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Proceedings of the Eleventh Annual Research Symposium

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INCINERATION AND TREATMENT OF HAZARDOUS WASTE

Proceedings of the Eleventh Annual Research Symposium
at Cincinnati, Ohio, April 29-May 1, 1985

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and
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Project Officer:

Harry Freeman
Alternative Technologies Division
Cincinnati, Ohio 45268

HAZARDOUS WASTE ENGINEERING RESEARCH LABORATORY
OFFICE OF RESEARCH AND DEVELOPMENT
U.S. ENVIRONMENTAL PROTECTION AGENCY
CINCINNATI, OHIO 45268

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FOREWORD

Today's rapidly developing and changing technologies and industrial products and practices frequently carry with them the increased generation of solid and hazardous wastes. These materials, if improperly dealt with, can threaten both public health and the environment. Abandoned waste sites and accidental releases of toxic and hazardous substances to the environment also have important environmental and public health implications. The Hazardous Waste Engineering Research Laboratory assists in providing an authoritative and defensible engineering basis for assessing and solving hazardous waste problems. Its products support the policies, programs, and regulations of the Environmental Protection Agency, the permitting and other responsibilities of State and local governments, and the needs of both large and small businesses in handling their wastes responsibly and economically.

These Proceedings present the results of completed and ongoing incineration and treatment research projects. Those wishing additional information on any of the projects discussed in these proceedings should contact the Alternative Technologies Division.

David G. Stephan, Director
Hazardous Waste Engineering Research Laboratory

PREFACE

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

ABSTRACT

The Eleventh Annual Research Symposium on Land Disposal, Remedial Action, Incineration and Treatment of Hazardous Waste was held in Cincinnati, Ohio, April 29-May 1, 1985. The purpose of the symposium was to present to persons concerned with hazardous waste management the latest significant findings of ongoing and recently completed research projects funded by the Hazardous Waste Engineering Research Laboratory's Alternative Technologies Division and Land Pollution Control Division.

This volume is a compilation of speakers' papers for Session B concerning hazardous waste incineration and treatment. Subjects include thermal treatment and destruction, air pollution control, biological and chemical treatment, bench and pilot scale research, industrial processes and boilers, and economics and institutional studies.

This document covers Hazardous Waste Incineration and Treatment only. A separate document for Session A, Hazardous Waste Land Disposal, is available from the Hazardous Waste Engineering Research Laboratory.

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EPA'S HAZARDOUS WASTE RESEARCH PROGRAMS: 1985

(Keynote Address)

Carl R. Gerber
Office of Environmental Engineering & Technology
U.S. Environmental Protection Agency
Washington, DC

This morning I would like to discuss EPA's hazardous waste research programs -- in light of the recently passed Resource Recovery and Conservation Act (RCRA) Amendments -- to highlight what I believe are some of our successes; to touch briefly on our ongoing and new programs; and to share with you where I think the Agency's hazardous waste research is going in general terms.

First, however, I would like to acknowledge the work of Dave Stephan and the staff of the Hazardous Waste Engineering Research Laboratory -- HWERL, as we call it -- in putting this 11th Annual Research Symposium together. Francis Mayo also deserves credit for his work in previous symposia and for the early stages of this one. As many of you probably know, a reorganization of EPA's engineering research program late last year basically moved all the hazardous waste and Superfund engineering research into one laboratory.

This meeting has become one of the major national meetings for hazardous waste research professionals, and certainly reflects well on the Agency in general and our Cincinnati-based operations in particular. I understand that although the date has not yet been set for next spring's meeting, the commitment has already been made to hold the meeting. I am pleased to hear this and hope the meetings will continue to happen and grow in the future.

Exchange or dissemination of information should be the goal of all government research programs, but is particularly important, if not critical, in a field like hazardous waste where developments are occurring rapidly and there is a great need for effective means of dealing with the problems.

You need go no further than a town newspaper to document environmental problems, or potential problems, caused by the disposal of hazardous waste, and to appreciate that this is a major national problem. In fact, with so many stories, it is all too easy to conclude that nothing significant is being done, or that there have been no technological solutions developed to mitigate these problems. While such feeling is certainly great for keeping us motivated, it can lead at times to counterproductive feelings of frustration or helplessness.

Fortunately, progress is being made. First, the enactment into law of the RCRA Amendments last November signaled a whole new national commitment to preventing the occurrence of hazardous waste problems. This new law not only extends the existing law, but provides a whole new impetus to the Agency in regulating the storage, treatment, and disposal of hazardous wastes.

In addition to specifically directing the Agency to address such problems as, underground storage tanks, the use of hazardous waste as fuels, small generator exclusions, management of used oil, and mining and other special wastes, the law directs the Agency to put into place regulations that would prohibit the disposal of certain substances in landfills. Such direction reflects a different approach to waste management; one that directs the country towards alternative

hazardous waste treatment and disposal processes, rather than land disposal, as the ultimate answer to many waste disposal problems. This is having a significant effect on our research programs, which I will address later in this talk.

But the revised law aside, what have we learned, or what technology has been developed, that can be viewed as successful? We have, through the combined efforts of the Agency's Office of Solid Waste and Emergency Response (OSWER) and the Office of Research and Development (ORD), determined that high temperature incineration is an acceptable disposal option for the overwhelming majority of liquid organic hazardous wastes. Based on this determination, the Agency has issued final regulations for incineration. These regulations are intended to ensure that disposal practices for organic hazardous wastes are upgraded throughout the country. We have also determined what types of boilers are suitable for using hazardous waste as fuels; and determined what industrial processes are suitable for waste disposal. Papers presenting findings in these areas are being given at this symposium.

We have developed, and are currently field testing, a mobile incinerator that appears to be a very promising technology for treating soils, as well as liquids, contaminated with hard-to-destroy substances such as dioxins. We are also actively involved in furthering the development of biological organisms for decontaminating soils in place. This work, which is also the subject of papers at the symposium, could lead to very attractive technological options for clean-up operations.

As all of you know, landfills and surface impoundments have been used for years as an inexpensive way of storing or disposing of wastes. Through either a lack of information or foresight, design of many of these sites was not based on presently accepted or even uniform criteria. Consequently, many of today's hazardous waste problems are related to land disposal operations; most importantly, contamination of groundwater.

Today, because of the research programs carried out over the past 10 years by the Agency, we know much more about disposal operations and what works and what does not. We have learned and documented that putting liquids in landfills is extremely risky, even in the best designed landfills, and consequently this is no longer allowed by the Agency. We have also learned and documented that it is highly probable that certain highly mobile, toxic, or persistent chemicals should not be placed untreated into the land. Although work is continuing to determine more about the effects of placing these substances in landfills, I believe we can safely say that many of these chemicals will be banned from land disposal, and that land disposal operations in this country in five years will be markedly different from those of previous years. A significant reason for this will be the result -- as summarized in the Technical Resource Documents -- of work at HWERL.

We have also witnessed significant advances in the development of the knowledge base and technology related to clean-up of Superfund sites. HWERL has produced a series of guidance documents related to clean-up operations that have been used extensively as textbooks in major universities around the country. These documents have also been widely used by the remedial action industry in structuring clean-up programs for Superfund and other abandoned disposal sites.

While we have realized successes in our programs we, of course, cannot rest on our laurels. Given the high visibility and magnitude of hazardous waste problems and the substantial risks to the environment posed, we must press forward on many fronts.

In the time remaining, I would like to highlight the activities in six of our programs: the Alternative Technology Research Program, the Land Disposal Research Program, the Remedial Action Technology Program, the High Temperature Incinerator Research Program, the Large Volume Waste Management Program, and the Leaking Underground Storage Tank, or the LUST, Program. This last program, technical considerations aside, will undoubtedly be a contender for best acronym of the year award.

ALTERNATIVE TECHNOLOGY RESEARCH PROGRAM

The 1984 amendments to RCRA require that within 66 months -- or by May 1990 -- EPA either ban the disposal of hazardous wastes to the land or ascertain that certain wastes or forms of wastes are acceptable for land disposal. In order to implement provisions of the legislation, the Office of Solid Waste (OSW) must determine that acceptable alternatives to land disposal of hazardous wastes exist. Through its alternative technology research program, HWERL is providing support to OSW to identify, evaluate, and develop alternative technologies to treat hazardous wastes. Chief among the wastes being studied are compounds that are very difficult to degrade without subjecting them to some extraordinary process. They may be not only resistant to degradation, but also may be inaccessible to reagents, bacteria, etc., by virtue of being bound in some way to the medium, or matrix in which they exist. It therefore becomes apparent that effective innovative treatment processes must be developed that will not only destroy these materials in bulk, (or concentrate them so that they may be more efficiently destroyed) but will also treat contaminated soils, buildings, etc., as well.

Since, up to this point, the Agency's regulatory process has been focused primarily on thermal destruction and land disposal of hazardous wastes, much less is known about other processes that may be used to treat these wastes. Information is needed on what treatment processes exist, what types of wastes can be handled by different processes, what residuals and environmental discharges are produced by these processes, and what costs will be incurred. Assessments of alternative treatment processes are required so that OSW can be certain that wastes that will be banned from land disposal can be adequately treated.

This is a relatively new program area for OSWER and for ORD. In Fiscal Year 1984, a program to conduct performance evaluations of existing alternative treatment systems was initiated. That program's first year of major activity is the current fiscal year. Several technologies have already been evaluated for removal of metals from hydroxide sludges and electrochemical and electrodischarge machining wastes. We are also in the initial stages of a large field assessment project to gather environmental data on existing commercial scale treatment facilities.

Some of our current objectives for the alternative technology research program are:

- To provide performance evaluations on a sufficient number of alternative hazardous waste treatment systems to allow OSW to direct that these systems be used instead of, or as pretreatments for, land disposal for selected hazardous waste streams;

- To develop and refine physical/chemical treatment techniques for dilute aqueous waste streams and those solid wastes containing water, such as soils and harbor or river sediments; and

- To assure the demonstration of promising alternative hazardous waste treatment technologies, so that these technologies may be recommended to and utilized by regulatory and industrial organizations.

In a related area, hazardous waste minimization, the Agency is supporting a small program to identify and encourage the adoption of process and treatment technology for reducing the generation of hazardous waste. As regulations limiting the characteristics and quantities of waste come into effect, I expect this area to become more important and the Agency's efforts in recycling and source reduction to increase.

LAND DISPOSAL RESEARCH PROGRAM

Our Land Disposal Research Program has been, and continues to be, a major part of our total program. The purpose of this program is to produce guidance on design, operation, maintenance, and closure of hazardous waste treatment, storage, and disposal facilities. An exciting aspect of this program is the development of user friendly, artificial intelligence systems that will standardize

the review of applications submitted to the Agency. These systems, which are in very early stages of development, will be based on the experience of experts and field proven techniques.

The Land Disposal Program currently addresses all aspects of land disposal operations, including such areas as cover systems, waste modifications, waste leaching, and liners. Some of current objectives for this program are:

- To develop and evaluate the effectiveness of various cover systems in relation to their functional requirements, for actual field application.
- To continue to evaluate the effectiveness of chemical stabilization and encapsulatory processes; and
- To evaluate the effectiveness of various types of clay and membrane liners in containing leachates.

A new objective authorized by the RCRA Amendments is investigation into municipal solid waste disposal, an area where we have considerable prior experience.

Each objective mentioned above presents a challenge that has knowledge gaps and will present difficulties. The biggest hurdle to overcome is field validation, as data from field sites are often difficult, if not impossible to obtain. However, such data are necessary if predictive models are to be verified and performance proved with time. Traditionally, our longer-term research has been measured in terms of two to three years, but needs to be revised to an eight to 10 year time frame if field results are to be meaningful. Retrospective studies, unfortunately, are either impossible to conduct or yield data of uncertain quality.

The main thrust of this research program to date has been with landfills. While much of these data are transferable to surface impoundments, surface impoundments offer unique problems that have not been fully addressed. Consequently, existing database for surface impoundments is limited and needs to be expanded to develop control and design technology.

Regardless of the obvious problems created by past land disposal operations, as long as waste is generated, there will be a need for final disposal of materials, even if the material is residuals from treatment operations. For that reason we envision a continuing highly visible land disposal program.

LEAKING UNDERGROUND STORAGE TANK PROGRAM

Billions of gallons of petroleum products and other hazardous materials are stored in underground tanks. The basic problems associated with these storage systems are leaks, and the costs, dangers, and potential environmental threats associated with those leaks. The primary causes of leaks from underground storage tanks are corrosion, poor fabrication and installation, and poor operating practices. The RCRA legislation of 1984 requires EPA to promulgate regulations to control underground storage tanks containing "regulated substances."

EPA must set final standards for existing tanks that cover leak detection and tank testing, record-keeping and reporting, corrective action, financial responsibility, and closure. Regulations for new tanks must include design, construction, installation, release detection, and compatibility standards. Research is required to establish a strong technical foundation not only to meet mandated regulatory deadlines, but also to reduce the rate at which the environment is being threatened. We in ORD are jointly working with OSW in this effort. The initial venture was a state-of-the-art document on leak detection that is now being finalized. Importantly, it revealed that the data presently available and the accuracies of various detection methods and devices are not acceptable, leading to a need to improve our ability to detect existing leaks. A leak detection method evaluation facility comprised of actual underground storage tanks is planned for construction in the very near future at our Releases Control Branch located in Edison, New Jersey.

INCINERATION AND HIGH TEMPERATURE PROCESSES

We are continuing our research studies of existing and new thermal destruction technologies to develop a high

degree of technical understanding and confidence in this kind of treatment process. The program continues to investigate laboratory, pilot, and full-scale environmental performance issues on a broad range of incineration and alternative thermal treatment devices. A combination of theoretical, hypotheses-based studies; studies on pilot and full scale operations; and overall environmental emissions work results in a coordinated approach to the overall technology. While the Agency's thermal destruction program began with early field tests in the mid-1970's, it became identified as a formal effort in 1980, and now exists as a major continuing segment of our hazardous waste research operations.

Over $20 million in thermal destruction research has been conducted since 1980. A major portion of this work has concentrated upon the assessment of the ability of existing thermal destruction facilities (incinerators and high temperature industrial processes) to meet RCRA performance standards for destruction and removal efficiencies for hazardous materials. These studies have produced an extensive performance database, which indicates that these facilities typically meet RCRA standards under ideal operating conditions.

In addition to studying existing systems, it is necessary to conduct more controlled studies if we are to truly understand the thermal destruction phenomena and to be able to apply technology to a wide range of wastes in a cost-effective and safe manner.

To this end, we have constructed or adapted several unique research facilities for thermal destruction studies. The Combustion Research Facility (CRF) in Jefferson, Arkansas provides highly instrumented, pilot-scale incinerators for the evaluation of the causes and consequences of process failure, while keeping actual net environmental emissions of hazardous constituents to within RCRA requirements. Experimental facilities at the Center Hill Facility here in Cincinnati -- which you can visit as a part of this meeting -- and at the Air and Energy Engineering Research Laboratory in Research Triangle Park, enable the conduct of studies essential to understanding the basic physical and thermochemical processes involved in effective waste destruction and the minimization of hazardous PIC formation.

Extensive technical support has been provided to regulatory program offices in the development of regulations and standards and to EPA's Regional Offices in the issuance of permits. Handbooks and guidance documents have been prepared on incineration, permits, and sampling and analytical methods for stack emissions measurement of trace organic compounds. In addition we have developed, as I mentioned earlier, a mobile incinerator at our Edison, New Jersey facility which should enable the Agency to carry out research and demonstration projects while cleaning up contaminated sites.

Among the current objectives in incineration research are:

- To assess the performance capabilities (destruction and removal efficiencies) of existing thermal destruction facilities which have not been evaluated (e.g., asphalt plants and carbon furnaces) to form the technical foundation for Agency policies and regulations with respect to these thermal destruction options;

- To define easily monitored incinerator facility operating parameters that correlate with incinerator performance;

- To project sampling and analytical methods for assessment of thermal destruction process performance; and

- To evaluate and develop innovative thermal treatment and destruction technologies that may represent improvements to the conventional waste incineration process or may be applicable to wastes that resist incineration.

LARGE VOLUME WASTE MANAGEMENT

We have recently initiated a program that addresses environmental problems related to the "large volume" wastes from mining, drilling, fossil fuel combustion,

cement kilns, and extracting and processing minerals. This work, which is specifically called for by the RCRA Amendments, will result in various special reports to the Congress. Although much work has been done by the EPA and others to date on mining wastes, much remains to be learned about the other "large volume" waste streams. Work in this area should continue at least through 1990.

REMEDIAL ACTION RESEARCH PROGRAMS

As a part of the Agency's Superfund Programs to clean up abandoned hazardous waste sites, HWERL is responsible for a research program to develop and evaluate various remedial action technologies.

To date, EPA has identified some 18,000 potentially hazardous waste sites. This number is expected to rise to 22,000 by the time the Agency completes its survey. Of those sites, 552 have been placed on the National Priority List.

A problem that has been found at almost all sites is contaminated soils. Frequently, large volumes of soils with low levels of contaminants are present; however, in several cases the contamination is at a high concentration.

Remedial actions for contaminated soils have usually been removal and burial in a secure landfill; or isolation on-site, e.g., covering with clean soil. Both of these methods have shortcomings. Removal and burial has transportation-related problems, high cost, and long-term liabilities, i.e., the landfill of today may be the Superfund site of tomorrow. Isolation techniques are frequently only partially effective, and the waste is not destroyed. Alternative methods are needed to solve this national problem.

In-situ technologies such as surfactant washing, grouting, thermal fusion, and microbial application have had very little acceptance at uncontrolled hazardous waste sites, because the technologies are still in the developmental stages and/or have not had field verification. From an institutional standpoint, we have problems of conducting tests on existing hazardous waste sites because of the inaccessibility of sites, the cost and time associated with permitting the studies, the risks associated with working with hazardous waste sites, and our inability to predict precisely the results of such field work. As a result of all these factors, EPA, the states, and industry are reluctant to use cleanup methods that are unproven. Thus, the role of ORD is to encourage and assist the development of new and innovative methods, and to assist in the verification of the cost/effectiveness of these methods, to assure their acceptability for remedial actions at Superfund sites.

Emphasis in future years will be on the development and/or field evaluation of primary technologies such as thermal, vegetative, extraction, exchange and chemical and biological degradation.

Another need identified by the Agency for uncontrolled sites is improved containment technologies for minimizing releases from these sites. We are currently pursuing a program to evaluate the effectiveness of containment technologies. The immediate objective is to screen all applicable technologies that might show promise. The longer term objective is to pilot- and field-scale demonstrate the most promising technologies, or assist in such demonstrations. The end objective is to provide the user community with improved, more economical, long-lasting, and low operation and maintenance cost recommendations for containment technologies. Clearly, for all our Superfund related work we will draw on information and technologies being developed to address RCRA related problems.

CONCLUSION

Of course there are many other programs, any one of which could be a suitable subject for a talk such as this one. However, I have included these six to give you a flavor of our current and future programs. As I indicated, papers at this symposium will amplify and provide details on all these areas and many others.

So where do we go from here? Without a doubt I think public and government interest will continue in this area. Lee Thomas, our new Administrator, has stated repeatedly his support of hazardous waste programs. Recently before the Senate Committee on Environment and Public Works he stated that the reauthorization of Superfund was his top legislative goal.

With such clear direction, I believe we will continue our effort to provide the improved databases and technology necessary to solve our nation's hazardous waste problems. It will not be easy: technology-related tests, particularly full scale field tests, are expensive and subject to major failures. A better understanding of the basic chemical, physical, and biological characteristics of hazardous wastes and how they might be rendered "non-hazardous" is complicated by the very complexity of these wastes and the media in which they exist and will not come cheaply or even quickly. Challenges await all of us involved in hazardous waste related research and development, not only to provide data and technology to assure the safe handling and disposal of these wastes, which are an integral part of our society, but also to do it in a cost-effective manner, and in a way that instills public confidence. I leave that challenge with you.

EMISSION AND CONTROL OF BY-PRODUCTS FROM HAZARDOUS WASTE COMBUSTION PROCESSES

Robert A. Olexsey, George L. Huffman, and Gordon M. Evans
U.S. Environmental Protection Agency
Hazardous Waste Engineering Research Laboratory
Cincinnati, Ohio 45268

ABSTRACT

Data on emissions of products of incomplete combustion (PICs) from full scale incinerators and boilers burning hazardous wastes are presented. Emissions of volatile PICs from incinerators do not exceed the limitation of 0.01 percent of input of principal organic hazardous constituents (POHCs) that has been proposed by the U.S. Environmental Protection Agency. Volatile PIC emissions from three of the boilers tested would exceed the proposed standard. However, for both boilers and incinerators there does appear to be a trend toward reduced PIC emissions with increased POHC destruction and removal efficiency (DRE). Combustion conditions and control technologies which may result in reduction in PIC emissions are discussed.

INTRODUCTION

Combustion is an effective method for disposal of hazardous waste compounds. Hazardous waste incinerators, industrial boilers, and many industrial thermal processes have demonstrated the ability to destroy principal organic hazardous constituents (POHCs) in compliance with EPA's required detruction and removal efficiency (DRE) of 99.99 percent. However, it is theoretically possible for a given combustion device to eliminate POHCs but, at the same time, produce hazardous by-products, or products of incomplete combustion (PICs). While emissions of such PICs are not currently subject to regulations, they are of concern because these compounds would be POHCs if they were present in the feed to the combustion device.

This paper addresses the issue of emissions of PICs from hazardous waste combustion processes. Data on PIC emissions are presented from full-scale tests of hazardous waste incinerators and industrial boilers burning hazardous wastes. Combustion conditions and control technologies which may result in reduction in PIC emissions are discussed.

FORMATION OF PRODUCTS OF INCOMPLETE COMBUSTION

The objective of incineration is to convert organic compounds to carbon dioxide (CO_2) and water. In actual practice, combustion is never "complete," that is combustion by-products are produced in the reaction. The most prevalent combustion by-products are partial combustion products such as carbon monoxide (CO). In fact, the most widely accepted measurement of combustion completeness, or efficiency is the ratio of CO_2 to CO_2 + CO in the exhaust gas from a combustion reaction.

In the context of incineration of hazardous wastes, as regulated under the Resource Conservation Recovery Act (RCRA), the focus of concern with hazardous combustion by-products is limited to product compounds that are, of themselves, hazardous compounds under RCRA. Therefore, the PICs that we are concerned with are those combustion by-products that are listed as hazardous wastes in Appendix VIII of 40 CFR Part 261 (1). Therefore, for purposes of our discussion and, in a regulatory sense, CO is not a PIC. Total unburned hydrocarbon (THC) is not a PIC. Only

fractions of THC that are listed as a RCRA hazardous waste are PICs.

Under EPA's RCRA incinerator regulations, an incineration unit must achieve a destruction and removal efficiency (DRE) of 99.99 percent for each principal organic hazardous constituent (POHC) in the waste material that is fed into the incinerator. PICs, therefore, are compounds present in the incinerator exhaust gas which are not present in the waste fed into the incinerator, but which would be classified as POHCs if they were present in the waste.

Emissions of PICs from hazardous waste incinerators are not currently regulated by the USEPA. However, in 1981, EPA did propose a regulation on "hazardous combustion by-products" that would limit PIC emissions to 0.01 percent of total POHC input to an incinerator (2). To date, this regulation has not gone past the proposal stage.

The mechanisms of PIC formation are complex and not particularly well understood. PICs are suspected to occur through any one or all of three reaction mechanisms (3):

1. Breakdown Of individual POHCs Into PIC reaction products. This mechanism has been documented through laboratory experimentation which has found that some materials, when subjected to temperature, consistently produce specific by-products. A case in point is the production of hexachloro-benzene (HCB) as a breakdown reaction product of kepone (4).

2. Complex recombination or substitution reactions. Through this mechanism, PICs are formed through chemical reactions among constituents in the feed. The reactions are enhanced through exposure of the reactants to high temperature and to catalytic materials which may be present in the reaction mixture. PICs produced through this mechanism will normally be high molecular weight compounds.

3. Universal combustion by-products. All fuels, including fossil fuels, can produce hydrocarbon by-products. Most fuels, including fossil fuels, contain trace quantities of many compounds, including halogenated materials. In any combustion process, hazardous PICs can be produced. Most often, these PICs are aromatics such as benzene, but chlorinated materials, particularly chlorinated methanes, such as chloroform, can also be found.

Formation of PICs is the result of some "failure" in the combustion process. The predominate mode of failure is most likely inadequate exposure of the molecule of waste material to a sufficiently high temperature to break the molecule and its derivatives down and then drive the combustion reaction through to completion (carbon dioxide and water). Even though nominal combustion temperatures may appear to be adequate, the range of temperatures that the molecules may experience may be such that small quantities of material may not be completely destroyed.

Inadequate mixing is a prime cause of insufficient temperature and inadequate oxygen and flame exposure for molecules of waste material. Material traversing a combustion zone in a plug flow configuration is more likely to produce regimes of low temperature and low oxygen exposure than will occur in a well mixed reactor with proper atomization of the waste material.

Short-circuiting and rapid exit of the combustion zone by waste material can lead to a situation where the POHC experiences insufficient residence time at temperature to destroy any PICs that may be produced. In addition, "quenching" of the flame through cold wall effect or improper feed point location for fuels can produce a situation where reaction products are "frozen" into the exhaust gas stream.

FULL-SCALE PIC EMISSIONS DATA

EPA recently completed and reported on a series of full-scale tests of incinerators and industrial boilers burning hazardous wastes (5, 6). The testing conducted under these full-scale programs was designed primarily to obtain data on POHC DRE to support EPA's regulation development. In addition to the POHC data, considerable data was obtained on emissions of PICs.

Table 1 describes the POHCs that were most frequently burned in the incinerator and boiler test programs. While eight incinerators and eleven boilers were actually tested under these programs, PIC data

TABLE 1

POHCs MOST FREQUENTLY BURNED IN COMBUSTORS

SEVEN INCINERATORS	FIVE BOILERS
Toluene	Carbon Tetrachloride
Tetrachloroethylene	Trichloroethylene
Trichloroethylene	Chlorobenzene
Carbon Tetrachloride	Tetrachloroethylene
Naphthalene	Toluene
Chloroform	1,1,1-Trichloroethane
Methylene Chloride	Methylmethacrylate
Methyl Ethyl Ketone	Epichlorohydrin
Phenol	Bis (2-Chloroethyl) Ether

from seven incinerators and five boilers is considered to be of sufficiently rigorous detail to be evaluated for analytical and comparative purposes.

Tables 2 and 3 list the volatile PICs which were most frequently found in the incinerator and boiler stack gases. All PIC concentration values in Tables 2 and 3 were obtained through analysis of Tenax resin samples of stack gas for Appendix VIII constituents through gas chromatography/mass spectrometry. Volatile PICs (boiling point $\leq$100°C) will be the subject of the remainder of this discussion. Although total PIC emission levels were determined for both the incinerator and boiler tests, very small quantities of semi-volatile PICs were found in the boiler stack gases. This is perhaps due to the fact that the wastes burned in the boiler tests were more heavily weighted with volatiles than were the incinerator wastes. Restricting the PIC discussion to volatile PICs will facilitate comparisons across combustor types. For the incinerators, volatile PICs accounted for about 73 percent of all PICs. At only three incinerators did semivolatile PICs amount to more than 3 percent of total PICs.

Tables 4 and 5 display summary data on PIC emissions, POHC input, POHC emissions, and site-specific mass-weighted POHC DRE for the incinerators and boilers, respectively. Values in Tables 4 and 5 are average values derived from 3 to 9 individual tests conducted at each site. Note that all of the incinerators and four of the boilers achieved mass weighted DREs in excess of 99.99 percent.

Tables 6 and 7 present data on ratios of volatile PIC emissions to POHC input and POHC emisisons. Data in the first columns of Tables 6 and 7 are given in percent in order to facilitate comparison with EPA's proposed PIC limitation of 0.01 percent of POHC input. From Table 6, it can be seen that for all seven incinerators the percentage of volatile PIC emissions to total POHC input is below 0.01 percent. However, the percentage of total PIC emissions (volatile and semi-volatile) to total POHC input for site 3 did equal 0.012 percent, which is in excess of the proposed limitation. From Table 7, it can be seen that sites E, F, and H emitted volatile PICs in excess of the 0.01 percent figure. From comparison of Tables 6 and 7, it can be seen that the boilers exhibited higher volatile PIC emissions to POHC emission ratios than did the incinerators. Where only two of the incinerators produced more volatile PICs than total POHCs, all of the boilers produced more volatile PICs than total POHCs.

The high ratio of volatile PIC emissions to total POHC input and total POHC emissions for the boilers could be attributed to a number of factors. The presence of watertubes in the boiler provides cold walls that could contribute to quenching of reaction products that enhance PIC production in these devices even though, generally, POHC destruction requirements are met. Also, for boilers, hazardous waste input generally accounted for less than 20 percent of the fuel input to the boilers. A notable exception was site G which was a specially designed unit that burned 100 percent chlorinated waste. It is possible that a significant amount of the PIC emissions from the boilers could be attributed to the primary fuel

TABLE 2

VOLATILE PICs MOST FREQUENTLY PRESENT IN BOILER STACK GASES

PICs	NUMBER OF FACILITIES	CONCENTRATION RANGE (ng/L)
Chloroform	5	4.2 - 1900
Tetrachloroethylene	5	0.3 - 760
Chloromethane	4	4.6 - 410
Methylene Chloride	4	83 - 2000
Benzene	3	9.4 - 270
1,1,1-Trichloroethane	3	5.9 - 270
1,2-Dichloroethane	3	1.3 - 1200

TABLE 3

VOLATILE PICs MOST FREQUENTLY PRESENT IN INCINERATOR STACK GASES

PIC	NUMBER OF FACILITIES	CONCENTRATION RANGE (ng/L)
Benzene	6	12 - 670
Chloroform	5	1 - 1330
Tetrachloroethylene	3	0.1 - 2.5
1,1,1-Trichloroethane	3	0.1 - 1.5
Toluene	2	2 - 75
Methylene Chloride	2	2 - 27

which was oil for sites D, E, and F and pulverized coal for site H. Emissions of PICs were not characterized for the baseline tests in which only fossil fuels were burned. Finally, for both incinerators and boilers, compounds that were present in the feed in concentrations less than 100 parts per million (ppm) were not considered to be POHCs. It is possible that the higher PIC emissions from the boilers could be attributed to compounds that were present in the feed in less than 100 ppm concentrations. It is possible, although it cannot be ascertained, that the boiler wastes contained more of these low concentration feed compounds than did incinerators.

Figure 1 represents the normalized PIC output data with respect to POHC DRE. The abscissa axis of the plot in Figure 1 displays total POHC DRE for the incinerators and the boilers. The ordinate axis displays the ratio of volatile PIC emissions to total POHC input for all the sites. The numerical designations and the symbol Θ refer to incinerator sites and the alphabetical designations and the symbol Δ refer to boiler sites. The vertical dashed line represents the DRE requirement for POHC destruction of 99.99 percent from the existing RCRA incinerator regulations. The horizontal dashed line indicates the proposed PIC limitation of 0.01 percent of total POHC input.

From Figure 1, a rough trend can be perceived of reduced PIC to POHC emissions

TABLE 4

INCINERATOR SUMMARY OF AVERAGE PIC AND POHC VALUES

SITE	TOTAL VOLATILE PIC EMISSIONS (mg/min)	TOTAL POHC INPUT (g/min)	TOTAL POHC EMISSIONS (mg/min)	MASS WEIGHTED POHC DRE (Percent)
1	68.00	9818	76.22	99.9992
3	9.00	780	48.00	99.9938
4	0.57	31	1.09	99.9964
5	1.36	1500	0.59	99.99996
6	0.23	323	6.60	99.998
7	228.00	8287	58.61	99.9993
8	0.71	1098	56.40	99.9949

TABLE 5

BOILER SUMMARY OF AVERAGE PIC AND POHC VALUES

SITE	TOTAL VOLATILE PIC EMISSIONS (mg/min)	TOTAL POHC INPUT (g/min)	TOTAL POHC EMISSIONS (mg/min)	MASS WEIGHTED POHC DRE (Percent)
D	205.70	5945	37.80	99.9994
E	567.36	2605	98.37	99.996
F	546.20	137	25.60	99.981
G	298.40	9436	13.26	99.9999
H	594.00	1020	96.00	99.991

TABLE 6

INCINERATOR PIC RATIOS

SITE	$100 \times \frac{\text{VOLATILE PIC EMISSIONS}}{\text{TOTAL POHC INPUT}}$ (PERCENT)	$\frac{\text{VOLATILE PIC EMISSIONS}}{\text{TOTAL POHC EMISSIONS}}$
1	0.0007	0.89
3	0.0011	0.19
4	0.0018	0.52
5	0.0009	2.31
6	0.00007	0.03
7	0.0028	3.89
8	0.00007	0.01

TABLE 7

BOILER PIC RATIOS

SITE	100 x VOLATILE PIC EMISSIONS / TOTAL POHC INPUT (PERCENT)	VOLATILE PIC EMISSIONS / TOTAL POHC EMISSIONS
D	0.0035	5.44
E	0.0218	5.77
F	0.3987	21.33
G	0.0032	22.50
H	0.0582	6.19

ratio with increased POHC DRE. In order to test the existence of such a trend, a computer was employed to conduct a simple ordinary least squares regression analysis with the POHC DRE as the predictor variable (X) and the PIC emission/POHC input ratio as the response variable ($\hat{y}$). In order to avoid problems with the computer algorithm, the DRE data points were transformed by subtracting the value 99.0 from each DRE, thus running the regression analysis utilizing just the decimal information. The resulting regression equation was $\hat{y} = 0.18862 - 0.18902x$ with an R^2 (adjusted for degrees of Freedom) of 79 percent, confirming this trend. The trend is more evident for the boilers than for incinerators. Point F is the only site that exhibits both a POHC DRE below the 99.99 percent and a PIC/POHC input ratio above 0.01 percent. Points E and H represent sites where DRE was in excess of 99.99 percent but the PIC/POHC input ratio was above 0.01 percent for volatile PICs. All the incinerator sites were above the required DRE and below the proposed PIC limitation. Points 6 and 8 represent sites where absolute values of volatile PIC emissions were extremely low, 3 ng/L and 5 ng/L, respectively.

CONTROL OF PRODUCTS OF INCOMPLETE COMBUSTION

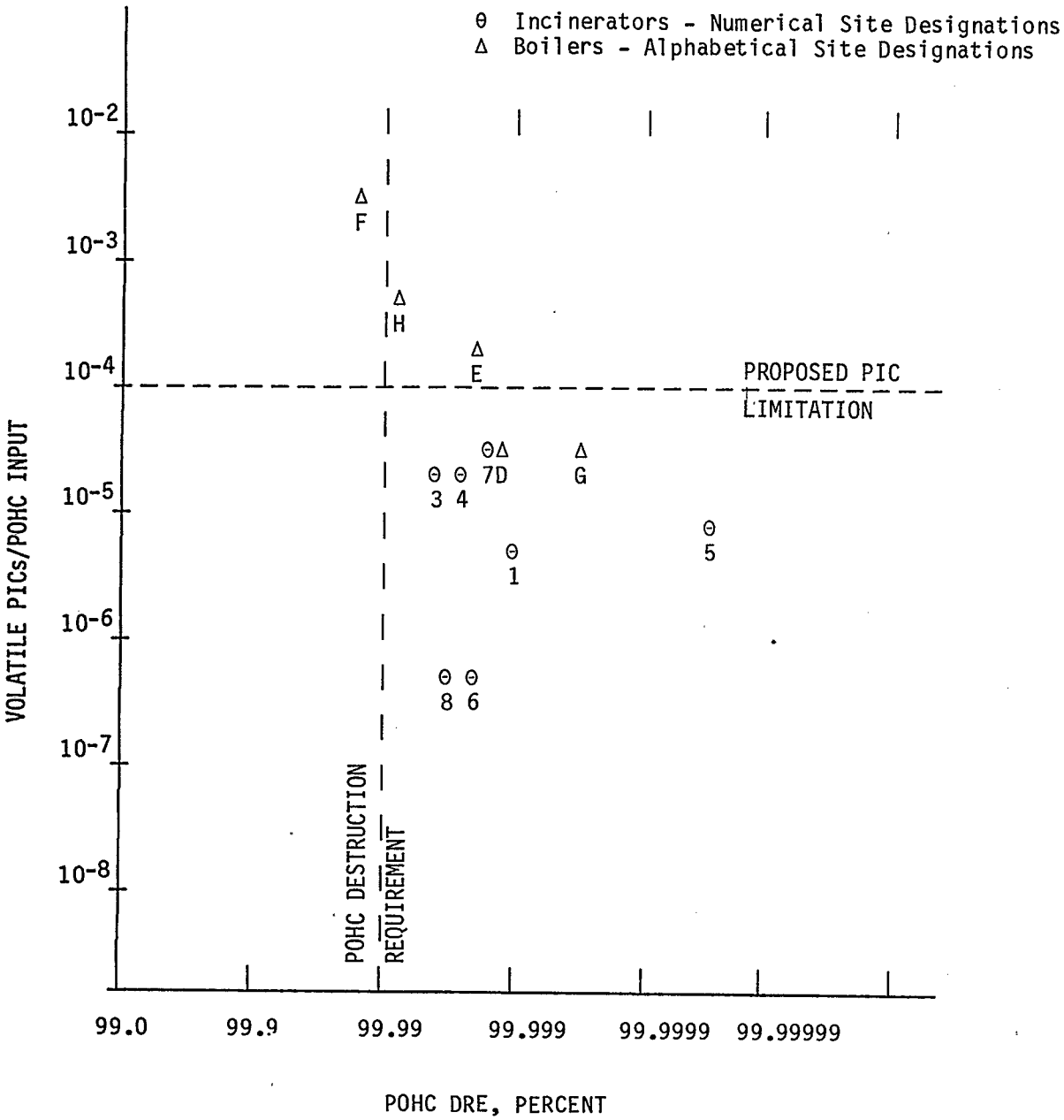
Much of the above deals with the amounts and types of PICs that are formed in various hazardous waste thermal destruction operations. But, perhaps a more pertinent question is "Given that PICs do form, what do we do about them --- i.e., how do we control them?" Little is known about how to answer this question. Data relative to how to control these potentially hazardous air pollutants is severely lacking. A significant amount of research is needed to fill this void. Nevertheless, some general statements can certainly be made.

Methods that have been proposed as potentially worthwhile, efficient, control techniques for PIC removal include: (1) Optimization of the combustion process itself to minimize the formation of PICs (2) Minimization of the amount of "cold" heat transfer surfaces that the exhaust gases see upstream of the "PIC Destruction Section" in the combustor; (3) Afterburning; (4) Enriched oxygen utilization; (5) Catalytic oxidation; (6) Scrubbing of the organic (gaseous, liquid or solid) PICs using organic scrubbing media and efficient contactors; and (7) Sorption of the organic PICs onto beds of activated carbon or other effective sorptive material. The first five of these are, of course, high temperature methods, whereas the last two are (generally) low temperature processes.

Regarding the optimization of the combustion process, suffice it to say that operation in the air-to-fuel regime where resultant PIC levels are low is a very reasonable objective as long as that regime is also the place where optimum POHC destruction occurs. A significant amount of research is needed here (on pilot and larger scales) to define the bounds of this regime as a function of combustor type.

Regarding the limiting of the amount

FIGURE 1



PLOT OF POHC DRE VS. RATIO OF VOLATILE PICS TO POHC INPUT

of "cold" surfaces that an exhaust gas sees upstream of the PIC destruction section, this is of course relevant primarily to new combustor designs; it would have limited applicability to retrofit designs.

Regarding the use of afterburning as a PIC control technique, this established practice should be quite useful in destroying some of (perhaps most of) the PICs that are formed in the primary combustor. However, this needs to be verified through additional research aimed at determining just how effective the various conventional afterburner designs are at destroying PICs.

Relative to the use of enriched oxygen as a PIC control technique, the applicability and effectiveness of this

method needs to be determined. Conceptually, the use of higher concentrations of O_2 in tearing apart complex organic molecules during combustion does seem to make sense. Nonetheless, experimentation is needed to prove whether this conjecturing is valid.

The authors feel that the catalytic oxidation option is particularly intriguing. This technique has enjoyed widespread success in many other applications. Directing combustor off-gases through a catalyst bed especially designed for gross PIC oxidation makes a considerable amount of sense, particularly for new combustor designs. Now, of course, "all" that is needed is for some process developer to find or develop an extremely versatile, low-cost, poison-resistant, sturdy, highly effective PIC oxidation catalyst --- the rest will be easy.

Regarding the (probable) low temperature option of scrubbing with organics, this technique can surely be developed if enough research is devoted to it. However, it does have the inherent draw-back of having to treat the scrubber liquors to remove the absorbed PICs prior to their final disposition.

Finally, relative to the dry sorption onto carbon option, this should be readily implemented and reasonably effective regarding PIC removal. Once again, however, this option does need additional research.

CONCLUSIONS

From the data presented here, it is apparent that the boilers tested had higher PIC emission levels and ratios than did the incinerators tested. For all combustors tested, there appears to be a trend toward reduced PIC emissions with increased POHC DRE.

Very little is known about the mechanisms of PIC formation in combustors. Similarly, little is known about the regimes of operation that tend to either produce or minimize PIC emissions from burners.

There is a need for more research into PIC generation mechanisms and PIC control technologies. Near-term research should be conducted at laboratory scale under ordered experimental protocols with controlled variables. In the longer term, additional full-scale testing that is directed toward proving out the small-scale hypotheses should be conducted.

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PRACTICAL GUIDE TO TRIAL BURNS AT HAZARDOUS WASTE INCINERATORS

Paul Gorman
Midwest Research Institute
425 Volker Boulevard
Kansas City, Missouri 64110

Donald Oberacker
U.S. Environmental Protection Agency
26 West St. Clair Street
Cincinnati, Ohio 45268

ABSTRACT

The U.S. Environmental Protection Agency contracted with Midwest Research Institute (MRI) to prepare a manual, "Practical Guide to Trial Burns for Hazardous Waste Incinerators," based on MRI's experience in conducting trial burns. Directed mainly to incinerator operators, the guide addresses the trial burn process, including planning and preparation, sampling and analysis, process monitoring, and data reduction and reporting. The guide concentrates on the most important, as well as the more troublesome, aspects of a trial burn. This paper is a condensation of some of the contents of the guide relative to planning for a trial burn and to problems that may be encountered when actually conducting the trial burn.

INTRODUCTION

The Resource Conservation and Recovery Act requires that hazardous waste incinerators effectively destroy hazardous organic compounds and maintain acceptable levels of particulate and chloride emissions. Owners and operators of these incinerators must demonstrate the performance of their facility by means of a trial burn. Consequently, industry and control agency personnel have become involved in planning for, conducting, and interpreting the results from trial burns.

Midwest Research Institute (MRI) has prepared a document, under contract to the U.S. Environmental Protection Agency (EPA), titled "Practical Guide - Trial Burns for Hazardous Waste Incinerators." This paper explains the purpose of the guide, describes the approach used in its preparation, and discusses selected areas and potential problems covered in the guide. Planning for and conducting a trial burn are emphasized in the paper. Several examples are included.

PURPOSE

The purpose of the "Practical Guide" is to assist incinerator operators and regulatory personnel who will be involved in trial burns but who may not have had experience in planning and executing a trial burn. The guide's intent is to convey information about the many complex and varied aspects of a trial burn, primarily those that are considered most important and those that frequently cause problems.

APPROACH

Experienced personnel at MRI first prepared a list of the most important parts of a trial burn, from planning through final reporting of results, and the most common problems that have occurred. Narrative descriptions of each identified part or problem were then written to describe how each could be handled and how problems could be avoided or minimized. The descriptions were kept brief in order to enhance clarity and conciseness, and tables

and figures were used whenever possible.

RESULTS

Anyone who is familiar with trial burns knows that there are many complex and varied steps involved, and numerous potential difficulties. The guide, consequently, was directed to the more important aspects of a trial burn and the problem areas that have been experienced.

The guide has a question-and-answer format to make it easier to use and more directly address the concerns of those who will be involved in trial burns. The questions asked and answered in the guide are listed below.

Planning for a Trial Burn

- What equipment or instrumentation is the incinerator required to have?
- How should trial burn operating conditions be selected?
- What types and quantities of waste are needed?
- How many runs are necessary?
- How many workers will be needed?
- How are stack sampling methods selected?
- What detection limits are required for the sampling and analysis methods?
- What quality assurance/quality control (QA/QC) measures need to be taken?
- What if the results do not meet Resource Conservation and Recovery Act (RCRA) requirements?

Conducting Trial Burns

- What is involved in preparing for the tests?
- What is involved in actual sampling?
- What is involved in analysis of samples?
- How are data converted to final results?
- How are the results usually reported?

Since all these questions cannot be answered in this paper, the most important areas and problems will be summarized in the following paragraphs, along with examples and some items of advice. Those related to planning will be discussed first, followed by those related to conducting the actual trial burn.

Planning for a Trial Burn

Much is involved in planning for a trial burn. Many aspects of the planning may be known, but their magnitude or complexity may not be realized. In addition, other aspects that need to be included in the planning activity are sometimes overlooked. Experience has shown that some of the most important or troublesome aspects in planning for a trial burn are:

Selection of operating conditions,
Pretests,
Number of runs and quantity of waste required,
Time requirements,
Sampling and analysis methods, and
Cost of a trial burn.

These aspects, which are discussed in detail in the guide, are summarized below.

Selection of operating conditions: The objective of a trial burn is to demonstrate compliance with the following RCRA requirements:

- Destruction and removal efficiency (DRE) $\geq$ 99.99% for the selected principal organic hazardous constituents (POHC)
- Particulate emission concentration $\leq$ 180 milligrams per dry standard cubic meter (mg/dscm)
- HCl emissions $\leq$ 1.8 kilograms per hour (kg/hr), or removal efficiency $\geq$ 99%

A major problem that is often slow to be realized is that these RCRA requirements need to be demonstrated under the worst practical operating conditions (worst case) because the operating conditions and waste characteristics during the trial burn usually become the limits specified in any subsequent operating permit. Some worst case conditions are listed in Table 1. It is difficult to achieve all the criteria shown in Table 1 because some are contrary to others (e.g., maximum air flowrate with minimum O_2 content).

TABLE 1. TRIAL BURN CONDITIONS

- Waste Characteristics
  - Maximum concentration of selected POHCs
  - Maximum Cl content
  - Maximum ash content
  - Minimum heating value (HHV) of waste feed
- Operating Conditions
  - Maximum heat input rate
  - Minimum combustion temperature
  - Maximum waste feed rate
  - Minimum O_2 concentration in stack gas
  - Maximum air input rate (maximum gas flowrate to yield minimum residence time)
  - Maximimum CO content in stack gas

When all, or most, of the worst case scenario is achieved, it will often represent an operating situation considerably different from normal operation. Burning a low heating value waste with high Cl and ash content at maximum feed rate, while trying to maintain all the other worst case conditions, has led to trial burn problems, if not inadvertent shutdowns. A common problem when burning high ash content liquid wastes has been frequent plugging of strainers. This has caused problems in maintaining maximum waste feed rate and even caused shutdowns during the trial burn. In another case, an incinerator operator burning a specific waste wanted to conduct one trial burn at maximum waste feed rate and minimum temperature. However, the operator realized that the incinerator always operated at lower temperature for lower feed rates. Revised operating procedures and a minor design change had to be made in order to operate at the higher temperature when burning waste at lower feed rates.

Realization of what must be done and good planning help minimize problems caused by the worst case situation represented in a trial burn. Wherever possible, the plant should be operated at the test conditions sometime prior to the actual trial burn.

Pretests: The major problem with operating at worst case conditions is that it maximizes the chance of failure (not meeting RCRA requirements). Since the plant wants to meet RCRA requirements, test conditions must be carefully selected, and plant operating experience is very important in making those selections. Pretests or miniburns are also highly desirable before the actual trial burn because they identify problem areas, one of the more common being failure to achieve the particulate emission limit, rather than failure to meet DRE. Mist carryover from alkaline scrubbing systems has often been an important factor in failure to meet the particulate limit. It is much better to discover such problems during a pretest, than to fail the official trial burn.

Number of runs and quantity of waste required: Other elements in the trial burn that have caused problems have to do with the number of runs and the quantities of waste required. EPA recommends three runs (at each set of operating conditions) for a trial burn. What is not usually recognized is that the operator should plan one run per day and that each run may require 8 hr of operating time. The quantities of waste feed necessary for three 8-hr runs are often large. If a plant is burning liquid waste at a rate of 5 gallons per minute (gpm), then the total amount required would approach 7,200 gallons. If, in addition, solids are being burned at a rate of one drum every 5 minutes, then a total of 288 drums may be needed. All these wastes must possess the characteristics required for the trial burn, and must be acquired and stored well in advance of the tests.

Time requirements: Many parts of the trial burn process require good planning and sufficient time for carrying out those plans. A list of the time factors is given in Table 2. Preparations for the actual sampling require considerable time, and analysis of samples after the tests usually requires at least 1 to 1-1/2 months, due mainly to complexities of POHC analysis. The analysis time is even longer when polychlorinated biphenyls (PCB) or dioxins must be analyzed in a PCB trial burn, under Toxic Substances Control Act regulations.

TABLE 2. TIME FACTORS INVOLVED IN A TRIAL BURN

- Receive notification to submit Part B application.
- Evaluate all conditions at which plant desires to be permitted (1 month).
- Prepare trial burn plan and submit to EPA (required 6 months after notification).
- Prepare responses to EPA on any questions or deficiencies in the trial burn plan (1 month).
- Make any additions or modifications to the incinerator that may be necessary (1 to 3 months).
- Prepare for trial burn.
  - * Prepare for all sampling and analysis (S&A) (2 to 3 months).
  - * Select date for trial burn, in concert with S&A staff or contractor (completed 1 month prior to test).
  - * Notify all appropriate regulatory agencies (1 month).
  - * Obtain required quantities of waste having specified characteristics.
  - * Calibrate all critical incinerator instrumentation (2 weeks).
- Conduct trial burn sampling (1 week).
- Conduct sample analysis (1 to 1-1/2 months).
- Calculate trial burn results (1/2 month).
- Prepare results for submittal to EPA (1/2 to 1 month). Include requested permit operating conditions.
- Obtain operating permit.

Sampling and analysis methods: Sampling and analysis results are the basis on which it is decided whether the incinerator did or did not achieve the RCRA requirements. It is for this reason that part of the "Practical Guide" is devoted to POHC sampling and analysis methods and procedures for estimating the detection limits necessary to demonstrate a DRE of 99.99%. The sampling and analysis that are required in a trial burn, and the associated QA/QC procedures, are among the most complex parts of the trial burn. Much of the guide is devoted to sampling and analysis, and covers many of the important aspects thereof, in a manner that, we hope, is relatively easy to understand, even though it must necessarily be technically oriented. However, because of their complexity, they are only briefly discussed in this paper.

Selection of sampling and analysis methods depends, of course, on the selected POHCs. One factor that is often not recognized is that the POHCs fall into the following three groups, that involve different sampling and analysis methods:

Group	Sampling and Analysis Method
Volatile POHCs	Volatile organic sampling train (VOST) and gas chromatography/mass spectrometry (GC/MS) or gas bag and GC/MS
Semivolatile POHCs	EPA Modified Method 5 (MM5) and GC/MS
Other POHCs	Special methods

When selecting POHCs, it is advantageous if all are in either Group A or Group B, since this will require only one sampling method and therefore mean reduced analytical costs. It is advantageous in most cases to avoid POHCs in Group C (e.g., formaldehyde).

After the POHCs have been selected, the detection limits required must be estimated to assure quantitation at the DRE level of 99.99%. A useful rule of thumb discussed in the guide is as follows:

100 ppm in waste feed ≅
1 μg/m³ in stack gas,
at 99.9% DRE

Higher concentrations in waste feeds yield proportionally higher concentrations in the stack gas. This rule of thumb is useful for estimating concentrations of POHCs in incinerator stack gas and for selecting the sampling and analysis methods with appropriate detection limits.

The VOST and MM5 methods usually can achieve the required detection limit, assuming no special interferences. However, the upper detection limit for VOST can be exceeded when the POHC concentration in the waste is high, even if the incinerator is achieving 99.99% DRE. When this happens, the DRE may have to be reported as a value like "< 99.995%." Clearly such a result is of no use. The solution to this potential problem is to estimate the stack concentration assuming a 99.99% DRE. Then, if the estimated concentration exceeds the VOST capability, gas bags will need to be used.

In general, gas bags should be used whenever the estimated stack concentration (at 99.99% DRE) exceeds 500 μg/m³. Referring to the rule of thumb just described, this could occur whenever the POHC concentration in the waste feed is 50,000 ppm (5%) or higher. Consequently, gas bags are often needed and are frequently used in addition to VOST.

Cost of a trial burn: One of the most surprising aspects of a trial burn, regardless of whether or not one uses a contractor, is the cost of sampling and analysis. In general, the cost ranges from $30,000 to $150,000 depending on the number of runs, number of samples taken in each run, and analysis required on each sample (i.e., the specific POHCs involved). The number of samples that are taken during a trial burn, including all replicates and blanks, is surprisingly large (in the range of 100 to 300). Each must then be multiplied by the respective number of analyses required. For example, each waste feed sample may be analyzed for heating value (HHV), Cl, ash, viscosity, and all POHCs.

The large number of samples and the number of analyses of each constitute the major parts of the cost for a trial burn. Cost is also significantly affected by the QA/QC that is specified.

Quality assurance/quality control: QA/QC must be adequate, but not excessive because of its potential impact on cost. More important, the QA/QC must be specific, clearly identifying:

- Number and types of samples to be analyzed in replicate;
- Number and types of samples to be spiked with POHCs or surrogates to assess recovery efficiency (accuracy);
- Number and types of blanks;
- Number and types of calibration standards; and
- Number and types of audit samples.

Conducting a Trial Burn

Some of the planning aspects for a trial burn discussed previously were directed toward avoidance of problems that

can occur in actually conducting the trial burn. First, of course, was having all the waste available with the desired characteristics. Second, was being able to operate the plant at the desired worst case conditions for the trial burn period. Other significant problems that can develop during actual trial burns have to do with the following:

Stack sampling facilities,
Cyclonic flow,
Recording of process data,
Documenting samples and analysis, and
Calculating and reporting of results.

These aspects, which are discussed in the "Practical Guide," are summarized below.

Stack sampling facilities: Stack sampling facilities must be adequate for all the test methods and equipment. Usually the degree of adequacy is determined during pretests or a pretest site survey by a sampling and analysis contractor. Even then, inadequate facilities often causes several hours of delay in starting the actual trial burn sampling. Lack of adequate electrical outlets and sufficient power for all the stack sampling equipment is the most common problem encountered.

Another problem the incinerator operators need to be aware of is that the trial burn requires a great deal of sampling equipment, which can have mechanical problems that cause test delays, especially if provisions have not been made for backup equipment and spare parts. More critical is the fact that the stack sampling equipment (Method 5) must pass a final leak check after a run has been completed. If a substantial leak is detected the run may be invalid and have to be repeated. This will mean an additional run, requiring additional quantities of the waste feed and additional time.

Cyclonic flow: One of the first checks done just prior to the actual trial burn sampling is a check for cyclonic flow in the stack. Cyclonic flow is not commonly encountered, but when it is, then installation of flow straighteners in the stack may be necessary. This is not a simple task and may require several days, if not weeks, to do. That possibility is another reason for a pretest, well in advance of the actual trial burn tests.

Recording of process data: Careful planning for all process data to be recorded, and by whom, is another seemingly minor but, important part of the actual trial burn. Usually these recorded data form a basis for DRE calculations (e.g., waste feed rates) and for subsequently specified permit operating limits. Close attention to the desired process operating conditions versus actual conditions during the tests is essential, along with actions to be taken if actual operating conditions are not within preselected operating limits. The advice here is to consider the "what if" situations and develop clear action plans. For example, if the operating temperature is to be held at 2000° ± 100°F, is sampling to be interrupted whenever the temperature goes outside that range (e.g., 1890°F)? Another example: if there is a momentary flameout, what action is to be taken? Examples like these may seem minor but many such incidents have taken place, and have caused difficulties during actual tests because there is then little time available for discussion.

Documenting samples and analysis: Many samples are taken during a trial burn and most of these samples must undergo multiple analyses and QA/QC. Therefore, an important requirement after the actual sampling is listing every sample and specifying exactly what analyses are to be performed on each sample and by what methods. That list and its requirements must be distributed to all those who have responsibility for analyses and final results. Without such a comprehensive list, it is easy to overlook some required analysis or step.

Calculating and reporting of results: The last part of the trial burn process is converting analytical results into final results for the test report. This involves several calculations which can cause problems or questions related to:

Blank correction procedures,
Rounding and significant figures,
Use of less-than or greater-values, and
Formatting of reported results.

The last section of the guide discusses all the above, together with recommended methods, and presents several sample tables of data to show how results are calculated, and how they may be presented.

CONCLUSION

We hope that the conclusion to be drawn is that the Practical Guide is worth reading, because it identifies problems that have been encountered in actual trial burns and the advice given in the manual may help minimize or avoid those problems in future trial burns. The Guide, which is in draft form and nearing completion of EPA review, should be available in a few months.

Carbon Monoxide and DRE: How Well Do They Correlate?

Laurel J. Staley
U.S. Environmental Protection Agency
Cincinnati, Ohio 45268

ABSTRACT

A series of six experiments were conducted in which five different organic compounds diluted in heptane were burned in a water-jacketed, bench-scale combustor. Excess air levels were varied to produce changes in the carbon monoxide (CO) concentration in the incinerator exhaust. Tenax trap samples were taken at various CO levels for purposes of determining accompanying Destruction and Removal Efficiencies (DREs) and levels of Products of Incomplete Combustion (PICs).

Results indicate that CO levels have only a tenuous relationship with DRE and vary with the compound being burned as well as with excess air and other combustion conditions. The highest levels of PICs and unburned POHCs (Principal Organic Hazardous Constituents) occurred at very high excess air levels and were accompanied by high CO levels.

INTRODUCTION

The Resource Conservation and Recovery Act (RCRA) regulations require that hazardous waste incinerator operators achieve 99.99% DRE (Destruction and Removal Efficiency) of the hazardous waste fed to the incinerator. Compliance with these regulations is generally determined by a trial burn in which the incinerator burns a hazardous waste stream representative of what the incinerator is intended to burn. Inlet and outlet mass flow rates for several selected chemicals, POHCs (Principal Organic Hazardous Constituents), chosen because they are thought to be relatively hard to burn, are determined. From these mass flow rates, the DREs of the POHCs are determined.

The trial burn method for determining compliance with RCRA has several problems. In spite of the fact that trial burns are expensive and time consuming, they provide only a "snapshot" of how well the incinerator is operating during the trial burn. No information is obtained about how the incinerator's performance might fluctuate with future changes in operating conditions or waste feed characteristics. Further, trial burns do not provide the incinerator operator with up-to-the-minute information on incinerator performance which would enable corrective action to be taken if incinerator performance deteriorates.

Several research groups are trying to correct this deficiency by determining whether a continuous indicator of performance, which would signal the onset of incinerator performance deterioration, can be found. These potential indicators are combustion intermediates or tracers spiked into the waste feed. The emission rates of these chemical intermediates and/or tracers can all be monitored. Theoretically, fluctuations in emission rates could then be used to signal changes in incinerator performance. Research is ongoing to determine the nature of the relationship between the emission rates of these chemicals and DRE, if, indeed, such a relationship exists.

One combustion intermediate under consideration as a DRE indicator is carbon monoxide (CO). Emission levels of carbon monoxide have long been used by operators of combustion devices to indicate performance levels in a very general sense. High CO levels are generally considered to indicate poor combustion and general operating problems with the incinerator. Conversely, low CO levels generally indicate that the combustor is operating well. In addition, inexpensive readily available and reliable monitors already exist for monitoring CO. Thus, because it seems economically and technically feasible, research is ongoing to attempt to tie DRE directly to CO levels.

Thus far, results indicate that the correlation between CO and DRE exists in the laboratory and in small-scale devices but not at full-scale. Researchers at the Energy and Environmental Research Corporation (EERC) in California have found that CO does not indicate minor changes in DRE, but does indicate general trends. In predicting general trends, EERC found that CO is a conservative indicator of DRE. That is, that CO increases long before DRE drops (2). However, full-scale tests at both hazardous waste incinerators and industrial boilers cofiring hazardous waste indicate that there is no apparent correlation between CO and DRE (1, 3).

Consequently, a set of experiments was conducted at the EPA-Cincinnati Thermal Destruction Laboratory (located at their Center Hill Facility) to further explore not only how POHC destruction varied with CO levels, but how the formation of Products of Incomplete Combustion (PICs) varied as well. We chose to study PIC formation in addition to POHC destruction because excessive PIC formation in hazardous waste incinerators can perhaps be a significant source of air pollution from these devices.

EXPERIMENTAL EQUIPMENT

The combustor used for the in-house EPA work is nearly identical to that used in the laboratory-scale research mentioned above which showed a correlation between CO and DRE. Figure 1 is a diagram of the Turbulent Flame Reactor (TFR) used in the in-house study. The TFR is water-jacketed and made of stainless steel. A mixture of test compound and heptane enters the TFR through a Delavan pressure atomizing nozzle. Nitrogen pressurization from bottled gas is the driving force for fuel flow. Combustion air supplied by a compressor enters the TFR through an International Flame Research Foundation (IFRF) windbox located at the bottom of the TFR. Adjustable swirl vanes allow for the control of angular and linear momentum imparted to the combustion air and afford some control over flame shape and stability.

Tenax-GC sorbent traps are used to collect POHC and PIC emissions from the TFR. The tenax sampling system used is shown in Figure 2. Sample gases enter through a 1/4" outside diameter (O.D.) stainless steel probe which penetrates the TFR exhaust duct. They then pass through a heat-traced length of 1/4" O.D. teflon tubing where the temperature is kept at 130°C. Prior to leaving the heat-traced length of tubing, sample gases pass through a particulate filter. Heat tracing ends roughly six inches upstream of the Tenax trap in order to allow the gases to air-cool from 130°C to 20°C. The gases then pass through a Tenax trap containing 1.5 grams of Tenax-GC resin which adsorbs all of the volatile organic compounds in the exhaust gas sample. After that, the gases pass through a pump, a rotameter and a dry gas meter prior to being exhausted to the atmosphere. The Tenax trap samples collected in this way were then analyzed by a gas chromatograph equipped with a Hall Detector.

To obtain continuous CO level readings, a Beckman Non-Dispersive Infra-Red (NDIR) monitor is used. A Beckman NDIR monitor is also used to continuously monitor CO_2 concentrations in the exhaust gas. Oxygen in the exhaust gas is monitored by a Beckman Paramagnetic oxygen monitor. Total Unburned Hydrocarbons (TUHC) are continuously monitored using a Beckman Flame Ionization Detector (FID) Total Hydrocarbon Monitor.

Figure 3 shows the continuous monitoring system employed for the experiments. Sample gas for CO, CO_2 and O_2

TURBULENT FLAME REACTOR

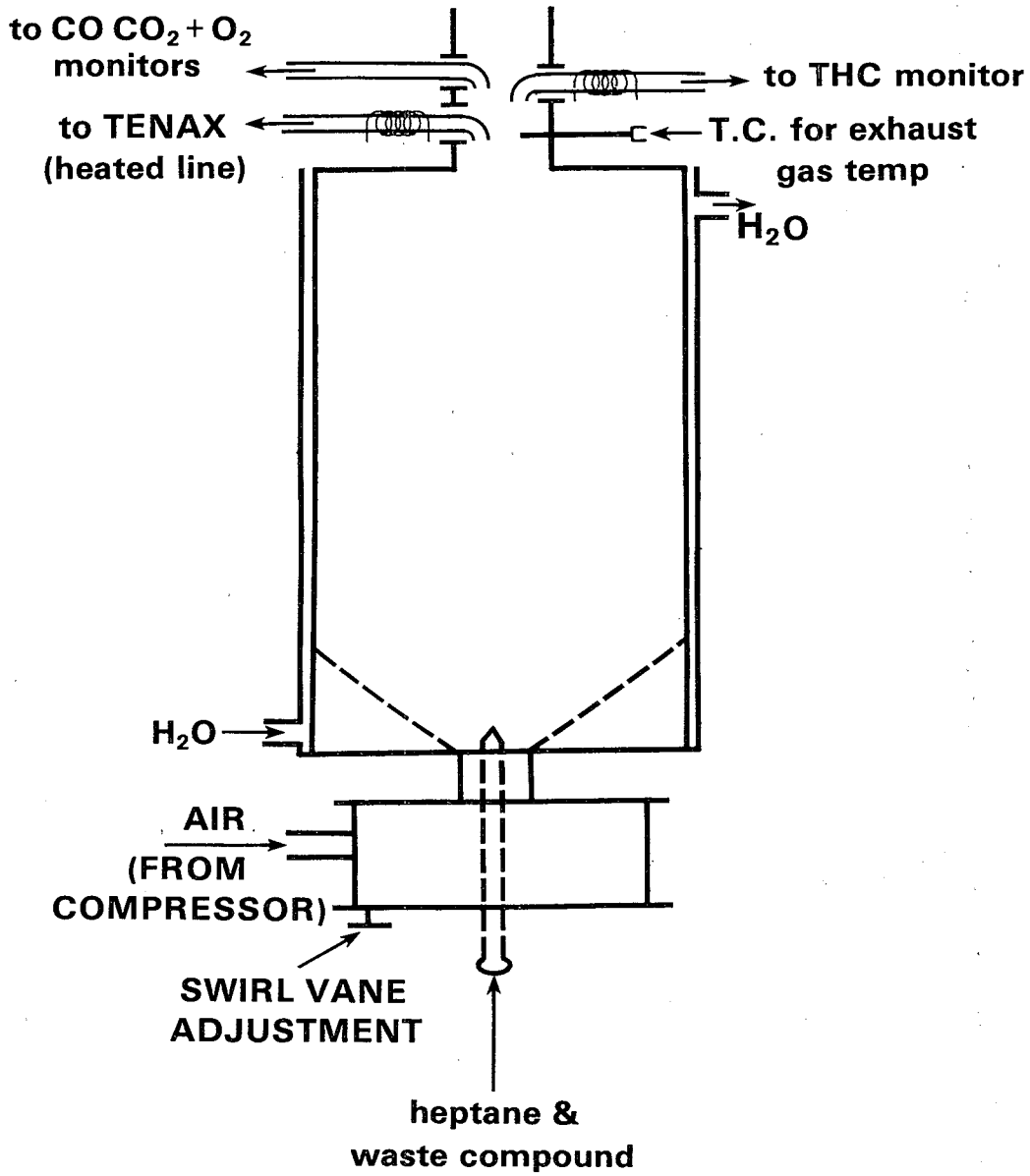

FIGURE 1

TENAX SAMPLING TRAIN

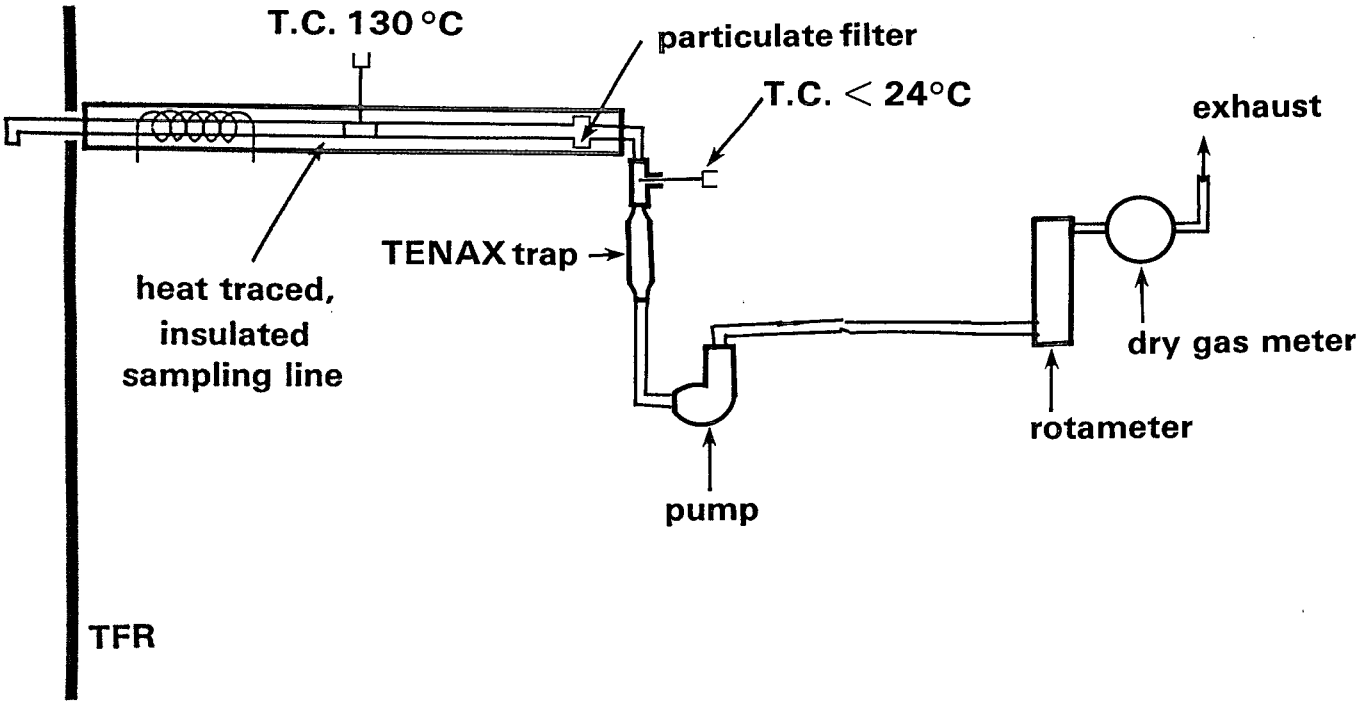

FIGURE 2

CONTINUOUS MONITORS

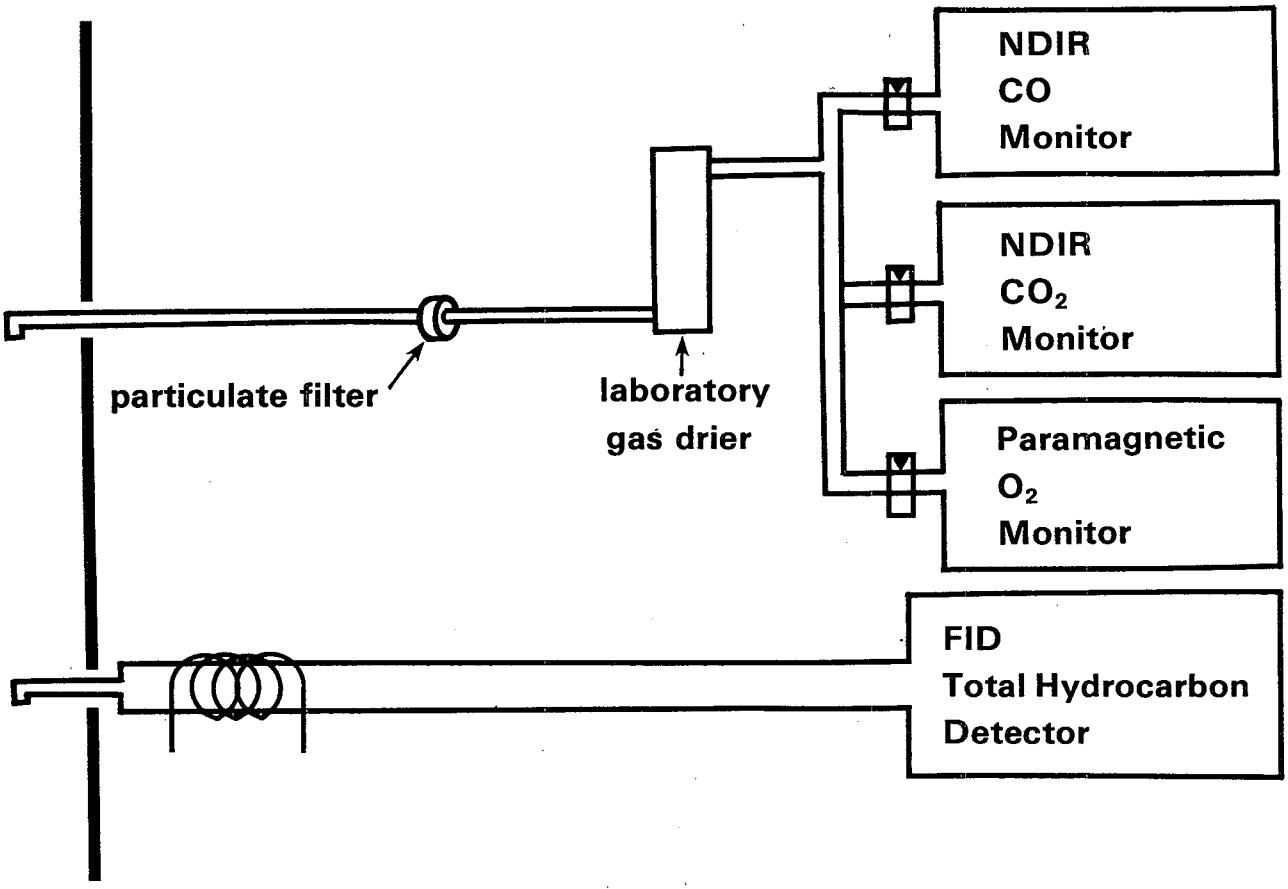

FIGURE 3

analysis is extracted from the TFR through a common sample line. Prior to entering the exhaust gas monitors, the sample gases pass through a particulate filter, and a laboratory gas drier filled with calcium sulfate.

Finally, three Type K thermocouples are used to measure TFR exhaust gas temperature and sample gas temperatures in the heated and unheated portions of the sample line upstream of the tenax trap.

EXPERIMENTAL DESIGN

The purpose of these experiments was to get a general idea of POHC and PIC levels in the exhaust gas of the TFR when that unit is operated under conditions that give rise to varying CO levels. This was primarily a "scoping" study intended to define areas in which future research might be most relevant and fruitful. Particular areas of concern included the following:

1. How well does CO level in the exhaust gas correlate with DRE?

2. How do POHC and PIC levels vary with changes in CO level?

3. How do POHC and PIC levels for long-duration failure modes such as improperly set combustion air compare to POHC and PIC levels for short-duration failure modes such as flame-outs, both of which are indicated by high CO levels?

4. Are there mixture effects which influence the relationship between CO level and DRE?

To address the above questions, a series of five compounds: trichloroethylene (TCE), carbon tetrachloride, tetrachloroethane, chlorobenzene and Freon-113 (1,1,2 trichloro-1,2,2 trifluoroethane) were each burned in the TFR separately in 2.0 mole percent solutions in heptane. We felt it would unnecessarily complicate the experiments to routinely use more than one POHC per test run at this early stage of our testing.

To test for mixture effects however, a test was conducted in which both Freon-113 and chlorobenzene were mixed together in heptane and burned. The same volumes of chlorobenzene and heptane were used in this test as in the previous tests where these compounds were burned separately (i.e., 2 mole percent each of chlorobenzene and Freon-113 resulting in 4 mole percent of total POHCs in heptane).

For each test, fuel flowrate was held at a constant level while the combustion air flowrate was varied to produce carbon monoxide levels that spanned the entire range of observable values. At five or sometimes six sets of operating conditions and observed carbon monoxide levels, five minute Tenax trap samples were taken of the TFR exhaust gas in order to determine unburned POHC levels, DREs and the levels of any (PICs) that may have been produced at those CO levels. In addition, carbon monoxide (CO), total unburned hydrocarbons (TUHC), carbon dioxide (CO_2) and oxygen (O_2) levels and exhaust gas temperature were continuously monitored.

At some point during each test, the flame was turned off during a sampling period. Sampling continued. The purpose of this was to see if the POHC levels and PIC species were significantly different for this sudden deterioration in incinerator performance (indicated by high CO) than they were for other more long-term failure conditions such as those arising from improperly set combustion air.

RESULTS

DRE Findings

For the most part, 99.99% DRE was achieved for the test POHCs in each of the six tests. In 62.5% of the cases DRE exceeded 99.99%. The rest of the time, DRE was at least 99.9%. Table 1 summarizes the DREs achieved.

Correlation Between CO and DRE

The correlation between CO and DRE is loose at best. DRE seems to be large ly determined by what POHC is being burned. Some POHCs burn easily;

Table 1. DRE Values and CO Levels vs. Excess Air Levels

Average CO Level	1000 ppm		300	200	300	400	500	800	1000	
Chlorobenzene and Freon		99.76* 99.998*	99.997 99.99	99.98 99.997		99.99 99.996			99.96 99.991	
Freon	99.998*		NA	99.992				99.994	99.996	
Chlorobenzene			99.994	99.99			99.98		99.76	99.92*
Tetrachloroethane		>99.999	99.992		>99.999		99.995		99.991* 99.97	
CCl_4		99.98	NA			>99.999		99.88	NA*	
TCE		99.994		99.98	99.97	99.78*				

% Theoretical Air: 110 120 130 140 150 160 170 180 190 200 240

* - Flameout
NA - Not Available

some do not. Results from this test series seemed to follow those obtained by EERC in their earlier studies. Namely, for hard to burn POHCs, CO levels increase without a concommitant decrease in DRE. Presumably, CO levels are increasing in advance of a decline in DRE (2). Figure 4 shows CO levels, excess air levels and accompanying DRE levels for all six tests. At excess air levels above 170% theoretical air, DRE for some POHCs does seem to decrease. For other conditions, however, DRE seems to remain above 99.99% even though CO levels again increase as excess air levels drop below 140% theoretical air. Above 170% theoretical air, CO levels, although elevated, are not at their highest levels even though POHC and PIC emissions are at their highest. Conversely, CO levels are at their highest below 130% theoretical air even though in this region DREs are consistently above 99.99% and PIC emissions are low.

Another indication that CO levels cannot closely predict DRE is that the high DREs in this test series were achieved at CO levels that are high in comparison to those found at full-scale incinerators. Minimum CO levels for these six tests ranged from 100 ppm to 300 ppm as seen in Figure 4. Full-scale incinerators typically operate at CO levels lower than 100 ppm (3).

Variation in POHC Destruction and PIC Formation With Changes in CO Level

Figure 5 shows a graph of POHC and PIC emissions for our tetrachloroethane test burn. Emissions for both the POHC for the test (tetrachloroethane) and the main PIC (trichloroethylene) increased with increasing excess air reaching their highest levels at 195% theoretical air. The average CO level under these conditions was about 800 ppm. Conversely, at 130% theoretical air, where the average CO level exceeded 1000 ppm, POHC and PIC emissions were at their lowest. This is contrary to what would be expected if the CO/DRE correlation were quite close.

Figure 5 also indicates that, even under conditions that result in low POHC emissions, it is still possible to produce comparatively large quantities of PICs when burning certain chemicals. Even though the emissions of tetrachloroethane are low, relatively high levels of TCE form. Even though no TCE was fed to the incinerator during this test, levels of TCE are always much higher than those of tetrachloroethane in the exhaust. Instead of being completely combusted to CO_2 and H_2O, a small portion of the tetrachloroethane seems to have been merely converted to trichloroethylene through the liberation of HCl.

Comparison of Flameout and Non-Flameout Conditions

Figure 5 shows that the levels of POHCs emitted at high excess air levels did not differ significantly from those emitted when the flame was extinguished. Nor did the types of PICs. This could be serious. When the flame goes out, there is usually only a momentary surge of soot and emission of exhaust gas laden with PICs. At high excess air levels though, the flame can be quite stable. Thus under high excess air conditions, large volumes of POHCs and PICs can be emitted over long periods of time resulting in a worse air pollution problem than a momentary upset like a flameout.

Mixing Effects

Table 2 which compares the results from Test 4 using chlorobenzene, Test 5 using Freon 113, and Test 6 using both chlorobenzene and Freon 113 shows that there are no major mixing effects which change the DREs achieved. Although the emissions of chlorobenzene (Test 4) and Freon (Test 5) differ slightly from the emissions in Test 6 (where both were burned together), the DRE for Freon was consistently higher than that for chlorobenzene. No mixing effects on CO levels were noted.

CONCLUSIONS

Any conclusions resulting from this work will need to be confirmed by future research. Nevertheless, we did identify some tentative conclusions. They are:

1. CO/DRE Correlation: Based on our tests, levels of CO do

FIGURE 4

CARBON MONOXIDE LEVEL VS. EXCESS AIR

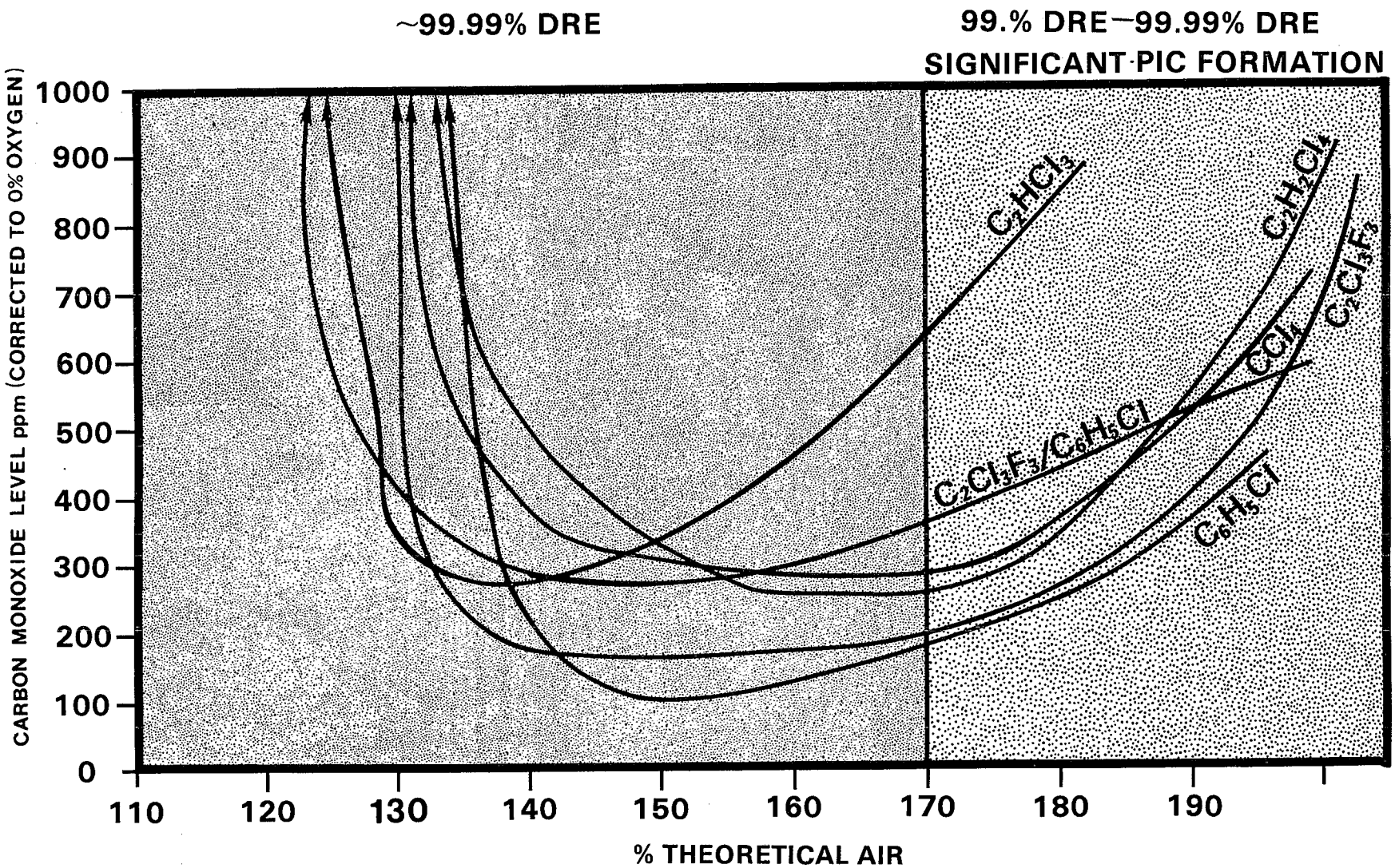

FIGURE 5

EMISSION LEVELS OF $C_2H_2Cl_4$ AND C_2HCl_3 VS. EXCESS AIR LEVEL

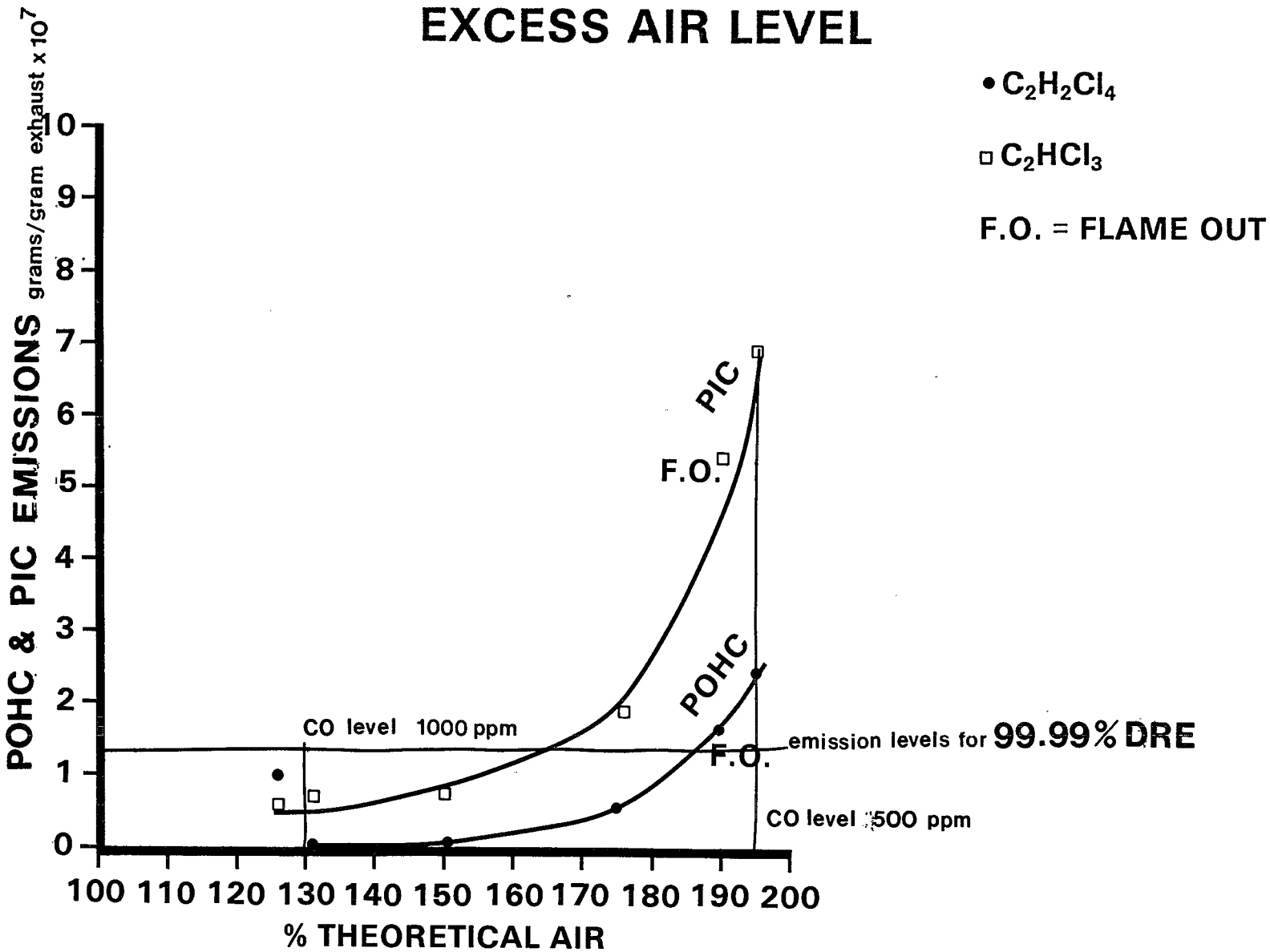

Table 2. Comparison of Freon and Chlorobenzene DREs for Combustion in Mixtures and Separately

% Theoretical Air	110	120	130	140	150	160	170	180	190	200	240
CO Level	1000 ppm		300	200	300	400	500	800		1000	
Test 4 Chlorobenzene (alone)			99.994	99.99			99.98			99.76	99.92*
Test 5 Freon (alone)	99.998		NA	99.992				99.994		99.996	
Test 6 Chlorobenzene (mixed)		99.76*	99.997	99.98		99.99			99.96		
Freon (mixed)		99.998*	99.99	99.997		99.996			99.991		

* - Flameout
NA - Not Available

not seem to correlate closely with DRE although they may indicate general trends in incinerator performance. High DREs (>99.99%) can be achieved in the TFR at CO levels considered high for hazardous waste and incinerators. The lowest DREs achieved occurred at the highest excess air levels and at elevated, although not the highest, CO levels.

2. POHC Destruction and PIC Formation: The highest PIC and unburned POHC levels of any of the conditions tested occurred at the highest excess air levels tested. We expected the highest emissions of POHCs and PICs to occur at low excess air levels. At low excess air levels and correspondingly high CO levels, POHC and PIC emissions did not increase even though high CO levels normally indicate incomplete combustion. Therefore, even though DREs remained high under these conditions, the POHCs may not have been completely combusted to CO_2 and H_2O. Instead the POHCs may have formed semi-volatile and non-volatile intermediates that were not detected using the available sampling and analysis methods. (The chlorinated species detecting GC/Hall Detector, or they may have formed semi-volatile PICs that we were unable to trap on Tenax-GC resin).

3. Flame-out Emissions vs. High Excess Air Emissions: Sudden deterioration in incinerator performance caused by extinguishing the flame (shutting off the fuel) did not result in significantly higher levels of unburned POHC or significantly different types of PICs than those produced under conditions of high excess air.

4. Mixture Effects: For the two chemicals tested together (chlorobenzene and Freon-113) there did not seem to be a significant mixture effect on DRE or CO level.

FUTURE WORK

The tentative conclusions outlined above will have to be supported by further experimentation. In doing these future experiments, we plan to take a closer look at PICs that may be formed under conditions of low excess air/high CO level. Further, we plan to examine the effect of post-flame heating and cooling on CO levels, POHC destruction and PIC formation. Both our studies and those of EERC (each using the TFR), show a tenuous relationship between CO and DRE (2). Field tests at full-scale boilers and incinerators show no correlation between CO and DRE (1, 3). One of the main differences between the two sets of tests is that the laborabory-scale work was conducted in a water-jacketed stainless steel device while the full-scale tests were conducted in refractory-lined vessels. The EPA Cincinnati has a refractory-lined device which is similar in firing rate to the TFR. Experimentation on this device should help resolve the discrepancy in results obtained from the laboratory- and full-scale work.

Hopefully, data gathered in this effort can be usefully integrated with data from other researchers both in the field and laboratory to finally determine the usefulness of carbon monoxide as a continuous indicator of Destruction and Removal Efficiency.

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SUMMARY OF TESTING PROGRAM AT HAZARDOUS WASTE INCINERATORS

Andrew Trenholm
Midwest Research Institute
425 Volker Boulevard
Kansas City, Missouri 64110

Donald Oberacker
U.S. Environmental Protection Agency
26 West St. Clair Street
Cincinnati, Ohio 45268

ABSTRACT

The Environmental Protection Agency's (EPA) regulatory impact analysis (RIA) on hazardous waste incinerator regulations included definition of the baseline performance of incinerators operating under normal conditions. As input to the RIA, a study was conducted to establish current baseline levels of performance through measurements of pollutant emissions (including over 40 Appendix VIII compounds) at eight hazardous waste incinerators and to analyze the data generated from these measurements to identify performance trends. The results of that study are described in this paper.

Tests were conducted at eight full-scale facilities to characterize all feed and effluent streams. Pollutants measured included EPA Appendix VIII hazardous compounds, particulates, hydrogen chloride, carbon monoxide, and total hydrocarbons. The data were analyzed to address questions on destruction and removal efficiency (DRE), products of incomplete combustion (PIC), pollutant emission levels, performance of air pollution control systems, and relationships of process parameters to destruction efficiency and emission levels. A large base of data on performance of hazardous waste incinerators was accumulated, and many possible relationships between parameters were explored. Conclusions included: DREs were generally above 99.99%; measured DREs tended to be higher when concentration of the hazardous compound in the waste was higher; the most frequently observed PICs were benzene, toluene, chloroform, tetrachloroethylene, and naphthalene; the particulate EPA regulation of 180 milligrams per normal cubic meter (mg/Nm^3) was not routinely met; and the hydrogen chloride EPA regulation almost always met.

INTRODUCTION

The EPA's Office of Solid Waste (OSW) conducted an RIA as part of EPA's hazardous waste incinerator regulatory development. The RIA includes definition of the baseline performance of incinerators operating under normal conditions and evaluation of the costs and benefits of alternative regulatory approaches. These analyses require knowledge of incinerator performance for different incinerator designs and operating conditions, a wide range of waste feed characteristics, and various combinations of air pollution control equipment. This study of eight hazardous waste incinerators was conducted to provide input to the data base that will be used to characterize performance.

Midwest Research Institute (MRI) conducted sampling and analyses for the eight sites, analyzed the data, and

reported the results. The results are available in five volumes from the National Technical Information Service (NTIS); Volume I is an executive summary; Volume II contains the program description and discussion of results; and Volumes III through V provide documentation of the methods used and data collected on the program (NTIS Numbers PB85 129500, 18, 26, 34, and 42, respectively). This paper summarizes the program and the results obtained.

PURPOSE

The purpose of this study was to establish current baseline levels of performance through measurements of pollutant emissions at the eight incinerators and to analyze the data generated to identify performance trends. The primary measures of performance during this program were DREs for principal organic hazardous constituents (POHC) and removal of HCl and particulates from the stack gases.

APPROACH

The eight hazardous waste incinerators tested had been selected by EPA to provide a broad representation of the incinerators in the country. These incinerators span a wide array of incinerator design and operating parameters, particulate and HCl control equipment, and waste feed characteristics.

The distribution of incinerator types and control devices is shown in Table 1. The facilities exhibited a wide range in capacity of 1 to 78 gigajoules per hour (GJ/hr) (1 to 74 million British thermal units per hour (Btu/hr)) heat input. Values for three key parameters, combustion temperature, residence time, and percent excess air or percent oxygen, also varied widely. Operating temperatures ranged from 650° to 1450°C and calculated residence time varied from 0.07 to 6.5 seconds. Excess air values fell within 60 to 130%. Corresponding oxygen content ranged from 8 to 12%.

Waste feeds with a wide range of characteristics were encountered at the eight sites. The heating values were below 4,600 kilojoules per kilogram (kJ/kg) (2,000 British thermal units per pound (Btu/lb)) for aqueous liquids and ranged from 14,000 to 37,000 kJ/kg (6,000 to 16,000 Btu/lb) for organic liquids, and from 0 to 29,000 kJ/kg (0 to 12,500 Btu/lb) for solid wastes. The organic liquids and many of the solids had a high enough heating value to sustain combustion without auxiliary fuel. Percent chloride in the wastes ranged up to 25%, with the highest values for organic liquids (chlorinated solvents). Little ash was found in aqueous liquids; values for organic liquids ranged up to 9%; solids had the most ash with values from 17 to 29%. Water content is obviously high for the aqueous wastes but ranged up to 50 to 60% for the organic liquids and solids.

TABLE 1. DISTRIBUTION OF INCINERATOR TYPES AND CONTROL DEVICES

Type or device	Number of facilities
Incinerator type	
Liquid injection	8
Rotary kiln - secondary chamber	2
Hearth	2
Gas injection	1
Control device	
None	3
HCl scrubber	5
Particulate control	4

This program encompassed a wide array of activities centered on testing at the eight hazardous waste incinerator facilities. These activities included evaluation and, in some cases, modification of sampling and analysis methods; multimedia sampling and analysis (S&A), and extensive data evaluation to assess the performance of hazardous waste incinerators.

The S&A activities characterized each input and output stream to the greatest degree possible. Typical input streams included waste feed, auxiliary fuel, and control system makeup and recycle waters. Output streams included stack gases, control device effluent (solid or liquid), and incinerator bottom ash. Each stream sampled was generally

analyzed for organic constituents, chlorides, particulate or ash, and, in some cases, metals. The S&A activities included full quality assurance/quality control.

The S&A activities generated extensive data of potential use to evaluate incinerator performance. Procedures were developed to reduce these data to a format usable for subsequent analyses. Activities included evaluating and defining procedures for calculating chloride and POHC input rates, blank correction procedures for POHC effluent rates, and calculating the most representative residence time and excess air for each of the eight facilities.

Specific technical issues related to incinerator performance were identified throughout the program. Engineering and statistical analysis techniques appropriate to each problem were selected and, to the degree possible within the available data base, conclusions were drawn. Pattern recognition data analysis was used to identify relationships between parameters that were not apparent from the overall examination of the data. These techniques were used primarily to identify the incinerator and waste characteristics that contributed most significantly to the achievement or nonachievement of 99.99% DRE.

PROBLEMS ENCOUNTERED

The sites and the specific incinerator operating conditions were limited by program constraints. Sites were those where access could be obtained, and operating conditions during the tests were those selected by the plants as their normal conditions. Thus, this study did not provide a complete characterization of incinerator performance for specific POHCs under varied operating conditions. A rigorous experimental matrix of incinerator parameters was not used nor were detailed facility characterizations prepared.

A number of S&A problems were encountered which are too detailed to present in this paper. The reader is referred to the full report for discussion of these problems and the solutions used.

RESULTS

This section presents the more significant results of the program. The discussion is divided into six subsections: POHCs, PICs, CO/THC monitoring, HCl control, particulate control, and metals emissions.

POHCs

One key element of this study was determination of DREs for any POHC (Appendix VIII compound) present at 100 micrograms per gram (μg/g) (approximate detection limit) or greater in any waste feed stream. The DREs span a wide range for both volatile and semivolatile compounds. The 134 volatile and 106 semivolatile data points (a data point is one test run for one compound) are distributed as shown in Table 2.

TABLE 2. DRE RANGE

DRE range	Type of POHC	
	Volatiles	Semivolatiles
< 99	2	3
99-99.9	12	5
99.9-99.99	30	20
99.99-99.999	51	46
> 99.999	39	32

The average DRE for the eight facilities was 99.992% for all volatile compounds. An average for semivolatile compounds could not be calculated because over half the stack measurements were below detection limits; however, most semivolatile compounds measured consistently achieved at least 99.99% DRE.

DREs < 99.99% tend to occur when one or both of two factors are present. The first factor is low concentration of the POHC in the waste feed (i.e., < 1,000 μg/g). The second factor involves compounds commonly identified as PICs (especially chloroform, methylene chloride, benzene, and naphthalene). The formation

of these compounds during the incineration of chlorinated organics increases their concentration in the stack gas, resulting in a lower DRE. Eighty percent of the volatile points and 96% of the semivolatile points below 99.99% DRE occurred in cases where one or both of these factors were present.

Three types of relationships between DRE and waste feed and incinerator operating parameters were addressed--the effect of waste feed concentration on DRE; the relationship between DRE and heats of combustion for specific POHC, and the impact on DRE of such incinerator parameters as temperature, residence time, and stack O_2 concentration.

The relationship between DRE and waste feed concentration was examined using linear regression analyses. Separate regression analyses were conducted for volatile and semivolatile compounds using the log transforms for both penetration (1-DRE) and waste feed concentration. For volatile compounds, the data were best fit by a line with a slope of -0.79. Figure 1 shows that no compounds below 200 µg/g in the waste feed achieved a DRE greater than 99.99% and no points above 12,000 µg/g failed to achieve 99.99% DRE. The correlation coefficient of -0.84 for the regression line is highly significant.

A similar comparison using the data for semivolatile POHCs showed the same basic relationship (Figure 2). The slope of -0.81 is comparable to that obtained for volatile compounds. A statistically significant correlation coefficient of -0.76 was obtained. Phenomena that might cause such a relationship were not identified.

The relationship between DRE and the heat of combustion of a POHC was examined using rank order statistics. The analysis was based on data from the four facilities which had sufficient quantifiable points to provide a meaningful analysis. If the incinerability of a compound were dependent on its heat of combustion, the DREs for compounds subject to the same incinerator conditions should be positively correlated with the heats of combustion of those compounds. None of the data for the four plants show a significant positive correlation.

Multivariate statistical analyses were used to examine the impact of four incinerator operating parameters--residence time, chamber temperature, heat input rate, and stack O_2 concentration--on DRE. The results of two types of multivariate analyses, factor analysis and discriminant analysis, indicate that the only operating variable strongly related to DRE is chamber temperature. However, the data were not sufficient to define a quantitative relationship between temperature and DRE. For the sites tested, factors such as waste feed concentration, specific compound kinetics, and PIC formation tend to mask relationships between incinerator operating conditions and DRE. These results indicate relationships which warrant further investigation; they do not establish definitive relationships between the operating parameters and DRE.

Measured DREs may also be affected by removal of POHCs from the gas stream by absorption in a scrubber. At one plant naphthalene was detected at 35 micrograms per liter (µg/L) in the scrubber effluent. Otherwise toluene, phenol, and naphthalene were present in effluents at several sites at concentrations less than 20 µg/L. These low levels suggest that scrubbers generally do not remove significant quantities of POHCs from the stack gas.

PICs

For this program, a PIC was defined as any Appendix VIII organic hazardous constituent that was not present in the waste feed at concentrations greater than 100 µg/g. Some 30 compounds were classified as PICs from the eight tests (Table 3). On the average, the PIC levels were slightly higher than the POHC levels, although this relationship varies widely from facility to facility. At only one of the eight tests were PIC output rates greater than 0.01% of POHC input rates.

Three explanations for the presence of PICs are: (a) the compounds were actually present at low concentrations (< 100 µg/g) in the feed and were destroyed at a relatively low DRE; (b) the compounds were introduced to the system from a source other than the waste; and (c) the compounds are

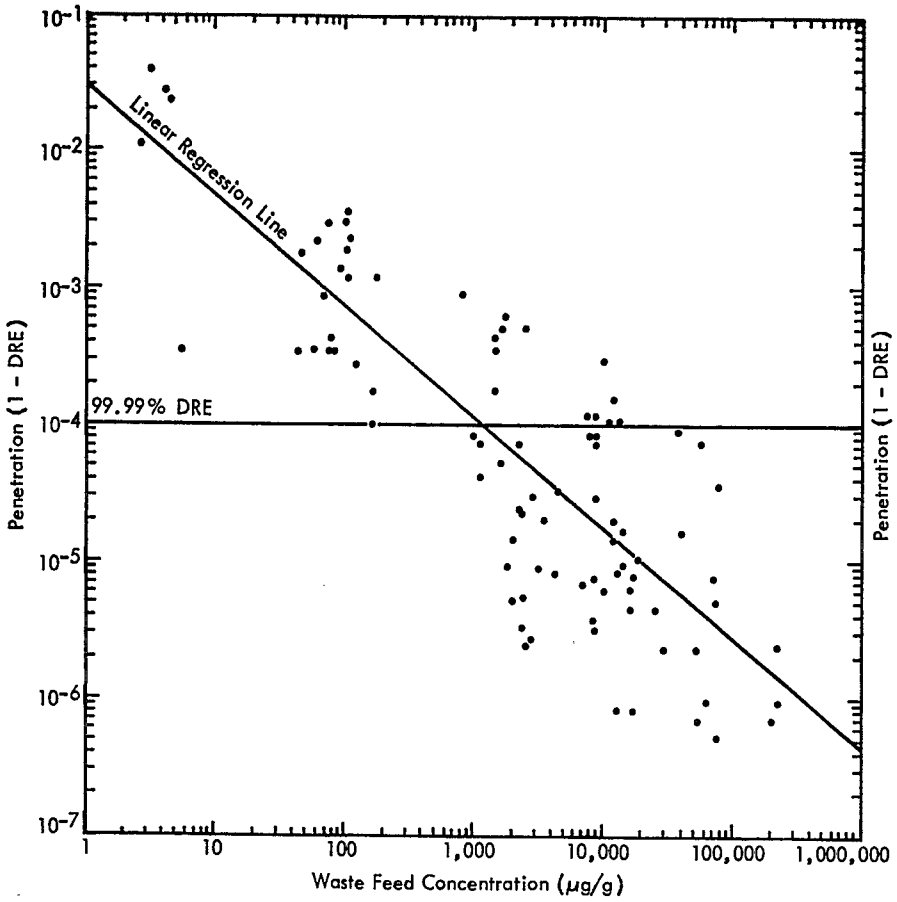


Figure 1. Penetration Versus Waste Feed Concentration - Volatiles.

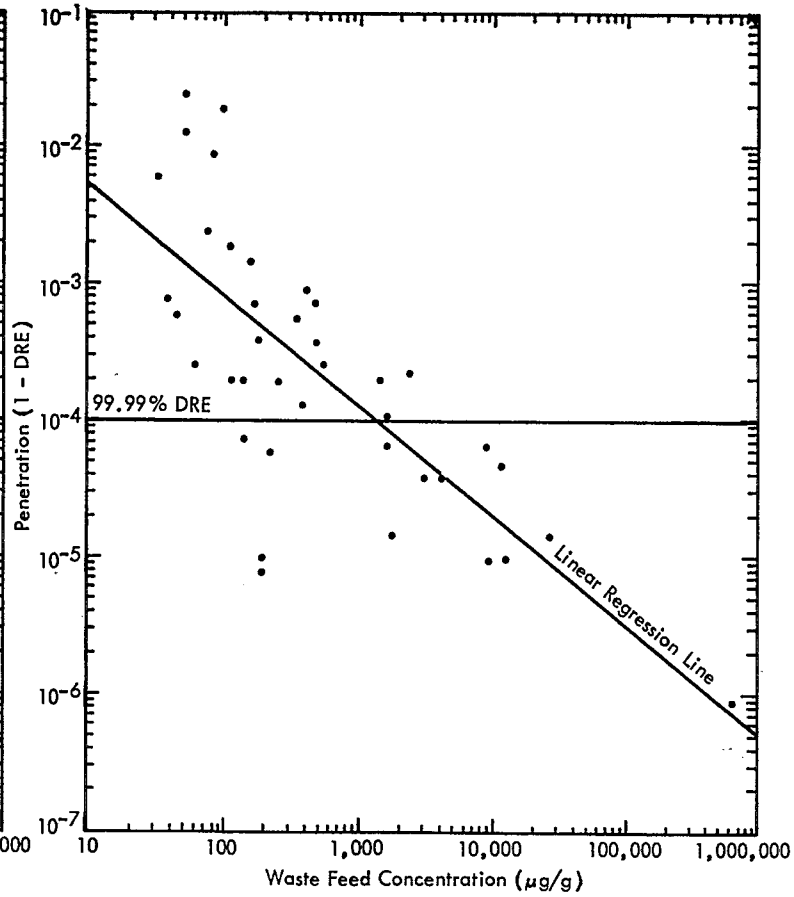


Figure 2. Penetration Versus Waste Feed Concentration - Semivolatiles.

TABLE 3. PICs FOUND IN STACK EFFLUENTS

PIC	No. of sites	Conc. (ng/L)
Benzene	6	12-670
Chloroform	5	1-1,330
Bromodichloromethane	4	3-32
Dibromochloromethane	4	1-12
Bromoform	3	0.2-24
Naphthalene	3	5-100
Chlorobenzene	3	1-10
Tetrachloroethylene	3	0.1-2.5
1,1,1-Trichloroethane	3	0.1-1.5
Hexachlorobenzene	2	0.5-7
Methylene chloride	2	2-27
o-Nitrophenol	2	25-50
Phenol	2	4-22
Toluene	2	2-75
Bromochloromethane	1	14
Carbon disulfide	1	32
Methylene bromide	1	18
2,4,6-Trichlorophenol	1	110
Bromomethane	1	1
Chloromethane	1	3
Pyrene	1	1
Fluoranthene	1	1
Dichlorobenzene	1	2-4
Trichlorobenzene	1	7
Methyl ethyl ketone	1	3
Diethyl phthalate	1	7
o-Chlorophenol	1	2-22
Pentachlorophenol	1	6
2,4 Dimethyl phenol	1	1-21

formed as products of combustion reactions.

The estimated stack concentration for a compound present in the waste feed just below the POHC limit of 100 μg/g and subject to a DRE of 99.9% is 10 nanograms per liter (ng/L). This low DRE becomes plausible when the trend of DRE versus concentration in waste feed is examined. The trend of decreasing DREs shows that many of the PICs detected could be explained by low concentrations in the feed.

Other potential sources of organic constituents in the stack gas are feed waters to pollution control systems, inleak air, and auxiliary fuel. In several cases, the control system added to the concentration of POHCs in the stack gas. The scrubber influent at three facilities contained about 100 μg/L of chloroform, while the effluent contained no measurable amounts. In all three cases, the quantity of chloroform lost from scrubber waters accounts for all chloroform detected in the stack. Scrubber waters also appear to contribute small quantities of other trihalomethanes to stack gases. Inleakage of air downstream from the combustion chamber may contribute to PIC emissions. Analysis of data from one facility where ambient concentrations of organic constituents were available and estimates of inleak air could be developed, indicated that inleak air could account for up to 10% of some organic constituents detected in the stack. Finally, analysis of auxiliary fuel oil at one plant indicated that this source could be a major contributor for some POHCs. Fuel oil streams can contain Appendix VIII compounds that are not present in the waste feeds.

The third mechanism, the actual formation of combustion reaction products, is the least understood of the three possibilities. The occurrence of simple stable compounds such as chlorinated methanes, ethanes, and benzene compounds in most stacks supports the hypothesis that PICs may be formed during combustion reactions. Primary candidates for this list on the basis of these tests include compounds which were present in all stack samples regardless of their presence in the waste feed: methylene chloride; chloroform; carbon tetrachloride; trichloroethylene; tetrachloroethylene; 1,1,1-trichloroethane; benzene; toluene; chlorobenzene; naphthalene; and phenol. Either benzene or toluene accounted for the highest measured stack concentrations of any compound at seven of the eight facilities.

CO and THC were monitored continuously during the testing at each of the eight sites. These data were subsequently reduced and compared to both POHC concentrations and DRE. The results indicated that continuous monitors for THC and CO may provide some indication of incinerator performance but that they are not good predictors of POHC concentrations either at specific plants or across plants. The results should be interpreted with caution in that the tests were not conducted in a parametric

fashion specifically designed to examine such correlations.

The results showed that CO is positively correlated with POHC concentrations when CO concentrations are above 50 ppm, but high POHC concentrations are also measured when CO concentrations are below 50 ppm. For THC, concentrations of POHCs are measurably higher when THC concentrations are above 10 ppm than when they are below 10 ppm. However, no correlations between THC concentrations and POHC concentrations were exhibited when THC concentrations were above 10 ppm.

Nonparametric methods were also used to compare CO concentrations to DRE. The analysis compared the average CO concentration for a run to the penetration (1-DRE) of a specific POHC for the same run using the data for carbon tetrachloride, toluene, trichloroethylene, and tetrachloroethylene. The concentrations of CO and penetration were not positively correlated for any of the four compounds.

HCl Control

Most hazardous waste incinerators that require add-on HCl control equipment use some type of countercurrent wet scrubber for HCl removal. Both water and water containing caustic for pH control are used as a scrubbing liquid. Five of the eight facilities had HCl scrubbers. Three of these systems were single-stage and two were multistage. Two of the systems used water only as a scrubbing media; the other three added caustic for pH control. While the systems did vary significantly, all five appear to be within normal ranges with respect to key design parameters.

The five facilities with HCl control complied with the standard except for a single run at one facility. Three of the facilities with packed towers achieved greater than 99% HCl removal and emitted less than 1 kilogram per hour (kg/hr) on all runs. One of the facilities which had only a venturi scrubber with mist eliminator consistently achieved 97 to 98% HCl removal and emitted less than 0.3 kg/hr of HCl. The one facility which failed to achieve the standard had a single packed bed scrubber. This facility achieved about 99% HCl removal efficiency and emitted less than 1 kg/hr of HCl on two runs. On the third run, the removal efficiency was 96% and the HCl emission rate was 2.0 kg/hr. No reason for the decreased performance on the third run was identified.

Particulate Control

The data collected during this study indicate that achieving the particulate emissions limitation of 180 mg/Nm³ (corrected to 7% O_2) may be more difficult than achieving either the HCl or DRE standards for hazardous waste incinerators. This conclusion holds true for incinerators with and without particulate control devices.

The data from three facilities with no particulate control device suggest that any facility firing wastes with ash content greater than 0.5% will clearly have difficulty achieving the particulate limit without add-on particulate controls. At ash contents of 0.2 to 0.5%, facilities may still have difficulty meeting the limit without controls. Each of these three facilities fired liquid organic wastes. One facility with extremely low ash (0.1% or less) easily complied with the standard. A second facility with wide ranges in ash content (< 0.005% to 0.5%) had mixed results. At < 0.05% ash, emissions easily complied with the limit; at 0.2% ash, emissions marginally complied with the limit; and at 0.5%, ash emissions exceeded the limit by a factor of 2. The third facility had ash contents ranging from 0.7 to 0.8%. Emissions from this facility exceeded the 180 mg/Nm³ limit by factors of 4 to 6.

Two of the five facilities with particulate control systems failed to comply with the emission limit and two achieved marginal compliance. The one facility with a venturi scrubber with an extremely high pressure drop (~ 30 kilopascals or 100 inches H_2O) easily complied with the limit. The results for four systems are summarized below:

Control type	Stack particulate conc. (mg/Nm³) Range	Avg.
Venturi scrubber	10.4-33.7	23.0
Ionizing wet scrubber	139-176	151
Venturi scrubber	102-290	169
Packed bed scrubber	183-217	200

Metals Emissions

Metals contained in the waste feed to incinerators eventually emit from the incinerator by one of three pathways--as part of the particulate emissions or as vapor from the stack, in liquid or solid effluents from the control device, or in the incinerator ash. Metals were analyzed in selected samples of these effluent streams from five of the eight facilities tested. The analysis focused on the 12 metals identified in Appendix VIII as hazardous constituents are shown in Table 4.

The data from these analyses were not sufficient to complete an overall materials balance for metals. A summary of the air emissions data for the five tests is presented in Table 4. These data are for particulate emissions only; they do not include metal vapor emissions.

ACKNOWLEDGMENTS

This project was jointly sponsored by the EPA's Hazardous Waste Engineering Research Laboratory and the Office of Solid Waste. The valuable assistance and guidance of Don Oberacker, Timothy Oppelt, Edward Martin, Benjamin Smith, and Gene Crumpler is greatly acknowledged. The cooperation of all test sites and the efforts of many individuals in MRI's Environmental Systems and Analytical Chemistry departments are also acknowledged.

TABLE 4. RANGES OF METALS EMISSIONS FOR FIVE HAZARDOUS WASTE INCINERATOR TESTS

Metals	Emission range: µg/g of particulate	Emission range: g/min
Antimony	< 1,200 - 15,200	< 0.012 - 1.2
Arsenic	ND*	ND*
Barium	41 - 3,090	0.0032 - 0.12
Beryllium	< 0.32 - 6	< 0.0001 - 0.002
Cadmium	140 - 4,300	0.0033 - 0.087
Chromium	668 - 47,500	0.0066 - 0.47
Lead	3,100 - 100,000	< 0.016 - 7.3
Mercury	56#	0.0043
Nickel	230 - 49,000	< 0.004 - 0.57
Selenium	< 500 - 61,600	< 0.046 - 4.5
Silver	7.6 - 1,880	0.001 - 0.0064
Thallium	**	< 0.004 - 0.012

* ND - not detected in all runs.

\# Detected during only one run; others not detected.

**Range could not be developed because of high < values.

TIER 4 DIOXIN TEST PROGRAM STATUS

Miles, A. J., Parks, R.M., Oberacker, D., Southerland, J.

ABSTRACT

The paper discusses the status of Tier 4 of the National Dioxin Study and focuses primarily on the identification and selection of candidate combustion sources for the test program. No laboratory results will be presented.

The Tier 4 program addresses the broad questions do combustion sources emit significant quantities of dioxin? If so, how much and what are the health risks associated with these emissions?

The approach taken to address these questions was divided into several steps. First, an extensive literature search was conducted, and all available dioxin emissions data were summarized. The information was then analyzed to attempt to identify factors which would affect dioxin emissions from combustion sources. The analysis indicated that the following factors could have an effect on dioxin emissions.

- Presence of dioxins in the feed;
- Presence of dioxin precursors in the feed;
- Chlorine in the feed;
- Combustion conditions (temperature, oxygen level, etc.); and
- Feed processing.

The analysis also indicated that combustion of waste products as opposed to fossil fuels was more likely to form dioxins. Using the factors listed above, in conjunction with a list of major combustion source categories and the available dioxin emissions data base, a ranked list of combustion source categories with the potential to emit dioxin was developed.

In conjunction with the development of the list, a source test program was devised. Ten to twelve sources are to be tested for dioxin emissions using a Modified Method 5 sampling train including an XAD-2 resin trap. The test program also includes sampling of feed materials and collected particulate; continuous monitoring of CO, CO_2, O_2, and THC; and acquisition of operating data over the period of each test. In addition, some 40 sites were selected for ash sampling and analysis to broaden the dioxin data base.

Site selection for the test program began in August 1984, and the first test was conducted in October. Two tests were conducted in November, and subsequent tests were conducted in December and January. All testing will be complete by June of 1985. No results from the test program are available.

INTRODUCTION AND PURPOSE

The Air Management Technology Branch (AMTB) within the EPA's Office of Air Quality Planning and Standards (OAQPS) is responsible for the development and implementation of a source testing program for Tier 4 of the National Dioxin Study. Technical guidance for the source test program is provided by IERL/HWERL in Cincinnati. The purpose of Tier 4 is to assess combustion source emissions of polychlorinated dibenzo-p-dioxin (PCDD), with a focus on the most toxic isomer - 2,3,7,8-tetrachlorodibenzo-p-dioxin (2,3,7,8-TCDD). Combustion source emissions of polychlorinated dibenzofuran (PCDF) will also be addressed in this study.

Radian Corporation, under task order contract, is providing support to the AMTB by collecting and reviewing available literature data on emissions of PCDD's and PCDF's from combustion sources. In addition, Radian will perform PCDD

emissions tests on twelve combustion sources. The samples will be analyzed by EPA laboratories for PCDDs and PCDF's. The source test plan addresses the following questions:

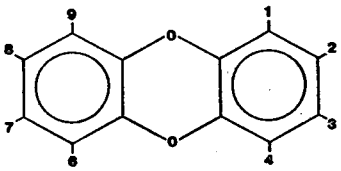
1. Which combustion source categories emit PCDD's (and PCDF's) to the atmosphere?

2. What range of concentrations and quantities of PCDD's (and PCDF's) are emitted from these source categories?

3. What are the estimated health risks associated with these emissions?

This paper describes development of the source test program including selection of candidate combustion sources. In addition, the status of the program as of April 1985 is discussed. Further details of the program can be found in the project plan (1), the initial literature review document (2), and the sampling guidance manuals (3, 4) developed for the program.

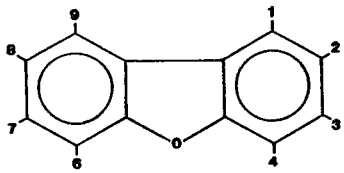
Dioxins are members of a family of organic compounds known chemically as dibenzo-p-dioxins. All dioxin compounds have a three ring nucleus containing two benzene rings interconnected by a pair of oxygen atoms. The structural formula of the dioxin nucleus and the convention used in numbering its substituent positions are shown in Figure 1a. Chlorinated dioxins can contain up to eight chlorine atoms and 75 different chlorinated dioxins are possible. Each congene has its own physical, chemical, and health effects properties.



DIOXIN CONFIGURATION

Figure 1a.

Dibenzofurans are a group of organic compounds that have a similar structure to the dibenzo-p-dioxins, except that the two benzene rings in the nucleus are interconnected with a five member ring containing only one oxygen atom (Figure 1b). Theoretically, the chlorinated dibenzo furan group can contain up to 135 different structural congeners, each with varying physical, chemical, and health effects properties.



FURAN CONFIGURATION

Figure 1b.

Of all the PCDD's and PCDF's 2,3,7,8-TCDD has received the most attention. However, in general, 2,3,7,8-TCDD repre- a small fraction of the total PCDD found in combustion source emissions. In addition, PCDF emissions can exceed 2,3,7,8-TCDD emissions by two to three orders of magnitude. For some sources PCDF's contribute significantly (over 80 percent) to the health risk associated with combined PCDD and PCDF emissions.

APPROACH AND SCOPE OF THE TIER 4 STUDY

The Tier 4 program was divided into three phases: (1) the literature evaluation and design of a test program and (2) the source test program including ash sampling, and (3) data summary and analysis.

The first phase of the Tier 4 study was accomplished in three general tasks. The first task was to obtain and review the available literature on PCDD emissions from combustion sources. Over 100 published and unpublished reports were obtained. In addition, contacts were made with key individuals to identify recently performed or ongoing studies that could be used to supplement the data base. The second task was to develop a ranked list of source categories with potential to emit PCDD's. The criteria used to develop the ranked list was based on information obtained from the literature review. The final task was to develop a testing program to assess PCDD (and PCDF) emissions from combustion sources. The results of these tasks are summarized below.

PCDD Emissions Data

A review of the literature has produced a list of 12 broadly defined source categories for which some dioxin

emissions data has been collected. Table 1 lists sources for which published dioxin data could be found and summaizes the measured TCDD concentrations. Although the National Dioxin Study is focusing on 2,3,7,8-TCDD, most of the data found in the literature addressed TCDD and total PCDD. Since 2,3,7,8-TCDD data are limited, TCDD was used during the evaluation of the data base as the best indicator of 2,3,7,8-TCDD emissions.

with over 100 ppm chlorine and normally some chlorinated phenol content. The highest TCDD emissions are generally associated with solid feed fuels and low combustion temperatures. Combustion sources burning fossil fuels tended to emit less TCDD's than those burning waste products.

TABLE 1.

COMBUSTION SOURCES IDENTIFIED IN THE 1984 LITERATURE SURVEY (2)

Source Category	Number of Facilities Tested	TCDD[a]			2,3,7,8-TCDD	
		Sample	Mean	Range	Mean	Range
Municipal Waste Combustors						
USA	6	Stack	3.5 ng/m^3	ND-240 ng/m^3	3.5 ng/m^3	0.30-9.1 ng/m^3
European	13	Stack	25.6 ng/m^3	ND-128 ng/m^3	b	-
Hazardous Waste Incinerators						
Incinerator Ship	2	Stack	ND[c]	ND	-	-
Land Based Incinerators	10(7)[d]	Stack	0.56 ng/m^3	ND-2.5 ng/m^3	ND	e
Sewage Sludge Incinerators	1	Stack	f	f	-	-
Utility Coal Boilers	7	Stack	ND	ND	-	-
Commercial Boilers (Waste Fired)	6(6)[d]	Stack	g	g	-	-
Industrial Boilers (Waste Fired)	6(1)[d]	Stack	10.13 ng/m^3	ND-40.5 ng/m^3	18,000 ppt[h]	ND-55,000 ppt
Activated Carbon Regeneration	1	Stack	0.013 ppt	ND-0.050 ppt	0.019 ppt	ND-0.083 ppt
Residential Wood Combustion	4	Scrapings	329 ppt	ND-777 ppt	242 ppt	26-600 ppt
Mobile Sources	9(4)[d]	Exhaust	4.0 ppt	ND-20 ppt	3.0 ppt	*
Wire Reclamation Incinerators	1	Scrapings	234 ppt	58-410 ppt	-	-
Lime/Cement Kilns (Waste Fired)	1(1)[d]	Stack	g	g	-	-
Accidental Electrical Equipment Fires	2	Wall Swipes	44 ppm[l]	ND-195 ppm	0.059 ppm,	*

[a]TCDD = Tetrachlorodibenzo-p-dioxin.
[b]Dash = No Data.
[c]ND = None detected (Detection limits vary).
[d]Number of tests have been performed, but the results have not been officially reported.
[e] = One datum, no range available.
[f]PCDD scan only. PCDD concentrations ranged from 483 ng/m^3 to 1,140 ng/m^3 with a mean of 739 ng/m^3.
[g]Results have not yet been officially reported.
[h]ppt = Parts per trillion by weight.
[i]Fuels include wood, wood/oil mixture, and natural gas.
[j]Fuels include diesel, unleaded and leaded gasoline. In one test series, exhaust scrapings were analyzed, in the other series, filter medium from exhaust samples.
[k]Includes PCB transformers and capacitor batteries.
[l]ppm = parts per million by weight.

A general characterization of each of the 12 source categories identified in the initial literature survey was made to identify similarities and differences that may affect the magnitude of PCDD emissions from each source. The following broad characteristics emerged. The source categories with the highest TCDD emissions were burning waste materials

Experimental Studies

In addition to gathering PCDD emissions data, all available experimental studies concerning PCDD formation mechanisms for combustion sources were obtained and reviewed in order to identify more specific factors that may contribute to PCDD formation.

There are several unproven hypotheses concerning PCDD emissions from combustion processes. Dow Chemical's "Chemistries of Fire" theory proposes that PCDD's are a natural byproduct of fire and will be formed at some quantities in all combustion processes (5). However, experimental results by Buser and Rappe (6) and an evaluation of data from the literature suggests that PCDD's are emitted only under limited conditions. The most prevalent theories, including Esposito's formation mechanism (7), involve the incomplete combustion of PCDD's or PCDD precursors. Although there is some disagreement of the definition of PCDD precursors, they are defined in this paper as chlorinated aromatics that can product PCDD's through bimolecular reactions and thermal rearrangements. Examples include chlorinated phenols and chlorinated benzenes. PCDD precursors may be thermally rearranged during incomplete combustion to form PCDD's. Also, when PCDD's are present in the feed to a combustion source, they can escape with the fine particulate if the destruction efficiency is low.

Neither the Dow hypothesis nor the precursor hypothesis is conclusively supported or refuted by the available data. Recent studies involving pyrolysis of wood with and without chlorination, in conjunction with studies of pyrolysis of chlorinated coal, suggest that any organic material combusted in the presence of high levels of inorganic chlorine may lead to PCDD formation under certain conditions.

Based on the literature review, the following factors are believed to affect dioxin emissions:

- Waste composition
  - PCDD In feed,
  - Precursors in feed,
  - Chlorine in feed,
- Combustion conditions
  - Residence time,
  - Oxygen availability,
- Waste characteristics
  - Feed processing, and
  - Supplemental fuel (variability and Btu value)

The interaction of these factors in PCDD formation mechanisms is not well understood. In addition, quantitative data concerning waste compositions is generally not available for many waste materials that are combusted and combustion conditions are not well defined for many combustion devices and are largely determined by site specific operating practices.

Source Category Prioritization

Despite these limitations the factors listed above in conjunction with available TCDD emissions data were used to subjectively rank all combustion sources for the purpose of the Tier 4 source tested program. A short list of combustion sources was developed by excluding those sources burning or using a relatively clean feedstock or fired with fossil fuels, such as coal, oil or gas, and those source categories which are fairly small or intermittent in nature, examples include incinerator ships and coffee roasting. The remaining sources were then divided into 4 groups ranked A-D using the rationale outlined in Figure 2. The ranks are defined as follows:

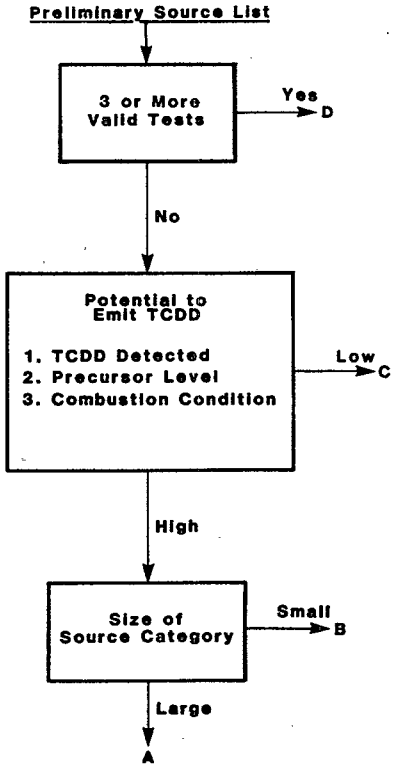


Figure 2. Ranking Flow Chart.

Rank A are large source categories (greater than 1 million tons of fuel and/or waste burned annually) with elevated dioxin precursor contamination of feed/fuel. These categories are judged to have a high potential to emit TCDD. Rank B are small source categories (less than 1 million tons of fuel and/or waste burned annually) or source categories with limited dioxin precursor contamination of feed/fuel. These categories have some potential to emit TCDD. Rank C are source categories less likely to emit TCDD. Rank D are source categories which have already been tested three or more times.

The ranked list was then used as the focus of the source test program. Preliminary cost estimates indicated that only 10-12 source tests could be performed with the available budget. With this limitation in mind, a decision was made to test three facilities for each of the two rank A source categories, and a single facility in each of the rank B categories. Through supplementary coordination with other in-house programs, samples were also planned for mobile sources and woodstoves.

Test site selection began in August 1984. This effort was initially focused on the rank A categories, sewage sludge incinerators and black liquor boilers. The site selection process involved identifying candidate sources from lists of sites provided by State and EPA Regional offices, trade associations and previous EPA studies. The lists were narrowed to three or four candidate sites using data on facility size, age, type of combustion device, etc. Each of the candidate sites on the short list was then contacted by telephone to explain the Tier 4 program, to gather further site specific information, and to ascertain if they were interested in participating in the program. Pretest survey visits were conducted at least two candidate sites per source category. For the rank A source categories, an attempt was made to pick at least one average source within the source category and one worst case candidate. For the rank B categories, attempts were made to select worst case sites with respect to PCDD emissions.

As the program progressed it became evident that it was very difficult to define the conditions which constitute worst case with respect to potential PCDD emissions. Very little if any PCDD or precursor information was available for the selected source categories, and the relative combustion conditions within the source category were not always known. For these reasons, a great deal of reliance was placed upon the total chlorine content of the primary feed materials to the combustion device as an indication of worst case conditions. For example, further information was found concerning the sources and levels of chlorides in black liquor circuits at Kraft pulp mills. During the initial source category selection process, black liquor boilers associated with the pulping of salt laden wood were suspected of having the highest chlorine content. After visits to numerous mills a brief literature survey and receipt of chlorine analyses for several mills it was discovered that very little wood is now stored in salt water prior to pulping. In addition black liquor with chlorine contents of 0.1 percent to 2 percent have been identified and a study was found with discussed the potential for chlorobenzene formation from combustion of black liquor (8). The highest chlorine content black liquor was associated with a mill that uses spent acid from the chlorine dioxide generator as a source of salt cake make up.

As the site selection process continued, additional source category specific data became available, and as a result, some changes were made to the ranked list. Table 2 presents the initial and final ranked list. The changes to the list are briefly discussed below. Commercial boilers firing waste oils were dropped from the rank A category because the proposed RCRA amendments would preclude the burning of waste oils blended with chlorinated solvents as other hazardous wastes. Combustion of wood treatment plant sludges containing pentachlorophenol and/or creosote (K001 waste) in boilers was identified as a rank B candidate in the initial list. Following contacts with the major wood treating companies and with various regulatory agencies, this category was dropped from rank B to rank C. All of the wood treatment companies claimed to be either landfilling the sludge or incinerating the sludge in a hazardous waste incinerator.

TABLE 2. RANKED SOURCE CATEGORY LISTS FOR PCDD TESTING

Initial List - March 1984	Current List - March 1985
Rank A	
Sewage Sludge Incinerators	Sewage Sludge Incinerators
Black Liquor Boilers	Black Liquor Boilers
Commercial Boilers	
Rank B	
PCP Sludge	Carbon Regeneration
Carbon Regeneration	Wire Reclamation
Charcoal Manufacture	Industrial Incinerators
Wire Reclamation	Salt-Laden Wood Fired Boiler
	Secondary Metals Blast Furnace
	Drum & Barrel Furnace
Rank C	
Mobile Sources	Mobile Sources
Wood Stoves	Wood Stoves
Wood Fired Boilers	Small Spreader Stoker
Small Spreader Stoker	Commercial Boiler
Hazardous Waste Incinerators	PCP Sludge
Lime/Cement Boilers	Lime/Cement Boilers
Rank D	
Municipal Waste	Municipal Waste
Industrial Boilers Firing Hazardous Waste	Industrial Boilers Firing Hazardous Waste
Hazardous Waste	

Charcoal manufacturing facilities were dropped from rank B to rank C because all facilities contacted were processing untreated forest scraps and not sawmill slabs that might have been pretreated with chlorophenols for Sapstain control.

In addition to these changes in the source category ranking, three categories were added to the source test program; these are industrial incinerators, secondary metals blast furnaces, and drum and barrel reclamation furnace.

Several industrial incinerators were identified during the course of the site selection process. Further investigation showed this to be a large category in terms of numbers of units nationwide (9). Solid waste materials burned in these units often contain appreciable levels of chlorine. In addition, most incinerators are fairly small and batch fed resulting in poor combustion conditions. One site selected for Tier 4 testing burns polyvinyl chloride (PVC) coated wood scraps that have been treated with pentachlorphenol. The secondary metals blast furnace source category was also added to the source test list. Some blast furnaces in the secondary metals industry process metal bearing scrap that contains plastics including PVC (10). PCDD has previously been detected in the baghouse dust from one such facility.

Drum and barrel reclamation furnaces were added to the list because of the large number of facilities, the diverse nature of wate materials combusted during the drum burning process and because of the relatively poor combustion conditions encountered (11).

The Source Test Program

A total of twelve complete source tests will be conducted as part of the source test sampling program. The anticipated schedule is shown in Table 3. In addition, one woodstove will be sampled and two mobile source samples will be analyzed. The test program is

complex and involves characterization of combustion device conditions using continuous emissions monitors in addition to Modified Method 5 sampling for PCDD's following the draft ASME protocol (12). Samples of the feed materials to the combustion device will be sampled and analyzed for chlorine and precursor content. Ash and soil samples will be collected and analyzed for PCDD's. The sample matrices for the first 5 tests are shown in Table 4.

All testing is expected to be completed by July 1, 1985. Only limited PCDD analytical results are available at this time. All results will be presented in the final Tier 4 report which is scheduled for completion in late 1985. Results of the study will also be included in a report to Congress scheduled for December 1985.

Ash Sampling

A total of 40 ash samples will be collected for combustion sources selected by EPA regional offices. Analysis of these samples will supplement the source test data.

TABLE 3. TIER 4 SOURCE TEST SCHEDULE

Test Number	Schedule	Source Category
1	October 1984	Sewage Sludge Incinerator #1
2	November 1984	Industrial Incinerator (Wood/Plastic)
3	November 1984	Sewage Sludge Incinerator #2
4	December 1984	Black Liquor Boiler #1
5	February 1985	Black Liquor Boiler #2
6	March 1985	Wire Reclamation Incinerator
	March 1985	Wood Stove*
7	April 1985	Wood Fired Boiler
8	April 1985	Black Liquor Boiler #3
9	May 1985	Industrial Carbon Regeneration Furnace
10	May 1985	Secondary Metals Blast Furnace
11	June 1985	Sewage Sludge Incinerator #3
12	June 1985	Drum and Barrel Reclamation Furnace or Coal Fired Spreader/Stoker Boiler

*This test is being conducted jointly with an AA EPA program, the integrated air cancer project.

TABLE 4. SUMMARY OF TIER 4 SAMPLE MATRICES

Sample Stream	Site 01 SSI-A	Site 02 ISW-A	Site 03 SSI-B	Site 04 BLB-A	Site 05 BLB-B
Primary Feed Materials	Sewage Sludge	Wooden Wastes	Sewage Sludge	Black Liquor	Black Liquor
Auxiliary Fuels	No. 2	No. 2	None Fuel Oil	None Fuel Oil	None
Combustion Air	Yes	Yes	No	No	No
Combustion Device Outlet	CEM, MM5	CEM, MM5, HCl	CEM	CEM, MM5	CEM, MM5
Control Device Outlet	MM5	NA	MM5	MM5, HCl	MM5, HCl
Combustion Device Bottom Ash	Yes	Yes	Yes	NA	NA
Emission Control Device Ash	Scrubber Blowdown	NA	Filtered Scrubber Blowdown	No	No
Other Plant Materials	No	No	No	Yes	Yes
Soils	Yes	Yes	Yes	Yes	Yes

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POWDERED ACTIVATED CARBON TREATMENT (PACT™) OF LEACHATE FROM THE STRINGFELLOW QUARRY

William M. Copa, Ph.D.[1]
Marvin J. Dietrich[1]
Patrick J. Canney[2]
Tipton L. Randall[1]

(1) Zimpro Inc., Rothschild, WI 54474
(2) Casmalia Resources, Santa Barbara, CA 93108

ABSTRACT

The PACT™ process, which incorporates the use of powdered activated carbon in a conventional activated sludge system, was used to treat leachate from the Stringfellow Quarry. Wastewater characterization of this leachate indicated that a high proportion of the organic content was biologically refractive but adsorbable on carbon. Laboratory screening tests indicated that this particular leachate was ammenable to treatment by the PACT™ process. Demonstration scale PACT™ treatment of the leachate was conducted at the Casmalia Resources landfill site using a 1000-5000 GPD (gallon per day) trailer mounted PACT™ unit. Stringfellow leachate was pretreated by lime precipitation for heavy metals removal prior to PACT™ treatment. Chemical Oxygen Demand (COD) reductions in excess of 72 percent, along with removal of organic priority pollutants, were achieved in this PACT™ demonstration study.

INTRODUCTION

The State of California has embarked upon an investigation of the feasibility of using alternative technologies to safely reduce, recover, treat, and destroy hazardous wastes, and thereby, reduce its dependency on land disposal of toxic wastes. The intent of the investigation is to document the availability of alternative waste management technologies and to help redirect the State's hazardous waste management program toward the development and implementation of these technologies. The alternative waste treatment technologies were categorized as follows:

- Physical Treatment
- Chemical Treatment
- Biological Treatment
- Incineration
- Stabilization/Solidification Treatment

The PACT™ wastewater treatment process, which combines powdered activated carbon with the biological activated sludge process, is one of the alternative technologies investigated by the State of California. In treating hazardous wastewaters, the PACT™ process offers a combination of physical treatment, biological treatment, and solidification treatment. The PACT™ process would appear to be ideally suited to the treatment of high-priority wastewaters containing pesticides, halogenated organics, or non-halogenated volatile organics.

The present study reports on the demonstration of the PACT™ process as an alternative technology for the treatment of leachate from the Stringfellow Quarry. The Stringfellow Quarry leachate can be classified as a high-priority wastewater containing halogenated and non-halogenated volatile organics as well as heavy metals. The PACT™ demonstration study consisted of a preliminary laboratory screening and waste

characterization followed by a continuous, large scale PACT™ treatment of the Stringfellow Quarry leachate at the Casmalia Resources landfill site in Santa Barbara, County, California.

THE PACT™ PROCESS

The PACT™ wastewater treatment process consists of the addition of powdered activated carbon to the aeration basin of a biological activated sludge system. The combination of physical adsorption with biological oxidation and assimilation, which is accomplished in PACT™ wastewater treatment, has been shown to be particularly effective in treating wastewaters which are variable in concentration and composition, highly colored, or contain materials which are refractive or potentially toxic to biological growth. The characteristic advantages of the PACT™ wastewater treatment process over conventional activated sludge are:

1. High BOD and COD removals.

2. Stability of operation with variability in influent concentration and composition.

3. Enhanced removal of toxic substances and priority pollutants.

4. Effective color removal.

5. Improved solids settling.

6. Supression of volatilization of organics.

The PACT™ wastewater treatment system operates in accordance with the flow diagram shown in Figure 1. Influent wastewater flows to the aeration tank where the wastewater is mixed with powdered activated carbon and biological solids. The wastewater-carbon-biological solids mixture is aerated for a sufficient period of time (Hydraulic Detention Time - HDT) to effect biological oxidation and assimilation of the biodegradable content of the wastewater. After aeration, the mixture flows to a clarifier where the powdered carbon and biological solids are settled and separated from the treated wastewater. The clarifier overflow (treated wastewater) is discharged from the PACT™ system. The clarifier underflow solids are returned to the aeration tank on a continuous basis to maintain a desired concentration of powdered activated carbon and biological solids.

A portion of the biological solids and spent powdered activated carbon is wasted daily from the PACT™ system. The wasted solids are directed to an aerobic digester for solids storage and stabilization. Solids remaining after aerobic digestion would be periodically wasted to a solids disposal system. Specifically for this PACT™ demonstration study, the wasted solids were dewatered in a filter press. The dewatered cakes were placed in drums and ultimately disposed of in the Casmalia Resources landfill.

Because powdered activated carbon is wasted with the excess biological solids, virgin powdered activated carbon addition is required, on a daily basis, to maintain the desired aeration basin carbon concentration. The addition rate of virgin carbon is determined by treatment requirements, waste load and wastewater characteristics.

LEACHATE CHARACTERIZATION

A composite sample of leachate from the Stringfellow Quarry was analyzed using standard wastewater examination methods(1,2). The composition of the leachate is shown in Table 1. The composite sample of leachate was acidic, brown colored, and contained some suspended solids.

The Stringfellow Quarry leachate was also analyzed for fifteen heavy metals. Both total and soluble heavy metal concentrations were determined on the initial composite sample (see Table 2). The precipitation of the heavy metals as their hydroxides was evaluated by the addition of sodium hydroxide to adjust the pH of the leachate to 7.0 and 9.0. The concentration of the heavy metals remaining in solution in the leachate at pH 7.0 and 9.0 is also reported in Table 2.

LABORATORY PACT™ SCREENING TESTS

Laboratory PACT™ screening tests consisted of generating physical and biophysical adsorption isotherms on the Stringfellow Quarry leachate. A physical adsorption isotherm was generated by adjusting the pH of the composite leachate to 7.0 and contacting this full strength material with varying concentrations of powdered activated carbon (ICI Hydrodarco H) for two hours. After the two hour contact period, the mixtures were filtered and the filtrates were analyzed for COD, Color, etc. A biophysical adsorption isotherm was obtained in a similar manner except that a small portion of activated sludge biomass, sufficient to effect a biomass concentration of approximately 2000 to 4000 mg/l, was added to each portion of leachate along with the varying amounts of powdered activated carbon. Also, the leachate samples were aerated during the two hour contact time. The filtrates were analyzed for COD, color, etc., just as in the generation of the physical adsorption isotherm. Data obtained in this manner are shown in Table 3. The adsorption isotherm data were plotted according to the Freundlich equation ($\log x/m = \log k + 1/n \log C$) to determine the isotherm constants (see Figure 2). Inspection of the physical and biophysical isotherms, Figure 2, shows that the physical isotherm is linear over the wide range of effluent COD values but that the biophysical isotherm deviates from the Freundlich equation at high loading rates (low carbon doses). This may imply that biological removal, by adsorption on the biomass or by biological assimilation, is the principle mechanism for removal of COD at low carbon doses but that physical adsorption is the principle mechanism at high carbon doses. The isotherms also show that a higher COD removal can be achieved in the biophysical system compared to the physical system with similar carbon doses.

The biophysical isotherm can be used, in conjunction with other waste treatment principles, to select operating parameters for the PACT™ process. Consider the biophysical isotherm shown in Figure 2. If a treated Stringfellow leachate effluent with a COD of 500 mg/l is desired, a powdered activated loading rate of approximately 115 mg COD/gram carbon is required. For an influent COD of 2000 mg/l, a mixed liquor carbon concentration of approximately 13 g/l would be required. With the choice of a nominal solids retention time (10 days) and a net biological cell yield (0.15 lbs. biomass/lb. COD removed), a practical food to microorganism (F/M) ratio can be targeted(3). The F/M ratio can then be used to determine the required wastewater hydraulic detention time for a given microorganism concentration. In this manner, all of the initial PACT™ process parameters can be established.

PACT™ DEMONSTRATION STUDY

PACT™ Process Equipment

The PACT™ demonstration unit, supplied by ZIMPRO INC., is a complete PACT™ wastewater treatment system mounted on a flatbed trailer (see Figure 3). The demonstration unit is capable of treating 1000 to 5000 gallons per day (GPD) of industrial or municipal wastewater, depending upon the strength of the wastewater and the degree of treatment required.

The demonstration unit was equipped with a six foot diameter (2580 gal.) aeration tank containing eight Sanitaire coarse bubble air diffusers. The air diffusers were fed by a variable speed Roots blower which has an output capacity of 40 to 100 SCFM of air. The demonstration unit also had an eight foot diameter clarifier, equipped with a collector rake mechanism. A 500 gallon tank is provided for collection of wasted carbon and biological solids. The demonstration unit is also equipped with a pH control system, three chemical feed tanks, and peristaltic pumps to feed chemicals, e.g. nutrients, polymers, etc. The PACT™ demonstration unit was operated according to the process flow diagram shown in Figure 1 throughout this demonstration test.

Two 20,000 gallon Baker portable storage tanks were installed to store the influent waste prior to treatment in the PACT™ demonstration unit. For the duration of the demonstration test, leachate from the Stringfellow landfill was received at the Casmalia Resources waste disposal facility. The leachate was stored in an open pond. On a batch basis, leachate was mixed with lime sludge (pH adjusted to 9.0) to precipitate heavy metals. After settling, the clear supernatant was then pumped to the Baker storage tanks for subsequent use in the PACT™ demonstration unit.

The PACT™ demonstration unit was equipped with a one square foot pilot filter press. The filter press was equipped with ten recessed, cast iron plates capable of producing 1 1/4 inch thick dewatered filter cakes. In operation, waste sludge was initially pumped to the empty press. The filtrate was discharged into the Casmalia Resources site evaporation ponds. The filter press run was terminated when the filtrate flow decreased to a small trickle. After pressure release, the moveable end of the filter press was retracted and the dewatered filter cakes were allowed to drop into a collection hopper. The dewatered cakes were drummed and deposited in the Casmalia Resources landfill, for ultimate disposal.

PACT™ Startup and Operation

The PACT™ demonstration study was initiated on July 18, 1984. The PACT™ demonstration unit was started by adding approximately 2300 gallons of mixed liquor obtained from the Lompoc, California wastewater treatment plant, to the aeration tank. Four 50 lb. bags of ICI Hydrodarco H powdered activated carbon were added to the mixed liquor and the entire mixture was aerated to sustain biological activity and provide uniform mixing. Acclimation of the PACT™ system to the Stringfellow Quarry leachate was initiated on July 19, 1984. The feed rate of Stringfellow leachate was initially set at a low rate, approximately 0.4 gallons per minute, and was gradually increased throughout the acclimation period.

The start-up and acclimation period required approximately forty five days and was confounded by reoccurring aeration blower malfunctions. Ultimately the aeration blower was replaced and, except for periodic plugging of the feed line, the remainder of the operation of the demonstration study proceeded smoothly. When the PACT™ system was acclimated to the Stringfellow leachate waste, as indicated by a substantial oxygen uptake of approximately twenty mg per liter per hour or greater, the operation was guided by controlling the selected PACT™ process parameters:

Hydraulic Detention Time (HDT) = 16 hours

Solids Retention Time (SRT) = 10 days

Mixed Liquor Suspended Carbon (MLSC) = 10,000 mg/1

Carbon Dose (CD) = 667 mg/1

The HDT was gradually reduced as the study progressed, to the desired value of 16 hours which corresponds to the maximum feed rate of 2.6 gallons per minute. The SRT was varied only when the wasting rate was interrupted because of decreased oxygen uptake. Throughout the PACT™ demonstration study, sodium hydroxide solution was added to the aeration basin to maintain a target pH range of 6.5 to 7.5. An automatic pH controller was used to facilitate this pH control.

Ammonia and phosphorus nutrients were added to the waste stream as ammonium chloride and di-ammonium phosphate. Levels of nutrient addition were adjusted in an attempt to obtain, at steady state operation, effluent ammonia nitrogen and phosphorus concentrations in the range of 1 to 5 mg/l. In the screening of Stringfellow leachate, both ammonia and phosphorus nutrient deficiencies were indicated but trace nutrient levels were assessed to be adequate.

PACT™ Operational Testing

During the acclimation and operational testing period, the PACT™ unit operation was monitored by implementation of a routine sampling and analysis schedule. Analyses performed three times per week were COD, BOD, suspended carbon, suspended biomass, total Kjeldahl nitrogen, ammonia nitrogen, and total phosphorus. The three time per week analysis schedule, showing sample streams and respective analyses performed, is outlined in Table 4. In addition, as shown on the analysis schedule, biweekly samples of influent and effluent were analyzed for specific toxic components, i.e. volatile organic chemicals, associated with the Stringfellow leachate.

PACT™ operational parameters that were determined on a daily basis are as follows:

1. Dissolved Oxygen (DO) in the aeration basin and clarifier.

2. Temperature of the aeration basin and clarifier.

3. pH of mixed liquor in the aeration basin.

4. Total hydrocarbon concentration in the aeration basin offgas - monitored only until the Santa Barbara County APCD was assured that hydrocarbon air emissions were not significant.

5. Influent and recycle flow rates.

6. Weight of powdered activated carbon added to the system.

7. Volume of mixed liquor wasted from the system.

8. Oxygen uptake of the mixed liquor biological solids.

Results and Discussion

The PACT™ demonstration study was conducted between July 18, 1984 and October 17, 1984 at the Casmalia Resources waste disposal facility. The wastewater that was used throughout this study was leachate from the Stringfellow Quarry. A sample of Stringfellow leachate was screened by laboratory testing and was shown to be treatable by the PACT™ process. The Freundlich physical and biophysical adsorption isotherms, which indicated carbon loading rates, organic removal efficiencies, and biological uptakes, were used to assess PACT™ treatability.

A performance summary for the PACT™ demonstration study is shown in Table 5. This summary shows operational and analytical data averaged for the entire study (7/18/84 through 10/17/84) and for the steady state period (9/10/84 through 10/17/84). This summary shows that, on the average, a 72 percent COD reduction, an 82 percent BOD reduction, and a 72 percent DOC reduction were achieved throughout the entire study. Similar average COD, BOD, and DOC reduction were achieved during the steady state operation, i.e., 74, 89, and 71 percent. The COD parameter of this particular wastewater, which had a low BOD:COD ratio, was the chosen parameter for monitoring overall treatment performance. The average COD removal for the entire PACT™ study period was 72 percent. A plot of influent and effluent COD, for the entire length of the study, is shown in Figure 4. As would be expected with a waste feed prepared on a batch basis, the influent COD was relatively constant with only small variations. Effluent COD values indicated consistently good removal efficiencies and varied between 345 and 733 mg/l. The plot of influent and effluent COD also indicates a consistent removal efficiency with increasingly stable values as the PACT™ process became fully acclimated in the latter half of the study. The COD removal data also indi-

cate that the mechanical problems (i.e. aeration blower malfunction) and the interrupted wasting of solids did not appreciably effect the COD removal efficiency. This overall result attests to the reliability of the PACT™ process, but more importantly, may indicate that the basic mechanism for organic removal may indeed be physical adsorption.

The influent BOD values were consistently low throughout the entire study. The influent BOD values ranged between 15 and 127 mg/1. These low BOD values reflect the difficulty in obtaining a culture of biological organisms (BOD seed) that can readily assimilate the complex organic compounds present in this wastewater. The effluent BOD values are quite variable, with values ranging between <1.0 and 73 mg/1.

The suspended solids in the effluent averaged 17.2 mg/1 for the entire study. This concentration of suspended solids is comparable to that obtained from an efficiently operating municipal wastewater treatment plant. Improved effluent quality, i.e. lower suspended solids, could be obtained by tertiary filtration of the effluent in a sand filter, prior to discharge.

Throughout this PACT™ demonstration study, color removal was relatively low. The PACT™ process is normally very effective in removing color from wastewaters. The lack of color removal in the PACT demonstration study is in direct conflict with the laboratory PACT™ screening test which indicated nearly complete color removal. The explanation of this conflicting data is not evident at the present time.

Organic priority pollutant analyses were obtained during this PACT™ demonstration study. The base neutral, acid fraction, and pesticide analyses of influent and effluent samples indicate that essentially all organic priority pollutants were removed by the PACT™ process. The effluent base neutral fraction did however contain certain phthalates which are believed to have been leached from the plastic pipe and tank coatings of the PACT™ demonstration unit.

Volatile organic chemicals (VOC's) were known to be present in the Stringfellow leachate and were designated as the specific toxic component of this wastewater. Analyses of the influent wastewater for VOC's indicates the presence of benzene, chlorobenzene, dichloromethane, chloroform, 1,2-dichloroethylene, trichloroethylene, tetrachloroethylene, ethyl benzene, and toluene in nearly all of the influent samples at detectable levels. Dichloromethane is the only VOC detected in the effluent samples and may be due to laboratory contamination. Dichloromethane is used in the extraction of base neutral and acid priority pollutant fractions and is commonly detected due to cross contamination in the laboratory. All other VOC's, present in the feed wastewaters, were completely removed (below limits of detection) by the PACT™ process.

The offgas from the aeration basin was monitored for total hydrocarbon (THC) concentration, to assess stripping of organics from the aeration basin. THC levels were shown to range between 2.5 and 11 parts per million (volume/volume) expressed as methane. This THC level is comparable to the background level of THC at the Casmalia Resources disposal facility, and verifies that the PACT™ process does indeed limit the volatilization of organics from the aeration basin.

A complete report on this study, which contains all of the tabulated operational parameters, analytical data, and the Quality Assurance Plan, has been submitted to the State of California Department of Health Services[4].

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Table 1. Composition of Stringfellow Quarry Leachate
(Values in mg/l except pH and Color)

Constituent	Composite Leachate (used for waste characterization)
COD	3550
BOD_5	<60
DOC	856
SS	6300
VSS	700
pH	3.27
Color (APHA)	860
Total Solids	31,200
Total Ash	24,200
TKN	32.6
NH_3-N	14.4
NO_3-N	14.0
NO_2-N	<0.5
Total Phosphate as P	2.5
Soluble Ca	407
Soluble Mg	540
Soluble Cl	303

Table 2. Metal Content of Stringfellow Quarry Leachate Before and After pH Adjustment (Values in mg/l)

	Composite Leachate		pH Adjusted Leachate	
	pH = 3.27		pH = 7.0	pH = 9.0
Metal	Total	Soluble	Soluble	Soluble
Cu	15.4	12.5	0.52	0.13
Cr	98.2	77.5	0.09	0.11
Zn	536	465	24.4	0.09
Hg	<0.002	<0.002	<0.002	<0.002
Pb	7.1	1.6	0.4	0.27
Cd	2.4	1.8	1.0	0.04
As	0.1	0.007	<0.004	<0.004
Sb	2.4	0.65	0.6	0.5
Co	3.6	3.2	0.2	0.17
Fe	851	363	162	2.1
Tl	0.14	0.9	0.8	0.7
Ni	15.8	15.8	0.5	0.002
Ag	3.0	0.06	0.4	0.05
Ba	1.6	0.07	0.3	0.08
Se	0.036	<0.002	0.022	<0.002

Table 3. Data for Physical and Biophysical Isotherms
COD and Color Removal from Stringfellow Quarry Leachate

	Physical Isotherm				Biophysical Isotherm			
Carbon Dose, g/l	COD mg/l	mg COD / gc	Color APHA	APHA / gc	COD mg/l	mg COD / gc	Color APHA	APHA / gc
0	2310	-	223	-	1930	-	148	-
0.8	2150	200	142	102	1870	550	94	161
1.6	2020	181	106	73	1690	388	75	92
3.2	1790	163	76	46	1563	233	64	50
6.4	1370	147	50	27	1520	123	49	27
12.8	870	112	16	16	617	132	20	16
25.6	410	74	13	8	279	79	8	8

Table 4. PACT™ Demonstration Study
Sampling and Analysis Schedule

Analysis	PACT™ Influent	PACT™ Effluent	Mixed Liquor	Aeration Tank Offgas
COD	3 times/week - C*	3 times/week - C		
BOD	3 times/week - C	3 times/week - C		
DOC	3 times/week - C	3 times/week - C		
TKN	3 times/week - C	3 times/week - C		
NH_3-N	3 times/week - C	3 times/week - C		
Phosphorus	3 times/week - C	3 times/week - C		
Suspended Solids/Ash	3 times/week - C	3 times/week - C		
pH	3 times/week - C	3 times/week - C	3 times/week - G	
VOC's	Bi-Weekly - G	Bi-Weekly - G		
Priority Pollutants	Once/Study - C	Once/Study - C		
Biomass/Carbon			3 times/week - G	
THC				Daily - G**
Oxygen Uptake Rate			Daily - G	
Dissolved Oxygen			Daily - G	

* C = Composite, G = Grab ** Daily until Santa Barbara County APCD advises otherwise.

Table 5. Performance Summary*
PACT™ Demonstration Study

	Study Dates	
	7/18/84 - 10/17/84	9/10/84 - 10/17/84
Pilot Plant Feed Rate, GPM	1.74	2.43
Hydraulic Residence Time, Days	1.03	0.74
Solids Residence Time, Days	29	15
Mixed Liquor, mg/l:		
Suspended Solids	19850	20780
Volatile Carbon	9150	9700
Volatile Biomass	3590	3240
COD:		
Influent, mg/l	1786	1788
Effluent, mg/l	498	467
Removal, %	72	74
BOD:		
Influent, mg/l	55.6	50.3
Effluent, mg/l	10.1	5.5
Removal, %	82	89
DOC:		
Influent, mg/l	556	535
Effluent, mg/l	154	154
Removal, %	72	71
Suspended Solids:		
Influent, mg/l	92.5	103
Effluent, mg/l	17.2	17.9
Color (APHA Units)		
Influent	174	177
Effluent	128	154

* All values are averages of data acquired throughout the indicated time periods.

FIGURE 1 - PACT™ WASTEWATER TREATMENT SYSTEM FLOW DIAGRAM

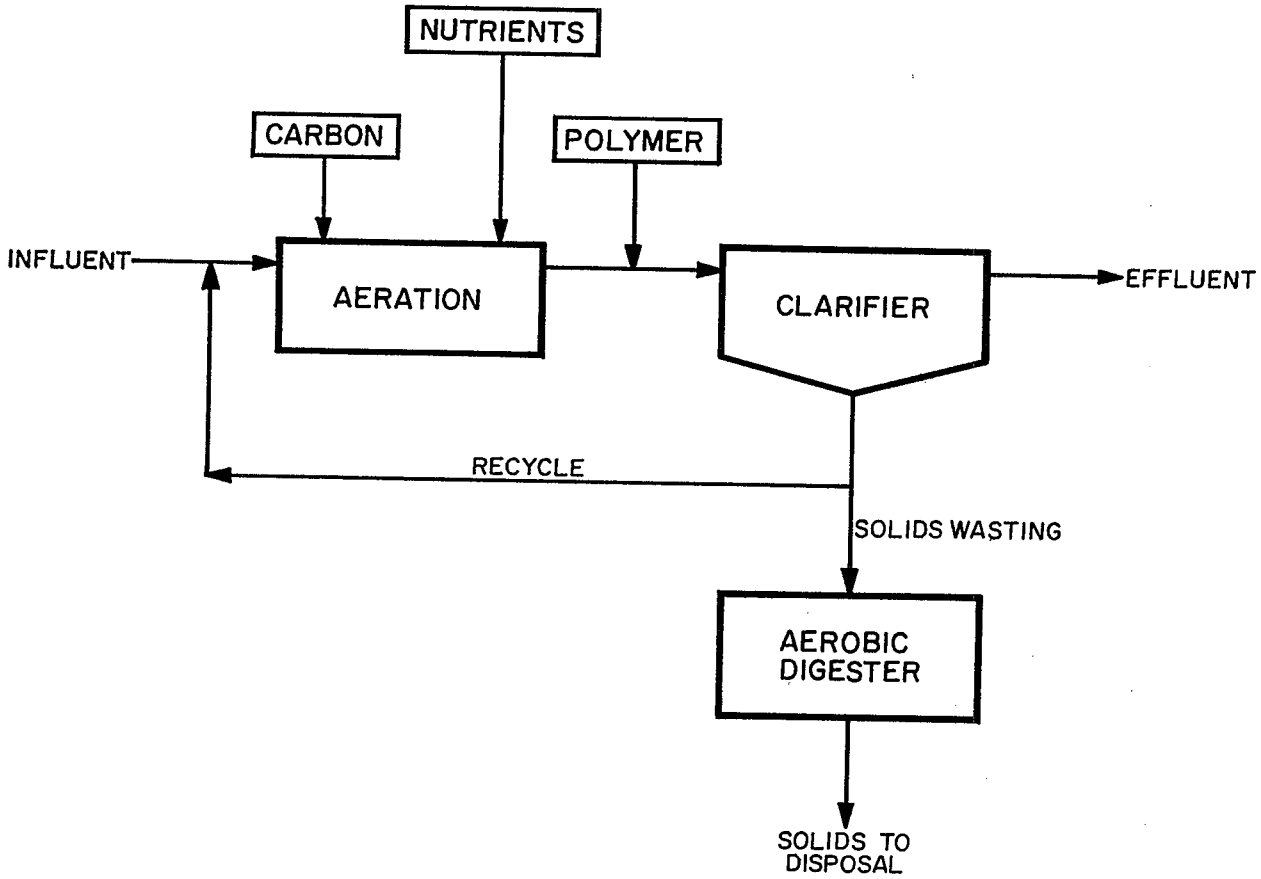


FIGURE 2 - PHYSICAL AND BIOPHYSICAL ISOTHERM
COD REMOVAL FROM STRINGFELLOW QUARRY LEACHATE

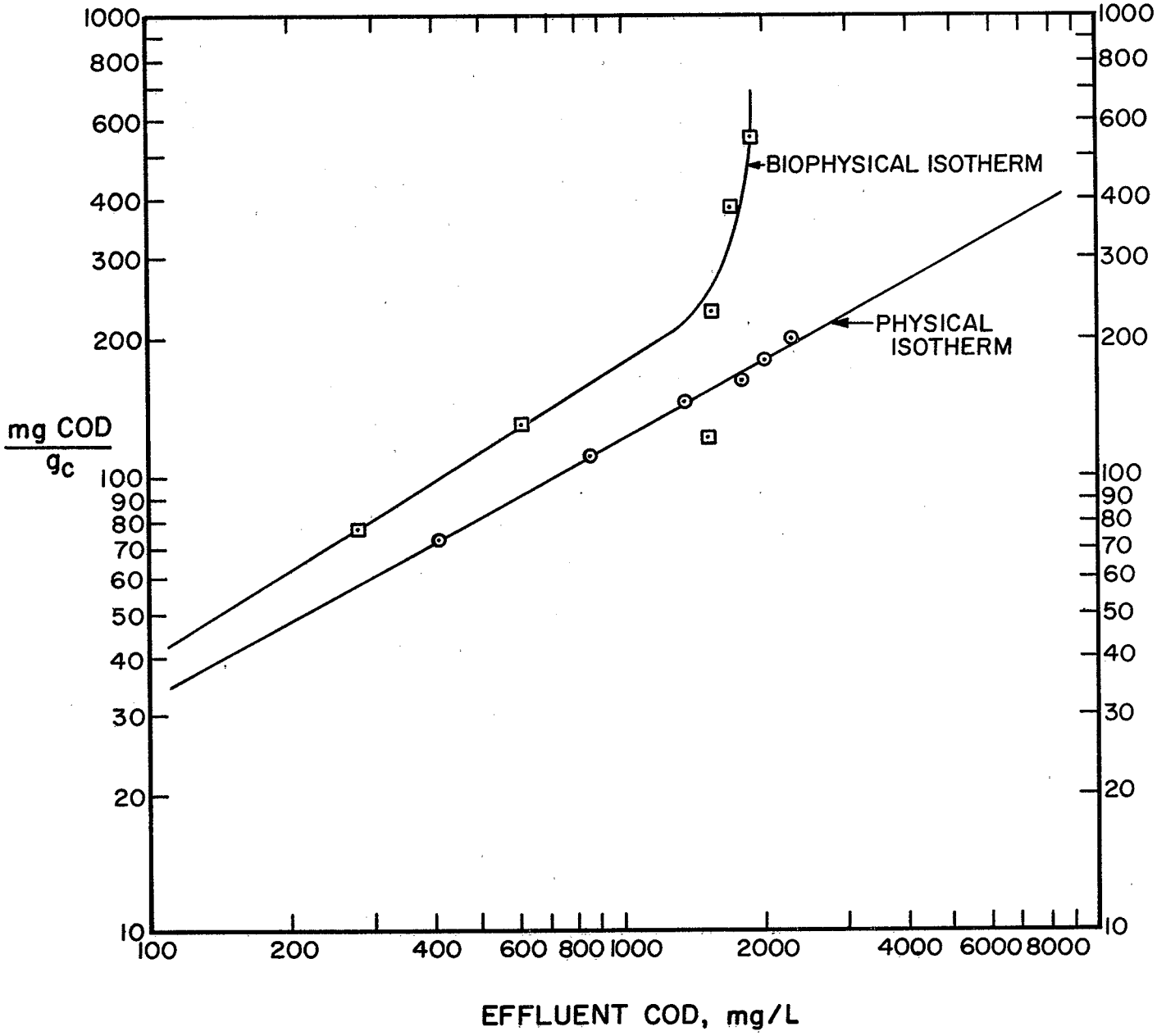


FIGURE 3 - PACT™ DEMONSTRATION UNIT

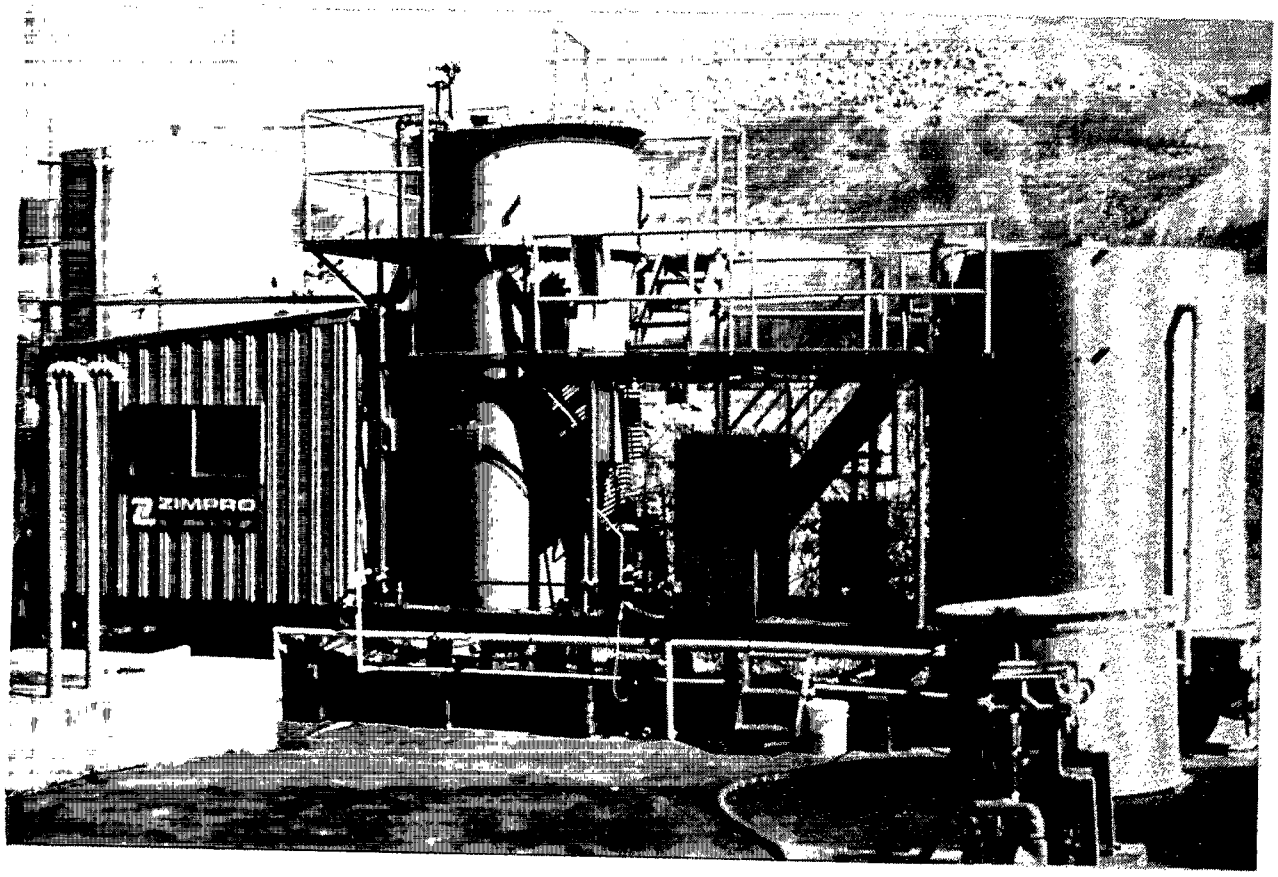
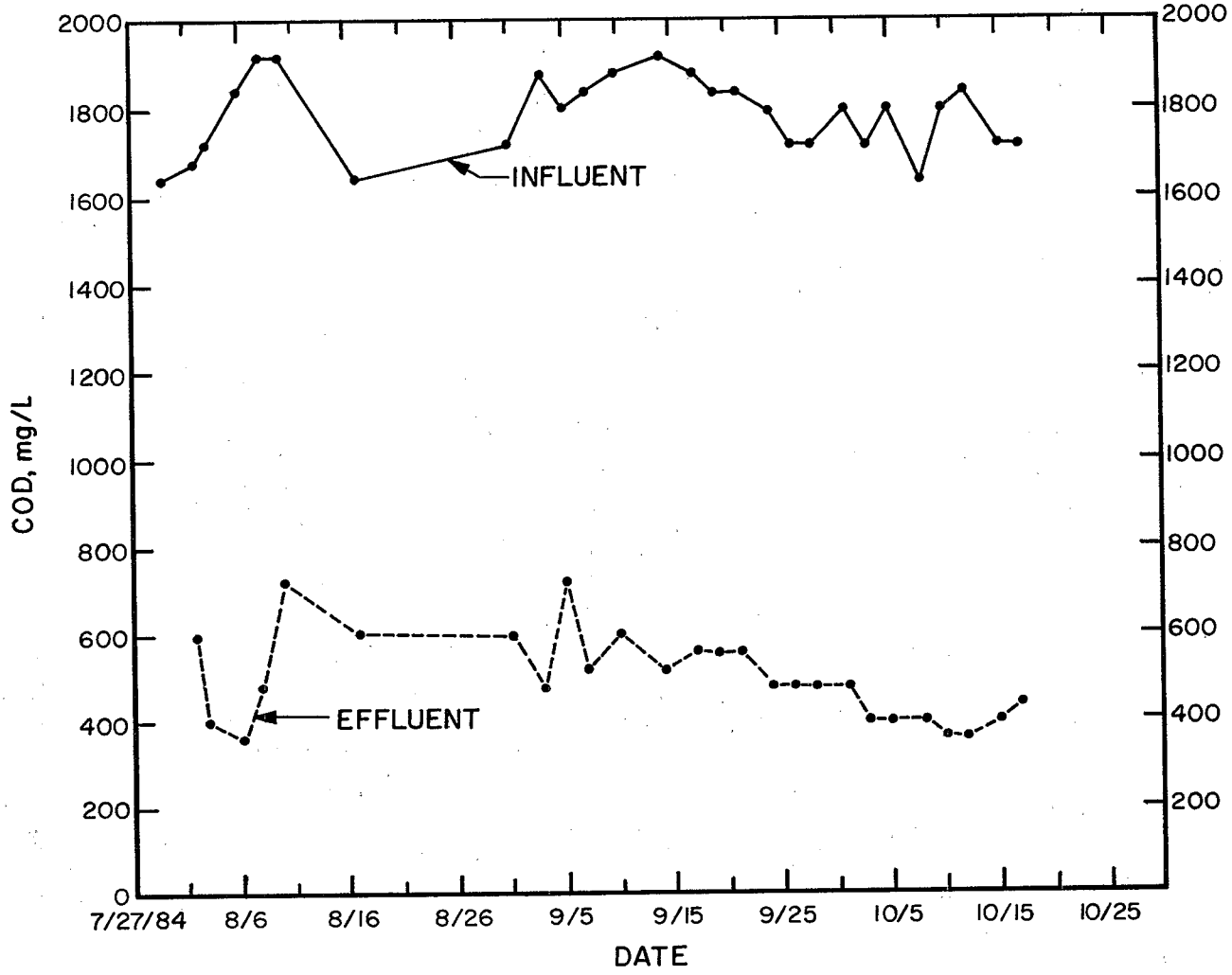


FIGURE 4 - PACT™ DEMONSTRATION STUDY
COD DATA



FIELD TESTING OF PILOT-SCALE APCDs AT A HAZARDOUS WASTE INCINERATOR

Wayne Westbrook
Eugene Tatsch

Research Triangle Institute
P. O. Box 12194
Research Triangle Park, North Carolina 27709

and

Lawrence Cottone

Engineering Science, Inc.
10521 Rosehaven Street
Fairfax, Virginia 22030

and

Harry Freeman
U.S. Environmental Protection Agency
Hazardous Waste Engineering Research Laboratory
Cincinnati, Ohio 45268

ABSTRACT

Pilot scale air pollution control devices supplied by Hydro-Sonic® Systems, ETS, Inc., and Vulcan Engineering Company were installed at the ENSCO, Inc. Incinerator in El Dorado, Arkansas in the spring of 1984. Each of these units treated an uncontrolled slipstream of the incinerator exhaust gas. Simultaneous measurement of the total particulate and HCl in the gas streams were made at the inlet to and exit from the units using an EPA Method 5 sampling train. Particle sizing at both locations using Andersen impactors was also done. The units supplied by Hydro-Sonics® Systems and ETS, Inc. exhibited a high degree of HCl and particulate matter control. The Hydro-Sonic® Tandem Nozzle SuperSub Model 100 gave the best overall performance for HCl and particulate control and ability to accommodate the variable composition of the exhaust gas.

INTRODUCTION

Much hazardous waste generated has characteristics that make incineration the disposal method of choice. Incineration of these wastes must be performed according to the applicable regulations of the Resource Conservation and Recovery Act (RCRA) and State and local regulations. The RCRA regulations specify the destruction and removal efficiency (DRE) that must be achieved for principal waste components and set limits for the emission rates of particulate matter and hydrogen chloride (HCl).

Advancements in air pollution control technologies is a continuing process. Improvements in existing technologies as well as innovative approaches are occurring. It is to be expected that advanced devices claiming better collection efficiency, lower energy consumption, or lower cost than current equipment will be marketed. It is likely that some of these devices are capable of providing better control of emissions from hazardous waste combustion than is now available.

PURPOSE

The purpose of this project is to evaluate innovative air pollution control devices and to test the performance of these technologies on commercial-scale facilities. The specific goals are to examine the cleaning capabilities of each device under specified operating conditions. The pollutants to be monitored are (a) particulates; total mass, and as a function of particle size, and (b) hydrogen chloride (HCl).

The data developed in the project will be used by EPA and others in the waste management technical community to assist in optimizing the control of air emissions from hazardous waste combustion.

APPROACH

Three vendors with pilot units meeting the project criteria agreed to participate. They are HydroSonics® System, Inc.; ETS, Inc.; and Vulcan Engineering. The Hydro-Sonic® pilot unit is a wet scrubber that operates by fine atomization of water into the gas stream resulting in HCl capture and particle growth with final removal by cyclonic action. The ETS, Inc. unit uses dry lime injection for particulate capture. The unit provided by Vulcan Engineering is a high temperature (>550° C, 1000° F) metallic weave filtration system. It is not currently designed for acid gas control. The Ceilcote unit applies an electric charge to the incoming particulate which then adheres to the packing material and is removed by water spray.

Several commercial hazardous waste incineration facilities were contacted to select the host facility for the tests. Of those companies willing to participate, ENSCO, Inc.'s incinerator in El Dorado, Arkansas best met the project criteria.

After a pilot unit was connected to the installed duct work, a slip stream of particulate-laden gas from the emergency bypass stack was drawn through the unit. Inlet and outlet gas streams were sampled simultaneously by EPA Method 5 for the concentration and total mass of the particulate matter and HCl. Particle size distributions were also determined at both locations.

Each APCD vendor operated his own equipment and was allowed to vary conditions to test the performance of the unit. ENSCO operated their facility in a routine manner during these tests. No special fuel blends on operating procedures were used to accommodate the units.

TEST SOURCE DESCRIPTION

The host plant for these tests was ENSCO, Inc.'s incineration complex in El Dorado, Arkansas. This permitted facility primarily incinerates polychlorinated biphenyl (PCB) contaminated oils and capacitors.

The plant is designed to receive and incinerate whole capacitors. The shredded parts are transported with into a rotary kiln. The kiln exit gas passes through a cyclone which removes much of the large suspended particulate matter. The gases then pass into a two-chambered afterburner referred to as the thermal oxidation unit (TOU). The upstream side of the afterburner can be fired with PCB-containing oils or other high Btu liquids.

Gases leaving the TOU are drawn into the custom-designed wet scrubber. This unit consists of two circulating water loops. The first, prequench, loop removes the bulk of the particulate and HCl. Lime slurry is added for pH control. Blowdown is routed to a pond for solids settling. The clarified water is recycled. The second loop is comprised of a jet eductor, knockout vessel, and demister. Fresh makeup water is added to maintain inventory. All blowdown from this loop is used as a makeup to the first loop. No water is discharged from this system except for that evaporated and carried out with the stack gas.

The incinerator typically operates 24 hours per day, 7 days per week. In general, wastes of a specific class are accumulated onsite until sufficient quantity is available for burns of at least one day. This permits achieving and maintaining steady-state incineration conditions. During these tests, wastes accumulated were incinerated on the schedule determined by plant management. No special wastes were burned or excluded. Close contact was maintained with plant personnel so that the APCD testing spanned only one operating condition, insofar as possible.

DESCRIPTION OF APCD CONNECTION TO PLANT

Connection was made to the emergency bypass stack. The stack, located between the TOU and the scrubber, is refractory

lined. Openings around the stack cap were plugged to prevent air infiltration into the stack. A stainless steel duct is connected to a flanged opening in the stack. The duct connects to a vertical section leading to a Hastalloy cooling section. Gas cooling is by direct water spray. A temperature control device mounted at the exit of the cooling section modulates the water flow. The cooled gas was then ducted to the APCD connection via a 12 inch ID 17 feet horizontal run of insulated carbon steel pipe. The APCD gas inlet sample ports are located near the midpoint of this duct. The two ports were on the vertical and horizontal axes perpendicular to the gas flow.

TEST METHOD DESCRIPTION

All emission measurements field work was performed by Engineering Science, Inc., Fairfax, VA, under subcontract to RTI. An RTI project coordinator was onsite to direct the test.

The test program was designed to withdraw a slipstream of incinerator exhaust gas and to test the APCDs performance in removing particulate and HCl. It was necessary, therefore, to measure these pollutants at the inlet to and exit from the air pollution control device (APCD). Sufficient equipment and personnel were available to conduct testing simultaneously at these two locations.

Both the concentration of total particulate in the gas stream and particulate mass per unit time were determined using EPA Method 5. The impinger solutions in the back half of the train were analyzed to obtain equivalent information for HCl. The particle size distribution at both the inlet and outlet test locations was determined using Anderson cascade impactors. Cascade impactors classify particles on the basis of their aerodynamic properties.

Due to the large difference in particle loadings between the inlet and outlet sites, it was not possible to obtain simultaneous impactor runs spanning the same time interval. Typically 5 to 7 minutes operation at the inlet site product optimum stage loadings. Operation for 60 to 90 minutes was required at the outlet location for collection of adequate sample. Impactor runs were arranged to coincide with one or more Method 5 runs.

An onsite laboratory was set up to reduce as much of the test data as possible. Facilities were available to properly clean all of the test equipment, recover samples, and to desiccate the particulate catches. A certified accurate balance was used to weigh all of the samples. A chloride ion-specific electrode and supporting electronics were available to measure chloride concentrations in the Method 5 train back-half impingers. Chloride audit solutions were onsite to audit this procedure.

The impactor data were processed at the conclusion of the test using the Particulate Data Reduction1 (PADRE) data program.

HYDRO-SONICS AIR POLLUTION CONTROL DEVICE

General Description

Lone Star Steel Co. originally developed this wet scrubber to control particulate emissions from various iron and steelmaking operations. It has been used on such sources as electric arc furnaces, coke oven emissions, open hearth steel furnaces, and sintering plants. The scrubbers have also been used on exhaust streams containing uranium hexafluoride and its hydrolysis products with particulate removal efficiency consistently exceeding 99 percent.

There are three versions of the scrubber: The Steam-Hydro, the Tandem Nozzle, and the SuperSub. All versions have the same basic concept. Water is atomized into the waste gas stream forming water droplets of about the same size as the particulate. The gas stream then enters a turbulent contact zone in which the particles are wetted and vapors are absorbed. Particle growth then takes place in an agglomeration zone. Because of the design, a single waste droplet may contain hundreds of micronic and submicronic dust particles. As a result of the growth of droplets containing particulate into increasingly larger size, the initial size of the particulate has only a small effect on its removal. Actual removal of the agglomerated particle is accomplished in a specially designed low-pressure-drop cyclone. Water and particulate are gravity drained from the cyclone bottom, and the cleaned gases exit through the top. Demisters are not required.

The Steam-Hydro employs a supersonic ejector drive to provide the energy for pumping and cleaning the polluted gas. Steam or compressed air is commonly

employed as the working fluid. The gas is drawn into the unit by the ejector nozzle which is fitted with a water injection ring at the exit of the nozzle. The expanding jet causes violent shattering of the water droplets and turbulent mixing of gas and water. The steam version is most attractive when there is a source of waste heat available to generate the high-pressure steam.

The Tandem nozzle scrubber uses a fan drive to pump the polluted gas and to provide the energy to generate the fine water droplets. The system used two subsonic nozzles and agglomeration sections in series. Both nozzles are equipped with water spray rings. The first section serves to condense vapors, remove the larger particulates, and initiate growth of the fine particulate. Additional water is atomized at the exit of the second nozzle and is turbulently mixed to continue the agglomeration of the particles.

The SuperSub version of the system is a combination of the above two system concepts. A small supersonic ejector (steam or air) is located upstream of the subsonic nozzle. The systems main driving force is fan power as in the Tandem Nozzle version. This arrangement provides good water atomization for fine particle control coupled with the lower energy requirements of the fan drive. Water consumption is about the same as a venturi scrubber.

Test Results

Test data for these units were collected between March 15, 1984, and March 23, 1984. Given in Table 1 are the removal efficiency data for total particulate and chloride organized by the APCD operating version. With the exception of two tandem nozzle runs (10 and 11), chloride removal for all combinations was greater than 98 percent. Runs made using recycle water from the ENSCO scrubber show higher removal of chloride than those using freshwater. Since the recycle water contained some alkalinity, this is not surprising. In a commercial application, alkalinity would be added to the scrubbing water. Thus, chloride removals of 99 percent or better should be expected for any version of this unit.

Particulate removal efficiency ranges from about 82 to 88 percent for the Steam-Hydro and Tandem Nozzle versions. The SuperSub version achieved a particulate removal efficiency of about 95 percent. It should be noted that these removal efficiencies refer only to the gas stream brought into the APCD and not the efficiency that might be obtained on the entire gas stream from the ENSCO incinerator. Since the APCD connection to the main gas duct should have resulted in a bias toward the smaller particles, we would expect that substantially higher removal efficiencies would have been obtained if the APCD had been treating the unbiased gas stream.

Shown in Table 2 are the percent mass less than 1 micron at the inlet and outlet of the unit. Much of the particulate matter exists below 1 micrometer, whether at the inlet or outlet of the control device. It must be noted that design philosophy of the unit is to agglomerate fine particles. Thus, it is to be expected that some the submicron particles entering the device exit as particles greater than 1 micron in size. These data indicate that the SuperSub configuration is the most effective of the versions tested for control of the submicron particulate matter from this source.

ETS, INC. DRY SCRUBBER

General Description

The unit has two major components: the dry reactor and a particulate collection device. The patented dry reaction has a number of unique components. The basic operating principles are as follows. Flue gas is directed cyclonically into the reactor. The rotating slinger unit (driven by a hydraulic motor) delivers the dry reactant (usually 200 mesh hydrated lime) perpendicular to the flue gas flow. This creates maximum mixing and intimate contact of the reactant and pollutants. An internal recirculator, with no moving parts, is located above the slinger. This device increases the contact time and enhances removal of the acid gases. The slinger then directs the dry reaction products down and into an expansion section where the larger particles are removed. The finer particulate matter is carried into the particulate collection device.

The particulate collector can be a conventional baghouse, an electrostatic fabric filter (ESFF) baghouse, or a Reduced Entrainment Precipitator (REP)

developed by ETS. The lime dust entrained in the flue gas continues to react with acid gas components throughout the transport ductwork. In addition, the lime dust aids in building a reactive filter cake on the fabric filters. This serves two purposes. First, reaction with acid gas components continues until final particu-particulate removal occurs. Secondly, the precoat assists in removing the fine particulate without excessive pressure drops across the filters.

This system is totally dry. The reactants are delivered as dry powder, not as a slurry required for the spray dryer type scrubbers. The reacted product is also a dry powder and can be handled much as one handles dust collected in a baghouse. Since no water is used at any point in the system, there are no mist carryover problem, little or no corrosion in the exhaust stack which remains dry and minimum loss of stack gas buoyancy since this energy is not used to evaporate water.

Unit Tested

The unit tested has a rated capacity of 2000 ACFM.

The dry scrubber was connected to a pulse jet baghouse which used Nomex® fabric cartridges. An inducted draft fan was located at the outlet of the baghouse forcing the cleaned gas into the 12-inch I.D. vertical exhaust stack.

Test Results

The ETS system was installed during the last week of March 1984. The system was operated and tested during two separate periods, April 1-10 and April 23-26, 1984. Two reactant materials, hydrated lime and nacholite were evaluated for HCl removal effectiveness.

Given in Table 3 are the particulate and HCl removal efficiency data for the two reactants at the various stoichiometries. Six of the nine tests using lime as the reactant indicate an HCl removal efficiency of over 98 percent. Only one of the tests using nacholite achieved over 90 percent HCl removal. The stoichiometric ratio (SR) ranges from 2 to 9 for the tests in which lime was the reactant. The data suggest that the SR for lime must be nearly 3:1 to insure scrubbing efficiencies of 99 percent.

Due to limitation in the feed equipment, nacholite was injected at much lower stoichiometric ratios. The HCl removal efficiency does not appear to correlate with the nacholite/HCl stoichiometric ratio up to a ratio of 1.7. Therefore, from these tests, it is not possible to determine the nacholite/HCl ratio required to achieve 99 percent HCl removal.

The particulate removal efficiencies are calculated strictly from the Method 5 data. No allowance has been made for the reactant materials added in the dry reactor. For most of the runs, the weight of reactant added ranged from about 40 percent to over 100 percent of the weight of particulate entering the system from the incinerator. The reactants added were 100 percent less than 200 mesh (74 micrometers). Obviously some of the material was much smaller and may have passed through the baghouse.

The calculated efficiencies for the first 10 runs were all greater than 90 percent with most in the 95 to 98 percent range. It should be noted that, due to the bias toward smaller particles caused by the slipstream sample withdrawal, this is the removal efficiency for the finer particles in the ENSCO incinerator exhaust gas. Since the unit would be expected to remove the larger particles more easily, the removal efficiency for the total gas stream would be expected to be even higher.

It is suspected that the low efficiencies measured for Runs 11 through 16 were due to persistent difficulties in sealing the cartridges in the baghouse. In addition, a tear was discovered in one cartridge after Run 11. We do not believe, therefore, that the particulate removal efficiencies reported for Runs 11 through 16 accurately reflect the particulate removal capabilities of the unit.

The particulate control capability of the ETS unit as a function of particle size was also determined.

Shown in Table 4 are the percentages of particulate matter less than 1 micrometer in size in the inlet and outlet samples. This implies better removal of fine particulate than coarse particulate. This is counter to the expected performance of a fabric filtration system. In our opinion, these data imply that a significant fraction of the particulate matter in the unit exhaust originated with the lime feed.

VULCAN ENGINEERING COMPANY HI-TAC FILTER

General Description

The high temperature air cleaning (HI-TAC) device was developed by Vulcan Engineering Company for the removal of particulate matter from gas streams at higher collector inlet temperatures than previously possible. The unit is not designed nor equipped to control HCl emissions. Although the HI-TAC unit looks much like a conventional baghouse, there are substantial differences.

The filter media is entirely metallic. This results in greater resistance to moisture, temperature, corrosion, abrasion, and pressure than is provided by conventional fabric media. Although temperatures below 500°F do not decrease the collection efficiency, the media is designed to operate in the 600°F to 1350°F range. Temperature excursions to 2000°F can be tolerated. The filter elements will even tolerate flame temperatures.

The unit was developed for use in the iron and steel industry to control particulate from the many high temperature sources. The initial tests on the unit were performed on exhaust gas from an iron cupola. The gas entering the unit was 750°F and contained 1.39 grains of particulate per dry standard cubic foot (dscf). The unit operated with an air-to-cloth ratio of 16:1 and collected 99.2 percent of the particulate.

Unit Tested

The unit tested is completely portable and self-contained. Connection to an electrical power source and the exhaust duct are the only setup requirements. The unit is mounted on a Talbert 47-ft double drop Tandem axle trailer.

Each of the four cleaning modules mounted on the trailer houses four removal cartridge elements. Each element consists of a metallic reinforcing framework covered with stainless steel mesh. The weave may be varied to determine appropriate design for a particular source.

Test Results

During this test program, there were three (3) types of weaves in the unit. These were:

Module I - 150 x 105 plain weave
Module II - 325 x 325 twilled weave
Module III and IV - 50 x 250 dutch weave

The total removal efficiencies for particulate matter and chloride are shown in Table 5. As can be seen, removal efficiency for particulate matter is quite erratic, varying from 34 percent to 98 percent. Excluding run number 1, the average removal efficiency is 89.7 percent. Inspections of the cartridges before and after test runs indicated that cake formation on the filter fabric was not reliable. During several inspections following cartridge cleaning, it was observed that a very large portion (about 70 percent) of the fabric surface was still covered by the filter cake, with about 20 percent of the surface clean down to the fabric. The sticky particulate from the incinerator interfered with proper cake formation and filter cleaning. It is possible that fabric weave changes or precoating of the fabric might correct this difficulty. The test program was not designed to adequately explore these options.

Particulate removal versus gas flow rate through the APCD and particulate removal versus air-to-cloth ratio showed no clear trends. It is suspected that the peculiar cake formation properties and resultant filter cleaning problems made these standard plots of little value.

Recognizing the difficulties cited above for particulate control, we attempted to assess, with much trepidation, the removal efficiency at various particulate size ranges. These data indicate 90 percent or better control of particles of less than 1 micrometer but decreasing efficiency as the particle size increases.

These apparently strange results may be due to the method used, determining small differences between highly variable numbers, or to agglomeration of fine, sticky particles passing through the filters.

In summary, the test results indicate that effective control of the fine particulates generated by hazardous waste combustion may be achievable by the Hi-Tac unit. Additional development work to address the problem of sticky particulate will be required.

CONCLUSIONS

1. All versions of the Hydro-Sonic units tested achieved excellent HCl control. Ninety-nine percent of HCl was obtained without adding

additional alkalinity to the ENSCO scrubber recycle water. With additional alkalinity, any of these units should be capable of well over 99 percent HCl removal.

2. The Tandem Nozzle SuperSub Model 100 achieved the best particulate removal of the three Hydro-Sonic units tested.

3. The ETS dry scrubber achieved both high removal efficiencies for HCl and particulate.

4. The ETS scrubber reagent consumption, hydrated lime, appears to be high (3 moles lime per mole HCl) but cannot be stated with confidence since no attempts were made to improve utilization through reagent recycle.

5. The ETS unit does not presently have capability to adjust reagent feed rate to accommodate rapidly varying HCl content in the gas to be treated.

6. The Vulcan Hi-Tac unit is not designed to, and cannot presently, remove acid gases from the exhaust gas being treated. Therefore, it is not applicable to incinerators burning significant amounts of halogenated hazardous wastes.

7. Further development work and/or emissions testing will be required before the Hi-Tac unit demonstrates the capability to reliably control sources which might product sticky particulate as encountered in the exhaust of the ENSCO incinerator.

8. Considerable variability was encountered in the ENSCO exhaust gas for particulate concentration, particulate size distribution, HCl concentration, flue gas moisture content, and exhaust gas temperature. It is necessary that any air pollution control device installed on a hazardous waste incinerator have design features that allow compensation for this variability.

9. Of the APCDs tested in this project, the Hydro-Sonic Tandem Nozzle SuperSub gave the best overall performance in terms of HCl and particulate removal and ability to accommodate variability in the gas stream being treated.

ACKNOWLEDGMENTS

This report was prepared under EPA Contract No. 68-03-3149. Research Triangle Institute (RTI) is the prime contractor. The field testing described was subcontracted to Engineering-Science, Inc. (ES) and was carried out under RTI direction. Mr. Harry Freeman of EPA's Thermal Destruction Branch, Hazardous Waste Engineering Research Laboratory, Cincinnati, Ohio, was the Project Monitor.

RTI and ES wish to acknowledge the technical contribution of ENSCO, Inc. Hydro-Sonic® Systems, ETS, Inc., and Vulcan Engineering and to express appreciation for their participation in this project.

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TABLE 1. PARTICULATE AND CHLORIDE REMOVAL EFFICIENCIES: HYDRO-SONIC SCRUBBER

Configuration[a]	Particulate efficiency (Percent)	Chloride efficiency (Percent)
SH/Lo/R	81.6	99.1
SH/Lo/F	87.4	98.7
SH/Hi/R	88.2	98.8
TN/-/R	92.1	99.8
TN/-/F	86.3	96.0
SS/-/F	95.4	98.3

[a]Configuration codes are: SH = Steam-Hydro; TN = Tandem Nozzle; S = Supersub; Hi= High energy input; Lo = Low energy input; - = not applicable to this version; Fresh = Freshwater used in APCD: R = Recycle water from ENSCO scrubber used in APCD.

TABLE 2. COMPARISON OF FINE PARTICLE (<1 MICRON) ENRICHMENT FACTORS (OUT/IN) FOR VARIOUS OPERATING CONDITIONS

Operating Condition	Inlet Impactor Run No.	Percent of Mass <1 Micron	Outlet Impactor Run No.	Percent of Mass <1 Micron	Out/In
SH/Lo/F	2	43	3	69	1.6
SH/Lo/F	3	57	4	67	1.2
TN/- /F	4	38	5	60	1.6
SS/- /F	5	64	6	36	0.6
SS/- /F	6	70	7	26	0.4

TABLE 3. SUMMARY RESULTS: ETS UNIT

Reactant used	Stoichiometric ratio	HCl Efficiency percent	Particulates efficiency percent
Lime	2.80	98.7	91
Lime	4.53	89.0	97
Lime	4.50	98.0	96
Lime	6.61	99.2	95
Lime	8.71	98.9	95
Lime	8.07	99.6	98
Lime	5.29	99.8	90
Lime	1.94	56.3	98
Lime	2.42	79.1	98
Nahcolite	0.70	93.2	96
Nahcolite	0.53	82.0	(1)
Nahcolite	0.87	54.7	76
Nahcolite	-	(2)	75
Nahcolite	0.56	53.8	85
Nahcolite	1.73	68.1	83
Nahcolite	0.98	33.1	38

(1) Torn baghouse cartridge.
(2) Sample lost.

TABLE 4. COMPARISON OF FINE PARTICLE (<MICRON) ENRICHMENT FACTORS OUT/IN FOR ETS IMPACTOR RUNS

Inlet percent (<1 micron)	Outlet percent (<1 micron)	Out/In
31.4	5.26	0.17
31.7	3.01	0.09
52.6	10.2	0.19
30.7	0.14	0.004

TABLE 5. VULCAN HIGH TEMPERATURE BAGHOUSE EFFICIENCY SUMMARY

Run number	System efficiency (Percent)
1	34.2
2	93.1
3	90.4
4	92.5
5	94.2
6	84.3
7	89.3
8	74.8
9	90.0
10	98.4

CASE STUDIES OF WASTE TREATMENT AT HAZARDOUS WASTE FACILITIES

C. Clark Allen
Research Triangle Institute
P. O. Box 12194
Research Triangle Park, North Carolina 27709

and

Benjamin L. Blaney
U.S. Environmental Protection Agency
Cincinnati, Ohio 45268

ABSTRACT

Commonly practiced commercial waste treatment processes were investigated for the removal of volatile organic compounds from waste. The effectiveness of thin film evaporators, steam stripping, and distillation to treat waste was evaluated by field sampling and analysis. The major sources of treatment process residuals associated with these treatment processes were also investigated.

INTRODUCTION

The EPA Office of Air Quality Planning and Standards (OAQPS) is developing regulations to control emissions from hazardous waste treatment, storage, and disposal facilities (TSDFs). The purpose of the OAQPS air emissions regulations is to protect human health and the environment from emissions of volatile organic compounds (VOCs), particulates, and aerosols.

The sources of TSDF emissions include storage tanks, treatment processes, surface lagoons, landfills, land treatment, and drum storage and handling facilities. There are approximately 5,000 locations in the United States where one or more of these activities are in progress at a TSDF.

To date, research has concentrated upon characterization of uncontrolled emissions from these sources through field measurements and upon determining the reliability of emissions models. Options identified for controlling emissions from TSDFs include banning the handling of wastes from sources where emissions rates are high, treatment of wastes to remove volatiles, and the use of in-situ (add-on) control techniques. In addition, changes in waste management practices (such as using holding tanks instead of ponds) may be a cost-effective control option.

Treatment of waste to remove the VOCs appears to be a viable emissions control option and is being used at several TSDFs. In general, it is attractive because it can be used by the waste generator or TSDF operator to remove volatiles from the waste before there is much opportunity for release of VOCs to the air. Treatment may be the most cost-effective control technique for sources with large surface areas, such as land treatment facilities and waste treatment and storage lagoons. Waste treatment may also serve to reduce ground water impacts from waste disposal in landfills or by treatment lagoons, etc, as well as to reduce the amount of wastes disposed.

This paper presents the results from field studies of three treatment techniques: thin film evaporation, steam stripping, and distillation. The processes investigated were located at waste recycling facilities. The data collected included volatile removal effectiveness, the disposal of residuals, and limitations of the technology.

VOC TREATMENT PROCESSES

Steam stripping will remove low levels (less than 1 percent) of volatile

organic compounds from oils and wastewater. Steam stripping can operate at a lower temperature than a thin film evaporator and is therefore more appropriate for some reactive materials. The volatile organic compounds can be recovered from the process by decanting if the organic phase separates from the condensed steam.

Thin film evaporators are used in many solvent recovery operations. Typically, 80 percent of the volatile materials can be recovered, with a sludge containing residual VOC obtained at the bottom of the evaporator.

Thin Film Evaporators

Samples were taken from the overhead, bottoms, and feed of wastes treated at three thin film evaporators (1,2,3).

The waste treated at Plant A represents a class of waste oils containing a small amount of solids and approximately 5 percent VOCs. During the visit to Plant A, a "batch" consisting of mixed chlorinated xylenes was being processed through the thin film evaporator (1). This material was relatively clean, and therefore 95 percent was being taken overhead, with the bottoms or treatment process product being acceptable for fuel.

The data obtained from samples of the feed, the bottoms, and the product are presented in Table 1. The headspace analysis demonstrated that the volatile organic material was removed by the thin film evaporator from the bottoms. The following removal effectiveness was estimated using a material balance from the information presented in Table 1 (based upon the headspace analysis and 95 percent product recovery):

Methylene chloride	99.1
Chloroform	>99.99
1,1,1-Trichloroethane	>99.5
Toluene	<85.0
Freon TF	80.0

The concentrations of the volatiles are reduced in the bottoms of the thin film evaporators. The vapor pressures of the more volatile compounds are more than 90 percent reduced by the treatment.

Sampling and analysis was carried out on another thin film evaporator at Plant B (2). The composition of the material evaluated was a volatile organic liquid composed of alcohol and aromatics. The composition of liquid samples is presented in Table 2. The bottoms materials from the thin film evaporator had a similar volatility characteristic as the feed, although the volume of the waste was reduced by about 50 percent. In general, the more volatile material was concentrated in the product stream and the less volatile materials tend to be more concentrated in the bottoms.

The waste being processed in the thin film evaporator at Plant C was acetone containing xylene, low levels of chlorinated solvents, and dissolved polymeric resins (3). The acetone and other low boiling point compounds were somewhat more concentrated in the distillate and xylene was enriched in the bottoms. The analysis is presented in Table 3. Because of the requirements to maintain the resins in solution, the VOCs in the bottoms at the end of the run was not substantially different than the VOCs in the feed and the concentrations in the vapor phase did not change significantly (a reduction of acetone concentration in the vapor from 378 to 308 mg/L) although the volume of waste was reduced by 10 percent.

Steam Stripping

Plant D stripped waste material by direct injection of live steam into a waste batch. The process of stripping continued until the desired concentrations were achieved in the waste (4). Four batches of liquid wastes were evaluated: [1] an aqueous xylene, [2] a chlorinated organic-oil mixture, [3] a chlorinated organic-water mixture, and [4] a mixed solvent-water mixture.

The test results for the aqueous xylene batch are presented in Table 4 and Figure 1. The rates of removal of all the compounds appeared to be roughly the same, with the heavier materials being somewhat more slowly removed. There was removal of all the VOCs to less than 300 ppm in the final treated waste.

In the chlorinated organic-oil mixture, there were two major components which were removed from the organic waste. These were the trichloroethane and chloroform. Chloroform was quickly removed from the process with only 23 ppm remaining after 80 minutes. The trichloroethane was somewhat more slowly removed with 4,000 ppm or 0.4 percent residual trichloroethane in the oil material at the end of the batch. Since the volume of the organic batch was changing as the more volatile component was removed, the

concentration of the trichloroethane did not drop initially but appeared to decrease much more rapidly in the later stripping as the batch temperatures increased. The average stripping rate of the chloroform and the trichloroethane was approximately the same.

When the batch of waste trichloroethane had been processed, a residual tank of condensed steam containing some of the volatile organics was collected in the MST. This chlorinated organic-water mixture was stripped and the concentrations of the volatile materials monitored. The results are presented in Table 5. In this batch of aqueous waste (which differed from the aqueous xylene batch in that there was no organic phase of xylene present during stripping), the stripping rates varied for the different compounds, with the more volatile materials such as chloroform and acetone stripped at a relatively faster rate. As seen from Figure 2, an approximately logarithmic decrease in the concentrations of the major volatiles was observed. The major component present in the aqueous waste was trichloroethane, and the waste was stripped down to 1 percent trichloroethane in 60 minutes. Approximately another 40 minutes of stripping would possibly be required to drop the trichloroethane level to .1 percent based the extrapolated curve in Figure 2.

The fourth batch was a mixed-solvents mixture produced by the project team to simulate a dilute aqueous waste stream containing miscible and immiscible solvents in the following approximate concentration: toluene (0.1 percent) and acetone (0.6 percent), trichloroethane (0.2 percent), and xylene (0.2 percent). The concentrations of each of the volatile components in this batch were reduced to less than .03 percent after 33 minutes of stripping. The toluene, xylene, and trichloroethane stripped at approximately the same rate, with acetone approximately twice as fast. The initial concentrations of toluene and xylene were not the same as initially charged to the batch, apparently because of inadequate mixing in the batch while the sample was taken.

For all four waste streams, the equilibrium concentration of the volatile organic compounds at equilibrium in the cool waste decreases as their concentrations decrease due to steam stripping. Based on a headspace analysis of the treated waste in the laboratory, it is apparent that the volatility characteristics of the wastes are dramatically altered by the steam stripping process. These volatility characteristics of the cooled wastes are of concern because of the relationship between the vapor pressure of the volatile components and its release into the atmosphere upon disposal. The waste material generally showed at least an order of magnitude decrease in the vapor concentrations at equilibrium with the waste.

Table 6 presents a summary of the data analysis of the four batches evaluated at Plant D. The correlation coefficient was relatively high for many of the rates of stripping. The steam rate influences the rate of stripping, so the rate constants are presented in a dimensionless form to account for the steam rate and batch size.

The values of the dimensionless rate constant were much smaller than would have been expected for dilute organic materials in water (Henry's Law). Table 7 demonstrates that the equilibrium vapor pressures were lower in the mixed waste system than in dilute concentrations. The rate constants were roughly the same for chloroform and 1,1,1-trichloroethane for each of the aqueous batches.

AIR EMISSIONS

Besides solid residuals produced by these treatment processes the significance of treatment process air emissions is also of interest. The treatment after disposal would be of little use if substantial quantities of contaminated residuals were produced. For these processes considered here, the principal residuals are in the form of either organic materials which could be incinerated or aqueous streams with the VOCs removed. A small amount of the VOCs were lost to the atmosphere.

Thin Film Evaporators

Air emissions were evaluated from three thin film evaporators and two steam stripping units. The major air emission source identified at the thin film evaporator process was the vent from the vacuum pump. It should be noted in the processes investigated that in all cases any air emissions were estimated as only a small fraction of the amount of the organics recovered; however, it is

possible for the system to have a relatively significant loss of some of the particularly volatile materials from the vacuum pump vent in a mixed volatile system.

The volatile materials, methylene chloride and chloroform, were present in the feed stream at Plant A in somewhat higher concentrations than in the product, and were not present to a significant extent in the bottoms. This suggests a possible loss of some of the more volatile materials to the atmosphere through the vacuum pump vent. The following list presents the estimated VOC losses (as determined by mass balance) to the atmosphere as determined by a material balance, according to boiling point:

Methylene chloride	57%, 40.7°C
Chloroform	97%, 61.3°C
1,1,1-Trichloroethane	-20%, 74°C
Toluene	-17%, 110°C

Negative values are attributed to uncertainty in the data (see below).

The exhaust of the vacuum pump did contain some volatile materials during startup. Carbon adsorption tubes were analyzed for VOCs present in air samples from the vacuum pump vent. Five tubes were analyzed, one 10-minute sample (85 mL/min), two 5-minute samples, and two field blanks.

The analysis of the gas samples of the vacuum pump discharge vent is presented in Table 8. Chloroform and 1,1,1-trichloroethane were present in the vent discharge with statistically significant quantities (relative to the field blank) of the higher boiling VOCs (toluene, ethyl benzene, xylene). The absence of methylene chloride captured on the carbon tube and the apparent insensitivity of the quantity of chloroform captured to the length of sampling time suggest that the quantities of the more volatile chlorinated compounds may be greater than reported in Table 8.

Although there is an expected error of 15 percent or less in the pollutant concentration data, and even greater error in differences and estimates based on gas partitioning, the data do suggest that the lower boiling VOCs may be subject to much higher process losses than higher boiling VOCs. These data suggest that thin film evaporators operating under a vacuum can have potentially significant VOC emissions. The emission rate would depend on the operating conditions of the still. The data reported in Table 8 was taken during startup and the concentrations observed were expected to be lower after the transitional period of startup. Some of the waste treatment plants visited indicated that control vent emissions could be reduced by multiple passes through the evaporator (2), or by using a second vent condenser (5).

At Plant B, the largest source of air emissions observed from the thin film evaporator was from the vacuum condenser vent. The concentrations of VOCs in the vent were roughly one-half the concentrations observed in the laboratory from equilibrium headspace analysis of the condensate. The concentration of air emissions would depend on the flow rate of noncondensibles out of the vent. This flow would depend on the concentration of noncondensibles in the waste and the magnitude of any potential system leaks (into the process).

The concentrations of VOC in the process vent of the thin film evaporator was evaluated for Plant C for comparison to the vacuum pump vent at Plants A and B. (The thin film evaporator at Plant C was operating at atmospheric pressure.) The analysis of the air samples from the process vent indicated that no significant (relative to the field blank) air emissions were observed from the process vent. The vent pipe was located perpendicular to the wind flow on the building exterior, and due to the wind gusts air flowed alternatively in and out of the vent (as measured by the Alnor velometer). No odors were detected at the vent.

At Plant C, the largest source of air emissions which was identified was the product storage tank. The product storage tank had a loose fitting steel top with a gap of approximately 8-3 cm (3-1 inch) and was 1 meter (4 ft) wide with an area of 620 cm^2 (0.67 ft^2). Acetone was the major component lost from the storage tank at 0.56 and 0.70 g/sec. Based on an emission factor of 2.0×10^{-5} g/mol/cm^2 sec and a vapor concentration of 383 mg/l (measured at 25°C in the laboratory), the estimated emissions for a fully exposed surface is 1.7 g/sec, greater than the field rate by a factor of 3. (At the time of the test of the produce storage tank, the plant was planning to replace the current receiver tanks with a more enclosed tank system.)

Steam Stripper

In contrast to the open product storage tank at Plant C, the product storage vessels at Plant D were enclosed inside a building with a vent to the roof from each tank. The air emissions from the process vents at Plant D were estimated on two batches, the xylene aqueous batch and the production waste trichloroethane batch. Air concentrations were measured, but no flow from the process storage tanks was detected. The concentrations of the vapor at equilibrium over the distillate obtained midway through the process corresponded with concentrations obtained approximately concurrently from the air in the vents. The volume emitted from the receiver vent was estimated on the basis of the data obtained from the dry gas meter readings. The emission factors were estimated by obtaining the ratio of the estimated grams of emissions to the total amount of wastes. The total VOC emission factor (g/g waste) was estimated to be 2.7 x 10^{-5} for the 1,1,1-trichloroethane production run and 3.8 x 10^{-5} for the aqueous xylene run. In both cases, the emissions were only a small fraction of the VOCs recovered from the process. The rate of emission of VOCs from the storage tanks was estimated a 0.006 g/sec.

The condensate receiver vent concentrations of the methylene chloride, chloroform, and trichloroethane from the 1,1,1-trichloroethane batch were much greater at the beginning of the process than at the middle of the process. This is not unexpected since the concentrations of these components in the condensate are much greater at the beginning of the cycle than midcycle, as determined from the waste analysis. The concentrations of the volatiles in the vent from the product storage and the MST tank vent were substantially lower than the concentrations obtained at equilibrium within the storage tank. This suggests that the air emissions are substantially lower than predicted from the equilibrium values of the tank contents.

The air emissions from the condenser vent were only a small fraction of the recovered VOCs. In addition, the air emissions from the storage tanks at Plant D were much lower than from the storage tank surface exposed to the flow of air at Plant C.

CONCLUSIONS

1. Thin film evaporators are useful for waste volume reduction and VOC removal in systems with high boiling point organics.

2. There are potential emissions from the condenser vent when volatiles are removed with high boiling organics in a thin film evaporator.

3. Thin film evaporators may not substantially alter the volatility characteristics of wastes containing primarily VOCs.

4. Steam stripping is effective for removing VOCs from wastes: [1] aqueous, [2] liquid organic/aqueous mixtures, and [3] liquid organic.

5. The air emissions from thin film evaporation and steam stripping were only a small fraction of the waste treated.

REFERENCES

1. Allen, C. C., and G. Brant, 1984a. Hazardous waste pretreatment for emissions control: field evaluations at Plant A. EPA Contract No. 68-03-3149, Work Assignment 25-1.

2. Allen, C. C., and G. Brant, 1984b. Hazardous waste pretreatment for emissions control: field evaluations at Plant B. EPA Contract No. 68-03-3149, Work Assignment 25-1.

3. Allen, C. C., and G. Brant, 1984c. Hazardous waste pretreatment for emissions control: field evaluations at Plant F. EPA Contract No. 68-03-3149, Work Assignment 25-1.

4. Allen, C. C., and G. Brant, 1984d. Hazardous waste pretreatment for emissions control: field evaluations at Plant C. EPA Contract No. 68-03-3149, Work Assignment 25-1.

5. Allen, C. C., and G. Brant, 1984e. Hazardous waste pretreatment for emissions control: field evaluations at Plant E. EPA Contract No. 68-03-3149, Work Assignment 25-1.

TABLE 1. THIN FILM EVAPORATOR WASTE COMPOSITIONS, PLANT A

	Bottoms*	Feed		Product	
	mg/L (in vapor)	Liquid (by vol)	mg/L (in vapor)	Liquid (by vol)	mg/L (in vapor)
Methylene chloride	0.03	2.0%	1.7	0.9%	0.97
Chloroform	<0.01	1.5%	5.1	ND	0.14
1,1,1-Trichloroethane	<0.01	0.7%	0.11	ND	0.14
Toluene	0.03	1.3%	<0.01	1.6%	0.04
Mixture of High Boiling Hydrocarbons	-	94.4%	-	93.9%	-
Freon TF	0.24		0.06	1.8	1.5

ND indicates compound not detected.
*Bottoms solid upon cooling.

TABLE 2. ANALYSIS OF LIQUID SAMPLES, THIN FILM EVAPORATOR, PLANT B

	Feed		Product		Bottoms*
	Liquid (by vol)	mg/L (in vapor)	Liquid (by vol)	mg/L (in vapor)	mg/L (in vapor)
Isopropyl alcohol	38.2%	0.75	53.8%	1.1	1.6
Freon TF	0.6%	38.	0.7%	62.	5.3
Toluene	0.4%	0.58	0.4%	0.94	0.32
Ethyl benzene	11.4%	5.5	8.4%	5.3	9.0
Xylenes	49.2%	22.	34.0%	19.	39.0

*Bottoms solid upon cooling.

TABLE 3. ANALYSIS OF LIQUID SAMPLES, THIN FILM EVAPORATOR, PLANT C

Compound	Feed		Distillate		Bottoms	
	Liquid (%)	Gas (ppm)	Liquid (%)	Gas (ppm)	Liquid (%)	Gas (ppm)
Acetone	74.3	378.0	82.2	383.0	60.6	308.0
Freon TF	0.1	2.0	<0.1	2.0	0.1	1.5
1,1,1-Trichloroethane	1.5	17.9	2.2	19.1	0.9	9.2
Trichloroethylene	0.2	0.1	0.3	0.1	<0.1	0.1
Toluene	0.5	0.3	0.9	0.2	0.9	4.1
Ethyl benzene		0.1	0.3	<0.1	0.3	0.4
Xylene	5.9	2.1	2.0	0.2	<0.1	<0.1
Tetrachloroethylene	0.6	2.4	0.5	1.6	13.6	5.0

TABLE 4. WASTE VOC CONCENTRATION DURING STEAM STRIPPING: AQUEOUS XYLENE BATCH

Process time (min)	Sample number	Concentration (mg/L)							
		Acetone	IPA	Chloro-form	TCEA	TCE	EB	Toluene	Xylene
0	45-3	39	960	5,200	170	290	360	86	2,000
15	45-5	10	640	2,300	99	230	560	32	480
64	45-6	<6	47	350	33	72	56	17	410
86	45-7	<6	<6	170	20	<20	100	42	270

IPA = isopropanol
TCEA = 1,1,1-trichloroethane
TCE = trichloroethylene
EB = ethyl benzene

TABLE 5. WASTE VOC CONCENTRATIONS DURING STRIPPING: 1,1,1-TRICHLOROETHANE MST BATCH

Process time (minutes)	Sample number	Concentration (mg/L)				
		Acetone	Chloroform	TCE	EB	IPA
0	45-29	290	1,600	180,000	44	37
22	45-31	71	250	71,000	30	<6
43	45-32	9	<34	28,000	24	<6
57	45-33	<6	<34	12,000	12	<6

TABLE 6. LINEAR CORRELATION OF THE LOGARITHM OF THE WASTE CONCENTRATION WITH THE STRIPPING TIME

Batch	Component	Correlation coefficient	Stripping rate constants	
			(min^{-1})	(dimensionless)
1	Isopropyl alcohol	-.974	.0507	14.7
1	Chloroform	-.9977	.0393	11.4
1	1,1,1-Trichloroethane	-.9971	.0242	7.0
1	Tetrachloroethane	-.9975	.0122	6.47
2	Chloroform	-.9974	.0998	19.7
2	1,1,1-Trichloroethane	-.9593	.078	15.3
3	Acetone	-.9925	.0806	10.0
3	Chloroform		.0844	10.5
3	1,1,1-Trichloroethane	-.9971	.0468	5.82
4	Acetone	-.9966	.28	25.4
4	Toluene	-.9377	.0657	5.97
4	Xylene	-.9875	.0859	7.8
4	1,1,1-Trichloroethane	-.990	.0684	6.21

*Dimensionless rate obtained by dividing the rate constant (min^{-1}) by the ratio of the steam rate (L/min) to the amount of waste (L).

TABLE 7. A COMPARISON OF THE RATE CONSTANTS OF STRIPPING TO THE HENRY'S LAW CONSTANT

Compound	H (atm)	K (Y/X)	Batch 1	Batch 3	Batch 4
Isopropyl alcohol		2.4	14.7		
Chloroform	186	2.0	11.4	10.5	
1,1,1-Trichloroethane	273	3.4	7.0	5.82	6.21
Tetrachloroethane	24	1.6	6.5		
Acetone		1.90		10	25.4
Toluene	360	2.8			5.97
Xylene	340	3.6			7.8

TABLE 8. ANALYSIS OF VENT GAS FROM VACUUM PUMP ON THIN FILM EVAPORATOR

	Process vent 10 minutes (mg/L)	Process vent 5 minutes (mg/L)	Duplicate process vent 5 minutes (mg/L)	Field Blank 1,2 (5 min basis)	
Chloroform	2.4	17.8	6.1	-	-
1,1,1-Trichloroethane	3.1	3.05	2.35	-	-
Trichloroethylene	0.87	0.59	0.61	-	-
Tetrachloroethylene	1.0	1.04	1.01	-	-
Toluene	27.1	23.5	25.8	-	-
Ethyl benzene	0.31	0.52	0.45	-	-
Xylenes	1.41	2.16	1.9	0.1	-

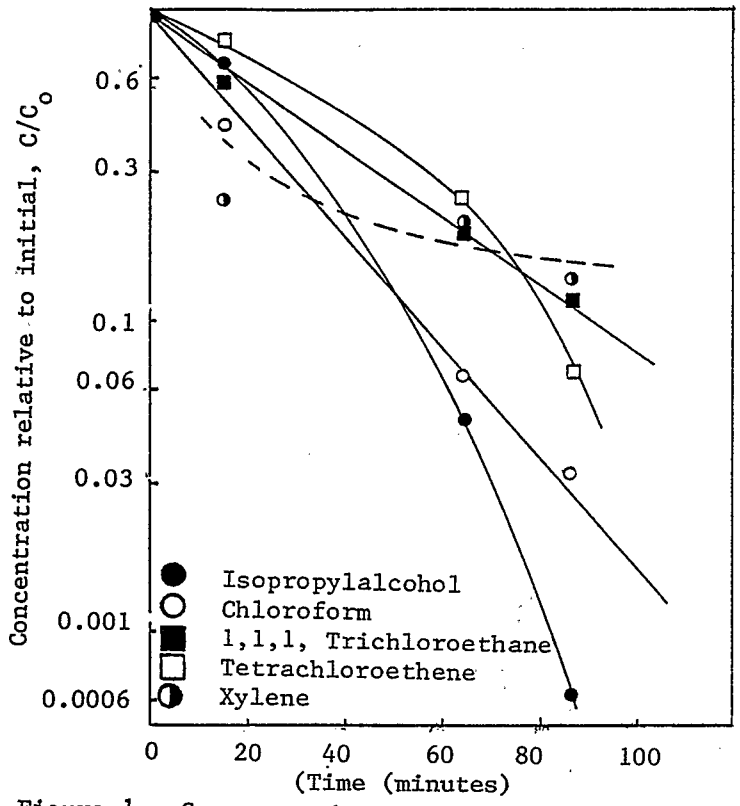

Figure 1. Concentrations in the batch of waste as a function of time: xylene MST.

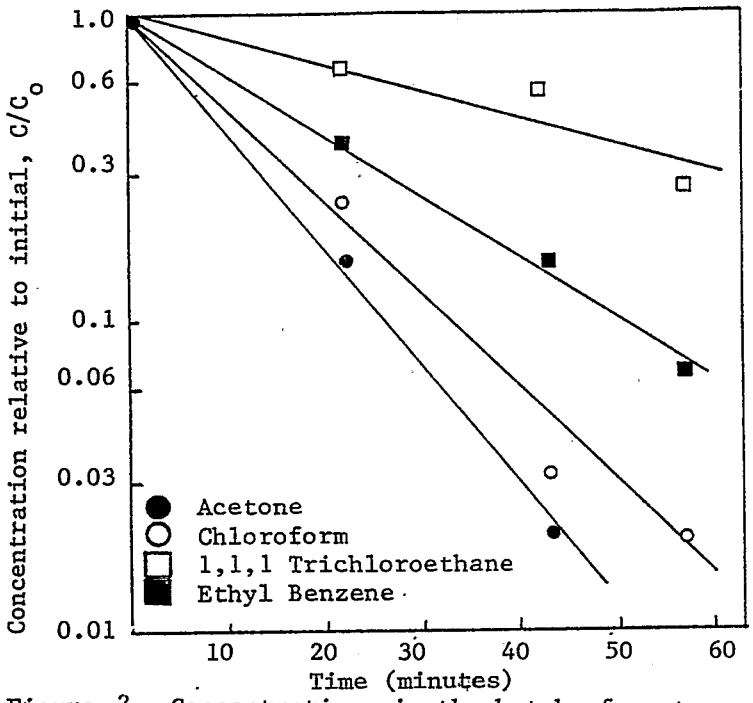

Figure 2. Concentrations in the batch of waste as a function of time: trichloroethane MST.

A CASE STUDY OF DIRECT CONTROL OF EMISSIONS FROM A SURFACE IMPOUNDMENT

R.G. Wetherold, B.M. Eklund and T.P. Nelson
Radian Corporation
P.O. Box 9948
Austin, TX 78766

ABSTRACT

Field measurements were taken to determine the effectiveness of a cover/enclosure in controlling VOC emissions from an aerated wastewater treatment lagoon. The control system included a carbon adsorption system for the air which was vented, under controlled conditions, from the enclosed system.

INTRODUCTON

The Hazardous Waste Engineering Research Laboratory (HWERL) of EPA has the responsibility of providing technical support to OAQPS in the area of atmospheric emissions from hazardous waste management. In this study, testing was performed at a specialty chemicals plant in the northeast. The aerated wastewater lagoon at this facility has been enclosed with an inflated flexible dome structure to reduce odors and to keep the lagoon warm during winter. A stream of air from the enclosure is vented through a regenerable carbon adsorption system. The effectiveness of the enclosure and carbon adsorption system in containing and controlling VOC emissions was evaluated in this study. Additionally, the fate of the VOC entering the aerated lagoon was estimated.

PURPOSE

The primary objective of this study was to determine, through field testing, the efficiency of a cover and associated carbon adsorption system in controlling the emissions of VOC from an aerated wastewater treatment lagoon.

APPROACH

Liquid and slurry samples were collected at various locations in and around the wastewater treatment facility at the chemical plant. The objective of the sampling was to gather enough data to perform a material balance around the system and, thus, determine the fate of the VOC entering the system.

Process Description--

A schematic flow diagram of the wastewater treatment system at the plant is shown in Figure 1. Specialty chemicals are produced in a number of separate batch processing areas within the plant. The wastewater entering the wastewater treatment system can come from a variety of sources, including reaction products, process washwater, and washwater used in cleanup operations. Waste solids are also associated with the wastewater.

Wastewater from the batch processing is quite variable in both flow rates and compositon. As shown in Figure 1, the wastewater from the plant first flows into two neutralizer tanks for pH adjustment.

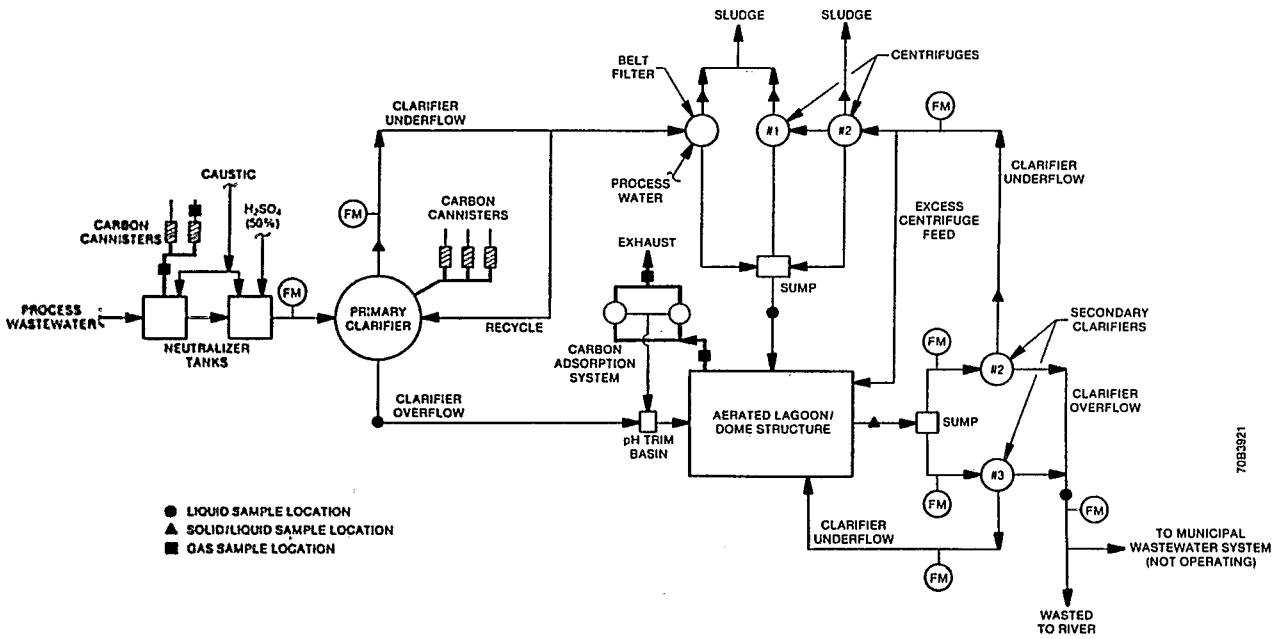

Figure 1. Wastewater Treatment Facility Sample Locations.

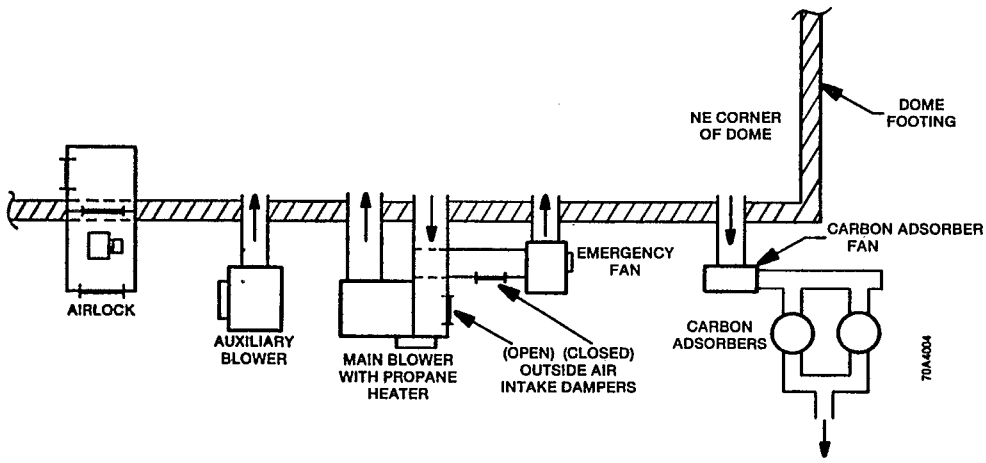

Figure 2. Dome Structure Fan Inflation and Exhaust System.

From the neutralizer tanks, the wastewater (including the waste solids) is pumped to the primary clarifier. The overflow from the clarifier is sent to a trim basin for additional pH adjustment and then to the aerated lagoon.

About one-third of the primary clarifier underflow is recycled back to the clarifier, and the remainder is directed to a belt filter for solids dewatering. The solids on the belt filter are washed with additional process water before being sent to a solids drying area. The recovered process and washwater are sent to the aerated lagoon through a sump. Hydrobac®, a freeze-dried bacteria designed to effectively attack aromatic/phenolic materials, is added in this sump to promote bacterial action in the lagoon.

From the aerated lagoon, the treated wastewater and resulting solids are pumped through a sump to two open-tank secondary clarifiers. Floc and powdered activated carbon are added in the sump.

The treated overflow from the secondary clarifiers is currently discharged to a nearby river. The major portion of the underflow from one of the secondary clarifiers is recycled to the aerated lagoon. The remainder of the underflow is sent to the solids centrifuge for dewatering. The recovered water is returned to the lagoon, and the solids are wasted to a solids drying area.

The aerated lagoon is approximately 46 x 130 meters. Aeration is performed with two 75-hp aerators and 25 smaller 7.5 hp aerators. Residence time in the lagoon is approximately 5 days at the normal depth of 1.5 meters. However, the lagoon level had been lowered to approximately 0.5-0.6 meters about two weeks before the testing. They residence time during the testing was approximately 1.5-2 days.

The entire aerated lagoon is covered by an inflated dome made of a PVC-coated polyester fabric. The structure is pressurized by a main blower with a capacity of 20,000 CFM. The integrity of the dome is maintained by steel cables strung over the fabric. The fabric is lined with Tedlar to minimize chemical attack and to reduce the permeability of the dome to the internal gases.

A purge stream of air from inside the enclosure is continuously vented to the atmosphere through a fixed-bed carbon adsorption system. A schematic diagram of the dome inflation and purge system is shown in Figure 2. The purge rate of approximately 1.4 m^3/sec (3000 cfm) provides a gas-phase residence time of 9.4 hours under the dome. The carbon adsorption system is a two-bed unit. During normal operation, one bed is adsorbing while the other is being regenerated with steam. The adsorption cycle lasts 24 hours, while the regeneration cycle consists of 12 hours of steaming and 12 hours of cooling. The recovered hydrocarbons and steam condensate produced during the regeneration cycle are returned to the aeration lagoon.

Liquid, slurry and gas samples were collected at various locations around the wastewater treatment facility. The sampling points are shown in Figure 1. The inlets to the system were considered to be the underflow and overflow from the primary clarifier. The outlet streams were the treated wastewater, the sludges (from the filters and centrifuges) and the exhaust from the carbon adsorption system. Key recycle streams were also sampled. The two secondary clarifiers were identical in size and operation. Only the outlet stream from one of the clarifiers was sampled.

The flow rates of the major process liquid and slurry streams were metered by the plant using flow meters as shown in Figure 1. Flow rates of some internal liquid streams were not measured, and these rates were estimated by plant personnel. The total gas flow rate at the outlet of the carbon adsorption system was measured by Radian twice each day. EPA Reference Method 2 Procedures were followed in making these measurements.

Sample Collection--

Liquid and sludge samples were collected from 2 to 8 times per day during the test period. These samples were collected in glass containers with Teflon-lined caps and stored at approximately 4°C until analyzed. Gas samples were continuously collected from the inlet and outlet air streams of the carbon adsorption system. The sampling system consisted of a rake-type in-stack probe, a heated pump and

heat-traced lines leading to the analytical instruments. The gas samples were analyzed on-site using two Byron Model 401 THC analyzers and a HNU Systems, Inc., Model 301 Gas Chromatograph.

Gas samples were collected for detailed off-site analyses to determine individual species. These samples were collected in evacuated stainless steel canisters 2-3 times per day from the inlet and outlet of the carbon adsorption system.

Sample Analysis--

The on-site analyses were limited to gas-phase samples. The Byron 401 Analyzers were used to monitor the total hydrocarbon (THC) concentrations. Analyses were performed on one-minute cycles. All data from the Byron Analyzers were automatically collected, stored and reduced using a microcomputer.

The HNU Systems, Inc., Model 301 GC was used to provide rudimentary on-site speciation as well as total VOC analyses of gas samples which were collected periodically from the carbon adsorption system air streams.

The solid, liquid and air canister samples were analyzed for C_2-C_{10} organic compounds at Radian's Austin laboratories. The air samples from the gas canisters were passed through a Perma-Pure drying tube and then through a trap cooled with liquid oxygen. A known amount of sample was then desorbed from the trap onto the analytical GC columns.

All analyses were performed on a Varian 3700 GC equipped with fused silica capillary columns. A flame ionization detector (FID) was used to detect and quantitate hydrocarbon species, while a photoionization detector (PID) was used to provide additional qualitative information. In addition, a second sample was resolved on a separate column and analyzed with a Hall Electrolytic Conductivity Detector (HECD) operated in the halogen mode. The FID/PID output from the GC was processed with a Varian 401 Chromatographic Data System (CDS) and an Apple II+ microcomputer.

The liquid samples were analyzed with a purge-and-trap technique. A stream of ultra-high purity nitrogen was passed through aliquots of the liquid samples. The resultant gas was passed through and trapped in the cryogenic traps of the analytical system. The analytical procedure followed after the cryogenic trapping was identical to that used in the analyses of air samples.

Solid samples (sludge and activated carbon) were extracted with tetraglyme, purged in 5 ml of deionized water to a cryogenic trap and then analyzed in the same manner as the gas samples.

RESULTS

Sampling and Analytical Results--

The results of the analyses of selected liquid/solid samples are summarized in Tables 1 and 2. The concentrations of compound classes and selected individual components in the primary clarifier overflow (aeration pond inlet) and the secondary clarifier feed (aeration pond outlet) are shown. Samples from several different days were analyzed.

Tables 3 and 4 contain summaries of the analyses of the inlet and outlet air streams of the carbon adsorption system. The concentrations of major compound classes and a few selected organic compounds are presented.

Emission Rates and Control Effectiveness--

A mass balance about the system was performed using average flow rates and compositions of the measured streams. The results of the mass balance for total nonmethane hydrocarbons (NMHC) are summarized in Table 5. The major emission point was the exhaust of the carbon adsorption system, accounting for 59% of the incoming NMHC. Fifteen percent of the incoming NMHC left the aeration pond in the effluent water stream. An additional 7 percent of the NMHC present in the feed to the aeration pond was carried from the system in the centrifuge sludge.

Biological activity in the aerated pond was assumed to be responsible for the difference between the measured inlet and outlet NMHC rates. The obvious assumption in this determination is that all significant sources of VOC emissions were

TABLE 1. LIQUID PHASE CONCENTRATIONS OF MAJOR CLASSES OF ORGANIC COMPOUNDS

	Liquid Phase Concentration (mg/l)							
	Primary Clarifier Overflow				Secondary Clarifier Overflow			
	Paraffins	Aromatics	Halogenated Organics	Total Nonmethane Hydrocarbons	Paraffins	Aromatics	Halogenated Organics	Total Nonmethane Hydrocarbons
15 Aug 1984	15.2	158	232	405	--	--	--	--
15 Aug 1984	5.2	98.6	77.1	181	--	--	--	--
15 Aug 1984	16.4	52.9	70.7	141	--	--	--	--
16 Aug 1984	33.5	140	61.2	234	25.2	2.9	2.4	42.9
16 Aug 1984	12.1	31.5	30.1	74.1	7.4	32.9	5.0	50
17 Aug 1984	20.4	93.2	90.1	204	17.5	0.35	6.3	25.3
17 Aug 1984	4.8	52.8	81.2	157	--	--	--	--
18 Aug 1984	15.9	86.3	44.5	147	--	--	--	--
18 Aug 1984	12.8	378	56.6	449	21.0	2.5	6.8	30.3

TABLE 2. LIQUID-PHASE CONCENTRATIONS OF SELECTED ORGANIC COMPOUNDS

	Liquid Phase Concentration (mg/l)									
	Primary Clarifier Overflow					Secondary Clarifier Overflow				
Sampling Date	Methylene chloride	Dichloro-ethane	Benzene	Toluene	Chloro-benzene	Methylene chloride	Dichloro-ethane	Benzene	Toluene	Chloro-benzene
15 Aug 1984	69.7	84.5	148	48.8	57.8	--	--	--	--	--
15 Aug 1984	0.0	42.4	50.7	4.6	25.3	--	--	--	--	--
15 Aug 1984	0.0	44.5	49.3	3.5	24.4	--	--	--	--	--
16 Aug 1984	0.0	55.2	135	3.1	1.6	0.0	0.0	1.8	0.28	0.0
16 Aug 1984	0.0	27.1	24.5	6.9	2.4	0.0	4.5	0.30	0.85	0.0
17 Aug 1984	0.88	58.1	87.8	5.4	4.2	0.0	6.2	0.0	0.0	0.0
18 Aug 1984	0.0	42.0	45.6	40.6	1.4	0.0	6.1	0.28	0.0	0.0
18 Aug 1984	0.0	54.0	34.9	56.5	1.6	--	--	--	--	--

TABLE 3. CARBON ADSORPTION SYSTEM: INLET AND OUTLET GAS CONCENTRATIONS OF MAJOR CLASSES OF ORGANIC COMPOUNDS

	Gas Phase Concentration, ppmv			
	Sampling Date			
	8/17/84	8/17/84	8/18/84	8/19/84
Carbon Adsorber Inlet				
Paraffins	63.2	10.4	153	--
Aromatics	33.1	11.2	117	--
Halogenated Organics	251	200	331	--
Nonmethane Hyrocarbons	348	222	607	--
Carbon Adsorber Outlet				
Paraffins	49.8	13.0	167	63.4
Aromatics	32.2	38.6	89.8	43.5
Halogenated Organics	251	264	409	46.1
Nonmethane Hydrocarbons	334	317	698	158

TABLE 4. CARBON ADSORPTION SYSTEM: INLET AND OUTLET GAS CONCENTRATIONS OF SELECTED ORGANIC COMPOUNDS

	Gas Phase Concentration, ppmv			
	Sampling Date			
	8/17/84	8/17/84	8/18/84	8/19/84
Carbon Adsorber Inlet				
Methylene chloride	4.0	5.1	4.3	--
Dichloroethane	204	172	240	--
Benzene	26.0	4.5	21.2	--
Toluene	5.7	5.1	92.1	--
Chlorobenzene	13.2	3.6	0.4	--
Dichlorobenzene	0.6	0.5	1.2	--
Carbon Adsorber Outlet				
Methylene chloride	4.2	5.1	2.1	0.1
Dichloroethane	205	231	355	15.3
Benzene	27.8	15.1	24.8	9.5
Toluene	7.5	19.6	54.1	24.0
Chlorobenzene	13.3	6.6	8.8	26.3
Dichlorobenzene	0.8	0.2	0.1	2.7

TABLE 5. SUMMARY OF MASS BALANCE RESULTS
(Based on Averages of the Data)

Source or Effluent	NMHC Flow (Kg/min)	% of Influent
Influent		
Primary Clarifier Feed	0.212	100
Effluent		
Dome exhaust	0.125	59
Effluent wastewater	0.032	15
Effluent centrifuge sludge	0.014	7
Biological oxidation*	0.041	19

*By difference.

TABLE 6. ULTIMATE FATE OF ORGANIC GROUPS

	Paraffins	Aromatics	Halogen	Total
Percent of Total Influent				
Primary Clarifier Feed	6.9	55.4	37.7	100
Percent of Total Effluent				
Dome Exhaust	11.6	8.2	39.2	59
Effluent Wastewater	8.2	4.4	2.4	15
Effluent Sludge	4.1	1.9	1.0	7
Biological Oxidation*	-(17.0)	40.9	-(4.9)	19
				100

*By difference.

included in the mass balance. As estimated by difference, biological activity in the pond appears to have accounted for approximately 19 percent of the incoming NMHC.

The large majority of the compounds detected in the streams around the wastewater treatment system fall into the paraffin, aromatic or halogenated hydrocarbon classification. Table 6 contains a summary of the fates of these three classes of compounds. The estimated loss by biological oxidation was estimated by difference.

Almost all of the halogenated compounds appear to be lost in the carbon adsorber exhaust. The small amount (4.9%) indicated by difference as actually being produced is probably due to measurement and analytical uncertainties. On the other hand, more than 70 percent of the incoming aromatic compounds are apparently destroyed through biological activity in the pond.

The influent paraffinic compounds seem to be relatively unaffected by the wastewater treatment. Indeed, there appears to be an increase in the amount of paraffins through the system. The relatively large amount produced (17.0%) appears to be significant, even when normal experimental and analytical uncertainties are considered. Some paraffin compounds may actually have been produced as a result of biological degradation of aromatic and halogenated compounds.

The effectiveness of the pond cover in containing VOC emissions could not be quantitatively assessed in this study. However, plant personnel indicated that the dome had a good seal around the base, and they estimated that the total leakage was about 0.14 m3/sec (300 cfm). A crude leak check of the dome by Radian personnel found only very small leaks around the dome base. Permeation of gas through the dome fabric is negligible according to information supplied by the manufacturer. Thus, it appears that VOC containment by the cover is virtually complete.

The results of the gas phase analyses around the carbon adsorption system show that this device is not removing any significant amount of VOC in the dome exhaust. In some cases, higher levels of VOC were observed in the outlet air than were detected in the inlet. These differences are presumed to be due to the variability of the inlet concentrations and to the operation of the carbon adsorption system. This result is not unexpected for several reasons. The carbon adsorption system was not designed for bulk removal of organic compounds from the air stream. It was installed for odor control and specifically for the removal of orthochlorophenol. The system appears to be effective in this application.

The air stream entering the carbon adsorption system is saturated with water at the temperature under the dome, which is generally warmer than the ambient conditions. Very high humidities drastically reduce the adsorptive capabilities of the activated carbon. There is probably actual condensation of water within the beds. Activated carbon is generally effective only on gas streams having relative humidities of 50 percent or less.

The results of this study support the following conclusions:

- The combination of the pond cover and carbon adsorption system is not an effective method for controlling VOC emissions because of the poor efficiency of the carbon adsorbers, as operated at this site;

- The carbon adsorption system is almost completely ineffective in removing significant quantities of VOC from the dome exhaust stream;

- Leakage around and/or through the cover over the aeration pond appears to be quite small;

- The aromatic compounds are effectively destroyed through biological activity in the aerated pond;

- The halogenated compounds are vaporized and lost in the purge stream through the carbon adsorption system; and

- The paraffinic compounds are virtually unaffected in wastewater treatment system and leave the system in the effluent wastewater.

PRODUCTS OF INCOMPLETE COMBUSTION - ANALYTICAL METHODS

M.M. Thomason, R.H. James, R.E. Adams
Southern Research Institute
P.O. Box 55305
Birmingham, Alabama 35255-5305

L.D. Johnson
Air and Energy Engineering Research Laboratory
U.S. Environmental Protection Agency
Research Triangle Park, North Carolina 27711

ABSTRACT

Products of incomplete combustion (PICs) may be formed during the incineration of hazardous wastes. The monitoring of principal organic hazardous constituents (POHCs) may be confused by the formation of PICs which are also POHCs. The total amount of hazardous PICs formed can easily exceed the total amount of the indicator POHCs detected in the exhaust gases of an incinerator. The compounds may be fragments of incineration feed constituents, products of complex recombinations, products of substitution reactions in the flame or post-flame zone, or compounds that enter the incineration process through other sources.

We have concentrated our efforts on applying previously developed general analysis methods for POHCs to the analysis of PICs. A large part of the current literature on PICs has resulted from finding polychlorinated dibenzo-p-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs) in incinerator effluents. Thus, we have specifically evaluated generalized GC/FID and GC/MS methods for PCDDs and PCDFs. Substituted polynuclear aromatic hydrocarbons (PAHs) are also frequently formed as PICs. We have also evaluated generalized analysis methods for a number of amino-, nitro-, alkyl-, oxy-, and halogenated PAHs. The compounds chosen are not yet included in Appendix VIII of 40 CFR, Part 261.

The results presented here give representative chromatograms, mass spectral conditions, and detection limits for these groups of compounds. Future work includes the identification of PICs in incinerator effluent samples with the extension of the general analysis procedures to high-priority compounds.

INTRODUCTION

During the incineration of hazardous wastes, compounds not identified in the waste feed may be formed. These compounds are known as products of incomplete combustion (PICs). The aim of incineration is to destroy all of the principal organic hazardous constituents (POHCs) in the waste and to make sure that harmful levels of PICs, which may be formed during combustion, do not escape into the environment. The total amount of hazardous PICs formed can easily exceed the total amount of the indicator POHCs detected in the exhaust gases of an incinerator. Trenholm (1) has defined PICs as any hazardous organic constituent detected in the stack gas of an incinerator but not present in the waste feed at a concentration of 100 μg/g or higher. PICs may be fragments of incineration feed constituents, products of complex recombinations, products of substitution reactions in the flame or post-flame zone, or compounds that enter the incineration process through other sources.

The combustion of chlorinated hydrocarbons has been shown to form PICs (2). In chlorinated hydrocarbon combustion, pyrolysis of the parent molecules forms dechlorinated intermediates because of the weak C-Cl bond. The dechlorinated intermediates may then undergo a variety of reactions: recombination to form other chlorinated hydrocarbons, further pyrolysis, oxidation, or polymerization. As the chlorine content of the hydrocarbons increases, the formation of soot is favored because of the weak C-Cl bond strength. Soot formation is undesirable because it is often related to the production of toxic compounds such as polycyclic aromatic hydrocarbons (PAHs). The combustion of chlorinated hydrocarbons has also been reported to produce polychlorinated dibenzo-p-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs) (3,4). PCDDs and PCDFs have also been found in incinerator effluents and fly-ash samples by several research groups (5-7).

Tiernan and co-workers (8) sampled and analyzed the effluents from an incinerator used to heat a steam boiler designed for energy recovery from the combustion of municipal refuse. Chlorophenols, chlorobenzenes, PCDDs, PCDFs, and traces of PCBs were found in the incinerator effluent. Karasek and co-workers (9) recently reported a detailed analysis of fly-ash extracts of municipal incinerators in Canada and Norway. They identified more than 200 organic components in the extracts. Compounds found included hydrocarbons, phthalate esters, PAHs, PCDDs, PCDFs, and other polychlorinated organic compounds.

The formation of PICs in an incinerator environment is probably a very complex phenomenon. The two classes of PICs which are under very close scrutiny at the present time are PCDDs and PCDFs. PCDDs and PCDFs are apparently formed from precursors such as PCBs, polychlorinated naphthalenes, polychlorobenzenes, and other chlorinated organic compounds found in the hazardous-waste load. Incinerator conditions also play a major role in the extent of PIC formation.

PURPOSE

We have concentrated our efforts on applying previously developed general analysis methods for POHCs to the analysis of PICs. A large part of the current literature on PICs has resulted from finding PCDDs and PCDFs in municipal incinerator effluents. Thus we have specifically evaluated generalized GC/FID and GC/MS methods for 10 PCDD isomers and 3 PCDF isomers which are frequently formed as PICs. We have also evaluated the generalized analysis methods for a number of amino-, nitro-, alkyl-, oxy-, and halogenated PAHs. The compounds chosen are not yet included in Appendix VIII of 40 CFR, Part 261.

EXPERIMENTAL APPROACH

- Preparation of Stock Standard Solutions of PICs

Stock standard solutions of the candidate compounds were prepared in appropriate solvents at a concentration of about 0.05 mg/mL. These stock solutions were serially diluted as required to prepare working standards. Methylene chloride, toluene, and isooctane were used as solvents.

- Description of General Operating Conditions

We developed the GC/MS generalized test method on a Hewlett-Packard Model 5985 GC/MS data system. The supplemental GC/FID work was performed on a Hewlett-Packard Model 5840 GC that was equipped for use with capillary columns.

The generalized GC/MS, GC/FID procedure is:

Instruments: HP 5985A for GC/MS and HP 5840 for GC/FID
Columns: Two SE-54 bonded-fused-silica capillary columns, 0.32-mm ID, 25-m length
Carrier gas: Helium, 2 mL/min
Injection: 2 μL splitless
Column temperature program: 60 °C for 3 min, then programmed at 20 °C/min to 300 °C and held at 300 °C for 15 min
Injection temperature: 290 °C
FID temperature: 300 °C
MS parameters: Scan 41 to 500 amu/sec, electron ionization at 70 eV, source temperature set to 200 °C, capillary column plumbed directly into the ion source.

The initial operating conditions chosen were a synthesis of conditions that would allow the separation and detection of as many compounds as possible. Modifications of temperatures and rates may be necessary or desirable to optimize the analysis for specific compounds.

PCDDs and PCDFs were also analyzed using selected-ion monitoring (SIM) GC/MS to improve the detection limits obtainable. Table 1 summarizes the ions monitored in the SIM studies. A 70 msec/ion dwell time was used.

- Optimization of the GC/FID and GC/MS Procedures

GC operating conditions were optimized by analyzing solutions containing selected PICs by the GC/FID technique. The column-head pressure was adjusted appropriately to allow adequate separation of the compounds of interest in less than 30 min.

Having established GC operating conditions by the GC/FID procedure, we then applied the method to the determination of the candidate PICs by GC/MS. The mass spectrometer was operated in a full mass scanning range (41 to 500 amu) in the EI mode. The scan time was maintained at ≤1 sec to enable the collection of enough scans to characterize each capillary GC peak. During SIM, the mass spectrometer dwelled on each selected mass for 70 msec/scan.

- Quality Control Procedures

We calibrated the GC/FID and the GC/MS procedures with standard solutions of the candidate PICs using anthracene-d_{10} as the internal standard. Four- to six-point calibration curves were prepared for each candidate PIC determined by gas chromatography. Each curve was a plot of the FID or the MS response (relative to anthracene-d_{10}) as a function of the quantity of the particular PIC injected on the GC column. Appendix A of reference 10 was used as a guideline for estimating detection limits for each candidate POHC.

The precision of determinations by GC/FID and GC/MS was assessed by triplicate injections of at least one standard solution of each PIC investigated by GC. Relative response factors (RRF) were calculated for each PIC relative to anthracene-d_{10}.

Recovery data were not applicable for this phase of the project because our analyses were done with standard solutions of PICs. We did not collect, prepare, or analyze field samples that required spiking of the matrix with surrogate standards of specific PICs.

RESULTS AND DISCUSSION

The generalized GC/FID and GC/MS methods for POHCs (11) were adapted for the analysis of 36 candidate PICs. Table 2 presents a summary of the GC/FID determinations of candidate PICs. The relative retention time (RRT) and on-column detection limit are given for each compound. The compounds are listed in the order of their elution from the GC column.

TABLE 1. IONS USED IN SELECTED-ION MONITORING OF SELECTED PICs

Compounds/Classes	PCDD Ions		PCDF Ions		Internal standard ions ($^{13}C_{12}$-TCDD)		Internal standard ion (anthracene-d_{10})
Mono-substituted PCDDs and PCDFs	218	220	202	204	332	334	188
Di-substituted PCDDs and PCDFs	252	254	236	238	332	334	188
Tri-substituted PCDDs and PCDFs	286	288	270	272	332	334	188
Tetra-substituted PCDDs and PCDFs	320	322	304	306	332	334	188
Hexa-substituted PCDDs and PCDFs	388	390	372	374	332	334	188
Octa-substituted PCDDs and PCDFs	458	460	442	444	332	334	188

Retention times are relative to that observed for the internal standard, anthracene-d_{10}. The on-column detection limit was estimated using experimentally determined calibration curves as suggested in Appendix A of Reference 10. Typical values were 2 to 40 ng.

The precision of determinations was assessed by triplicate injections of at least one standard solution of each PIC investigated by GC. RRFs were calculated for each PIC relative to anthracene-d_{10}. These results are also summarized in Table 2. The calculated values of the standard deviations (SDs) and relative standard deviations (RSDs) in Table 2 indicate that most GC/FID determinations gave acceptable precision. The percent RSDs range from 0.2 to 9.3%.

Table 3 summarizes the GC/MS determination of the candidate PICs. The five most abundant mass fragments of each compound, along with their relative abundance, were used for the establishment of detection limits and for the generation of calibration curves. RRTs and RRFs were determined for each compound. The RRTs for GC/FID and GC/MS were similar. The precision of the GC/MS determinations was also evaluated by triplicate injections. In general, the precision of the GC/MS determinations was poorer than the GC/FID determinations. The RSDs range from 3 to 27%.

Figure 1 is a representative total-ion chromatogram (TIC) obtained for several dioxin isomers. The candidate dioxin and furan isomers studied were also evaluated using SIM. The estimated limits of detection were 40 to 200 times lower using SIM instead of full mass acquisition.

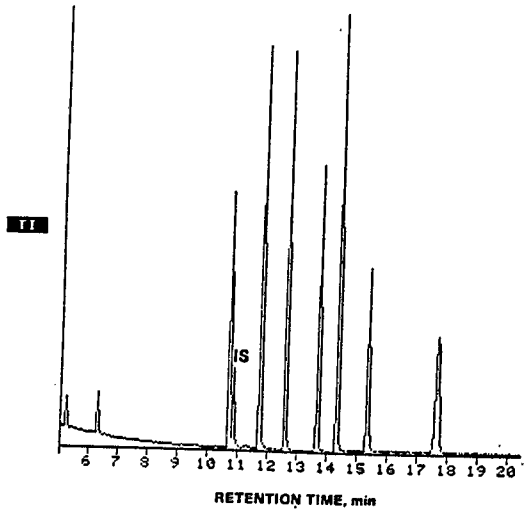

Figure 1. TIC of selected dioxin isomers.

TABLE 2. SUMMARY OF GC/FID DETERMINATIONS OF CANDIDATE PICs

Compound	Relative retention time[a]	On-column detection limit, ng	Precision of RRF[b]		
			Mean	Standard deviation	Relative standard deviation, %
1-Fluoronaphthalene	0.619	4	0.928	0.012	1.3
2-Bromonaphthalene	0.820	5	0.733	0.008	1.1
3-Bromoquinoline	0.825	2	0.543	0.0071	1.3
1-Bromo-2-methylnaphthalene	0.896	3	0.635	0.0050	0.79
1-Iodonaphthalene	0.899	2	0.540	0.0022	0.42
1-Bromo-4-methylnaphthalene	0.907	3	0.664	0.0070	1.1
2-(Bromomethyl)naphthalene	0.929	9	0.431	0.0095	2.2
1-Amino-4-chloronaphthalene	0.972	40	0.028	0.00012	0.42
2-Chlorodibenzo-p-dioxin	0.980	10	0.659	0.0014	0.22
1-Chlorodibenzo-p-dioxin	0.983	2	0.474	0.0013	0.28
9-Bromofluorene	0.991	10	0.379	0.0050	1.3
5-Bromoacenaphthene	1.01	5	0.554	0.0010	0.2
1-Amino-4-bromonaphthalene	1.02	4	0.548	0.0055	0.99
1-Chloro-8-nitronaphthalene	1.03	4	0.560	0.0058	1.0
2-Chloroanthracene	1.05	7	0.356	0.0015	0.42
3,6-Dichlorodibenzofuran	1.06	3	0.626	0.0044	0.71
2-Bromofluorene	1.06	10	0.595	0.0039	0.65
2,7-Dichlorodibenzo-p-dioxin	1.08	2	0.388	0.0020	0.52
2,3-Dichlorodibenzo-p-dioxin	1.08	10	0.553	0.0023	0.42
1-Chloroanthracene	1.11	4	0.743	0.0017	2.3
9-Chloroanthracene	1.11	4	0.678	0.0083	1.2
9-(Chloromethyl)anthracene	1.11	4	0.945	0.0034	0.36
1,2,4-Trichlorodibenzo-p-dioxin	1.16	5	0.352	0.0043	1.2
9-Bromophenanthrene	1.16	4	0.528	0.0011	2.0
9-Bromoanthracene	1.17	5	0.529	0.0053	1.0
9,10-Dichloroanthracene	1.20	4	0.638	0.0017	2.6
2,3,7,8-Tetrachlorodibenzofuran	1.23	2	0.356	0.0005	1.4
1,2,3,4-Tetrachlorodibenzo-p-dioxin	1.28	2	0.277	0.0077	2.8
6,9-Dichloro-2-methoxyacridine	1.28	5	0.318	0.0012	3.8
9,10-Dibromoanthracene	1.30	9	0.318	0.0009	2.8
3,6-Dibromocarbazole	1.37	8	0.178	0.0017	9.3
1,2,3,4,7-Pentachlorodibenzo-p-dioxin	1.40	10	0.379	0.0094	2.5
1,2,3,4,7,8-Hexachlorodibenzo-p-dioxin	1.57	8	0.190	0.0011	6.0
1,2,3,4,6,7,8-Heptachlorodibenzo-p-dioxin	1.83	40	0.118	0.0023	2.0
1,2,3,4,6,7,8,9-Octachlorodibenzo-p-dioxin	2.15	20	0.090	0.0077	8.5
1,2,3,4,6,7,8,9-Octachlorodibenzofuran	2.17	20	0.104	0.0073	7.0

[a]Relative to the retention time of anthracene-d_{10}.

[b]Relative response factor (RRF) = $(A_s C_{is}/A_{is} C_s)$.

TABLE 3. SUMMARY OF GC/MS DETERMINATIONS OF CANDIDATE PICs

Compound	Mol wt	Masses of characteristic EI ions (relative abundance) 1	2	3	4	5	On-column detection limit, ng
1-Fluoronaphthalene	146	146(100)	73(10)	147(10)	145(8)	125(8)	9
2-Bromonaphthalene	206	208(100)	206(90)	127(55)	126(14)	207(12)	5
3-Bromoquinoline	207	207(100)	209(94)	128(89)	101(33)	75(22)	4
1-Bromo-2-methylnaphthalene	220	141(100)	220(89)	222(86)	139(34)	115(32)	50
1-Iodonaphthalene	254	127(100)	254(98)	126(19)	255(12)	128(10)	5
1-Bromo-4-methylnaphthalene	220	141(100)	220(97)	222(93)	139(34)	115(26)	5
2-(Bromomethyl)naphthalene	220	141(100)	115(17)	139(14)	70(13)	142(12)	4
1-Chlorodibenzo-p-dioxin	218	218(100)	220(34)	219(14)	155(12)	221(5)	9
2-Chlorodibenzo-p-dioxin	218	218(100)	220(34)	155(30)	127(23)	109(18)	10
1-Amino-4-chloronaphthalene	177	177(100)	179(32)	115(28)	178(13)	149(11)	9
5-Bromoacenaphthene	232	153(100)	152(83)	76(67)	232(39)	234(38)	10
9-Bromofluorene	244	165(100)	166(15)	163(14)	82(13)	164(10)	10
1-Chloro-8-nitronaphthalene	207	172(100)	126(72)	207(40)	161(37)	149(25)	9
1-Amino-4-bromonaphthalene	221	223(100)	221(94)	115(51)	70(24)	114(16)	40
3,6-Dichlorodibenzofuran	236	236(100)	238(70)	173(20)	237(15)	240(12)	3
2-Bromofluorene	244	165(100)	246(63)	244(59)	163(24)	166(18)	5
2,7-Dichlorodibenzo-p-dioxin	252	252(100)	254(66)	189(28)	126(25)	253(13)	9
2,3-Dichlorodibenzo-p-dioxin	252	252(100)	254(63)	126(22)	189(22)	253(14)	3
1-Chloroanthracene	212	212(100)	214(32)	176(26)	88(20)	213(15)	4
2-Chloroanthracene	212	212(100)	214(37)	176(29)	177(18)	213(17)	7
9-Chloroanthracene	212	212(100)	214(33)	176(30)	88(18)	213(15)	8
9-Bromophenanthrene	256	256(100)	258(99)	176(57)	88(48)	177(34)	8
9-Bromoanthracene	256	256(100)	258(98)	88(61)	176(54)	177(29)	10
1,2,4-Trichlorodibenzo-p-dioxin	286	288(100)	286(89)	290(34)	223(23)	225(20)	10
9-(Chloromethyl)anthracene	226	191(100)	189(28)	226(21)	192(18)	94(17)	7
9,10-Dichloroanthracene	246	246(100)	248(73)	176(33)	247(18)	87(15)	4
2,3,7,8-Tetrachlorodibenzofuran	304	306(100)	304(77)	308(45)	307(11)	310(10)	9
1,2,3,4-Tetrachlorodibenzo-p-dioxin	320	322(100)	320(78)	324(49)	323(12)	257(11)	10
6,9-Dichloro-2-methoxyacridine	277	277(100)	234(78)	279(69)	236(51)	164(23)	10
9,10-Dibromoanthracene	334	176(100)	88(84)	336(52)	87(37)	334(26)	4
1,2,3,4,7-Pentachlorodibenzo-p-dioxin	354	356(100)	354(71)	358(63)	293(26)	291(22)	10
3,6-Dibromocarbazole	323	325(100)	323(54)	327)52)	246(24)	244(24)	4
1,2,3,4,7,8-Hexachlorodibenzo-p-dioxin	388	390(100)	392(86)	388(50)	394(36)	327(30)	8
1,2,3,4,6,7,8-Heptachlorodibenzo-p-dioxin	422	424(100)	426(99)	428(50)	422(41)	361(28)	10
1,2,3,4,6,7,8,9-Octachlorodibenzo-p-dioxin	456	460(100)	458(100)	142(77)	462(74)	167(57)	40
1,2,3,4,6,7,8,9-Octachlorodibenzofuran	440	442(100)	444(98)	446(72)	440(41)	154(40)	30

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EPA RESEARCH TO RECOVER TOXIC HEAVY METALS FROM WASTE STREAMS

S. Garry Howell
Hazardous Waste Engineering Research Laboratory
U. S. Environmental Protection Agency
Cincinnati, Ohio 45268

ABSTRACT

The Environmental Protection Agency (EPA) has sponsored several research programs with the goal of reducing heavy metal pollution of land, surface and groundwater. Past efforts were aimed at reducing discharges of heavy metals from electroplating operations, and investigating the possibilities of establishing centralized treatment and recovery systems for large metropolitan areas such as Cleveland, Los Angeles, and Milwaukee. EPA studies indicate that such facilities would be feasible, and that a large part, if not all, of their cost of operation could be met by sale of the metals recovered.

INTRODUCTION

Heavy metal wastes such as those produced by metal plating operations, have traditionally been discarded rather than treated for reclamation of metal values. Sludges and mill scales were usually landfilled, and plating wastewaters often discharged to the sewer. Various regulations have greatly restricted these practices, and the recent escalation of both metal and energy costs have made metal recovery not only a desirable environmental goal but the time is rapidly approaching when the value of recovered metals will cover the cost of pollution abatement, and in some instances yield a modest profit. The Environmental Protection Agency has sponsored research into metals recovery from several sectors of the metals (i.e., mill scale, grinding swarf) and metal finishing industry (plating wastes). This paper will cover only plating and the chemically closely related electrochemical machining wastes.

History and Background

There are an estimated 20,000 metal finishing shops in the U.S., about 80% of which plate copper, nickel, chromium, and zinc. In years past spent plating wastes were hauled to a landfill, or even diluted and poured into a sewer. Toxic effects of heavy metals on marine life, and pollution of drinking water has led to a number of laws and regulations restricting landfilling of sludges and liquids containing heavy metals. In addition to the ultimate cost to society in health effects, the economic loss suffered by discarding potentially valuable minerals is tremendous. As several of these minerals are mostly imported (nickel and chromium, and to a lesser degree copper) they are also of strategic value. Table 1, from a report by the Comptroller General to Congress, shows an estimate of metal values lost in 1980. Using the same amounts of metal discarded, and adjusting for 1985 prices, the total value is almost 58 million dollars.

It is obviously impractical to attempt to recover all the heavy metals shown in Table 1 (iron and aluminum are not economically recoverable in small quantities). The report from which this table was taken suggests that it would be technically feasible to recover 80 to 90 percent of the copper, 30 to 40 percent of the zinc, 90 to 95 percent of the nickel and 70 to 75 percent of the chromium. Economic feasibility is the prime obstacle; quite likely only 40 to 50 percent recovery could be obtained even under the best conditions.

TABLE 1. ANNUAL LOSS OF MINERALS IN ELECTROPLATING WASTES

Mineral	Amount (metric tons)	Value/Ton	Total Value
Iron	3,460	$ 77	$ 266,420
Copper	2,560	791	2,024,960
Zinc	3,718	748	2,781,064
Nickel	5,000	4,000	20,000,000
Aluminum	1,651	1,060	1,750,060
Chromium	6,357	2,000	12,714,000
Lead	756	462	349,272
Total	23,502		$39,885,776

RESULTS AND CONCLUSIONS

Operation of a pilot scale metal recovery unit has demonstrated that metal recovery from electroplating and electrochemical machining wastes is technically feasible, and in most cases, economical. If transport costs from generating sites to the recovery facilities are very low, as could be the case in some metropolitan areas, the value of metals recovered will often lower operating expenses, and in many cases yield a profit.

Profitability of a metals recovery operation is primarily dependent on the following factors:

- Metal type and concentration in the sludge; for instance, high concentrations of high value metals such as nickel and chromium can be sold, yielding enough profit to support the rest of a recovery operation.
- Availability of large quantities of high metal content wastes within a reasonably short range. Hauling distances that averge over 25 miles can greatly increase recovery costs to the point where recovery is no longer economically feasible.
- An economical and reasonably flexible recovery process; some variability in composition is to be expected in metal wastes fed to the operation. This cannot always be offset by blending to achieve homogeneity of feed material.
- The actual viability of a metal recovery operation in a specific area can only be determined by careful weighing of all the above factors plus the availability of capital and special tax considera tions often given to resource recovery facilities.
- The probable minimum economical size of a control recovery operation is 25-50 tons of 25% solids sludge per day.
- The most practical and economical overall process appears to be a series of unit operations tying together more or less conventional hydrometallurgical processes; pyrometallurgical approaches do not appear to be economical for small volume recovery operations.
- While sulfide precipitation yields effluent water with a very low metal content, the difficulty of and energy costs for separating and recycling sulfides makes it a poor second choice to hydroxide precipitation for metal recovery. In addition, EDTA must be added to

selectively precipitate metal sulfides, and organic coagulants must be used to produce filterable precipitates.

RESEARCH PROJECTS

The Environmental Protection Agency has sponsored research into metal removal and/or recovery from wastewaters and sludges for over ten years. Early efforts concentrated on water purification (10) but the wisdom of reclaiming metal was soon recognized as a means of reducing water pollution conserving metal/resources. Work done for EPA at Battelle Columbus in 1975 included a survey of plating facilities and the volume and types of metals discarded in sludges. As understanding of the problem began to develop, a series of investigations were funded, each adding to the overall bank of information. These projects are listed in reverse chronology below.

Metal Value Recovery from Metal Hydroxide Sludges (1)

The latest EPA projects were undertaken at the Montana College of Mineral Science and Technology (Montana Tech), and tied together much of the previous work. The first phase of the investigation was a carefully executed series of laboratory experiments to establish the processes needed to leach hydroxide sludges (the most plentiful type produced by electroplating (EP Shops) with sulfuric acid, and the various recovery methods required for copper, zinc, chromium, and nickel. Flowsheets were constructed and the unit operations required to make a complete recovery process were developed.

In Phase Two, a pilot assembly capable of processing 75-100 lbs. of sludge per day was built and operated at a large electroplating facility. While not entirely troublefree, the operation was smooth enough to allow confirmation of the possible commercial viability of the process, and development of a computerized mass balance.

The steps of the process were as follows:

- The sludge is leached with sulfuric acid.
- Iron, which is frequently present in EP sludges, was removed by precipitating as a potassium jarosite [$KFe_3(SO_4)_2(OH)_6$]. This must be done first, as iron interferes in many of the subsequent recovery steps. This step is in need of improvement, because in the process of precipitating the jarosite some anions such as chromate are removed, along with some heavy metal cations. Even though the volume of the jarosite sludge is much less than that of the starting material, the waste would be classed as hazardous, requiring special precautions and extra costs when landfilling. Because of these faults, it is proposed that a new program be instituted to attempt to remove iron without the inclusion of large amounts of other heavy metals.
- Conventional techniques were used to extract copper from the acid solution using an oxime in petroleum solvent. The copper was then stripped from the organic phase with stronger acid and electrowon or crystallized as sulfate.
- Zinc and cadmium were extracted with diethyl hexyl phosphoric acid (D_2EHPA), leaving chromium and nickel behind. Again, a sulfuric acid strip was used for zinc removal from the organic phase. Small amounts of residual iron are removed in early stages of extraction; ten extraction stages are required to remove iron-free zinc.
- Chromium was oxidized to Cr^{+6} with chlorine, then selectively precipitated as lead chromate which can be sold as a pigment or regenerated to chromic acid with sulfuric acid. The lead sulfate precipitate formed when chromic acid is regenerated may itself be recycled to precipitate more lead chromate. In some instances SO_2/O_2 oxidation of the chromium may be more desirable.
- Nickel is precipitated as sulfide, the only heavy metal in the process which is not directly recyclable back to a plating operation. However, several alternative techniques

are presented to yield a nickel ammine, or nickel sulfate may be solvent extracted with a mixture of chelating agents.

Recognizing that some improvements could be made in the various separation steps, first order cost estimates indicate that a 50 ton per day recovery plant could not only reduce landfill volume considerably, with consequent less chance of pollution, but in addition could yield a profit as shown in Table 2 below.

Metal Recovery from Electrochemical Machining and Electrodischarge Machining (ECM/EDM) Wastes (2)

These relatively new machining processes produce heavy metal wastes; ECM yields hydroxide sludges heavily contaminated with sodium chloride, and EDM finely divided particles of the alloy being machined. Both ECM and EDM are primrily used on hard alloys, often high in nickel, chromium, cobalt, molybdenum, etc. This project involved a survey of ECM/EDM shops, the volumes of sludge produced, metal content, and disposal practices and costs. Several recovery routes were studied, including the procedures outlined in Reference (1) above.

Cadmium Recovery from Electroplating Wastes (3)

This project was primarily concerned with methods and costs for recovering cadmium from plating shops which are able to segregate Cd from other sludges, or perhaps those whose only business is cadmium plating. The authors give very little thought to the fact that many platers use cadmium at least occasionally, and do not segregate their sludges. The recovery technique (melt and/or distill cadmium electromotively displaced with zinc metal) is most effective on low chromium and nickel sludges. While chromium is not displaced by zinc, nickel would have to be removed by distilling the zinc.

Coupled Transport Systems for Control of Heavy Metal Pollutants (4)

Coupled transport membranes are made by immersing a microporous membrane into a liquid complexing agent such as those used

TABLE 2. PROCESS COST: FIRST ORDER ESTIMATE (2)

UNIT OPERATION	COST ($)*			
	Factored Capital Cost Estimate	Annualized Capital Cost	Operation Cost Per Year	Total Cost Per Year
1. Leach, jarosite precipitation	430,800	119,500	223,500	343,000
2. Jarosite storage	390,500	108,200	25,400	133,600
3. Copper solvent extraction, electro-winning	336,100	93,100	205,900	299,000
4. Zinc, residual iron solvent extraction, zinc sulfate crystallization	661,600	183,300	269,700	453,000
5. Chromium oxid., chromic acid production	1,818,200	503,600	407,700	911,300
6. Nickel recovery	231,600	64,200	230,000	294,200
TOTAL COST	3,868,800	1,071,900	1,362,200	2,434,100
Profit (Gross)			1,071,900	

*Assuming a $1.00 per gallon credit for sludge from producers.

for liquid/liquid extraction of metals from solution. The liquid (often called a liquid ion exchanger) then acts as a transfer agent to move metal ions through the capillaries, using the driving force of the pH gradient across a membrane separating an acidic from a basic solution. Data are presented which suggest that a membrane unit having 450 to 500 square feet of surface could separate chromium from the rinse water of a medium sized plating line. The separation unit would cost about $5,000, compared to over $50,000 for an evaporative-ion exchange system as noted in Reference (5) below.

Evaporative Recovery of Chromium Plating Rinse Waters (5)

A demonstration of this process was given by Advance Plating Company, Cleveland, Ohio on the first of four counterflow rinse tanks. After first passing through a cation exchanger to remove metallic impurities, water from the first rinse tank is drawn into a vacuum evaporator, whose condensate is returned to the third rinse tank. Concentrated acid produced in the evaporator bottoms is returned to the plating bath. The value of recovered chrome has enabled the operator to pay off the equipment in two years or less, in addition, the chromic acid in dragout water is reduced by 99.98%.

Removal of Toxic Metals from Metal Finishing Wastewater by Solvent Extraction (6)

This short investigation of solvent extraction was primarily limited to one extraction agent, Alamine 336 (General Mills). By increasing acidity stepwise with HCl, selective removal of chromium, cadmium, and zinc from wastewaters was demonstrated. Copper and nickel could not be extracted with this reagent; several other high molecular weight amines were tried without success.

Reverse Osmosis Field Test: Treatment of Watts Nickel Rinse Waters (7)

Rinse waters from a Watts type (primarily nickel sulfate) nickel plating operation were passed through a polyamide membrane, effectively separating a concentrated nickel salt solution and recycling the rinse water. Results were very encouraging, indicating that the capital cost of the R.O. unit could be recovered in about a year, based on the reduction in water usage plus metal values returned to the plating bath. This process could be more accurately described as recycling or conservation since there is no chemical change of metals recycled to the bath.

Treatment of Metal Finishing Wastes by Sulfide Precipitation (8,9,10,11)

Although the process of sulfide precipitation has been known for many years, its use as a means of pollution control appears to be of fairly recent origin, and, is mentioned here primarily to illustrate an effective method of metal removal. A major disadvantage of sulfide precipitation is the lack of selectivity; it is apparently impossible to precipitate a single metal without major contamination by other metal sulfides. Use of a polymeric flocculant (preferably anionic) increased the settling rate, and adding a chelating agent such as EDTA (ethylenediamine tetraacetic) acid at the proper pH greatly aided selectivity.

Heavy metal sulfides, even if effectively separated, are extremely difficult to reduce to their corresponding metals by hydrometallurgical methods, and are generally recovered by smelting. The large volumes of raw material required to support such smelters makes plating waste metal recovery by this method impractical.

A Reclamation of Metal Values from Metal Finishing Waste Treatment Sludges (12)

A survey of plating opertions involving over 600 questionnaires (150 replies) revealed the extent of sludges generated by the industry, and even developed a "typical" analysis of metal content; the copper, nickel, and chromium contents were very similar to those found in subsequent studies. Some preliminary laboratory leaching and extraction studies led to the conclusion that metal recovery could be economically feasible only if the process could be carried out on a large, and preferably continuous scale. Based on then current (1971) metal prices, it was concluded that chromium and zinc recovery were uneconomic; the writers apparently did not foresee the ban on landfilling of heavy metal wastes now being implemented. (10) The only laboratory work done by these investigators were leaching experiments with ammonium carbonate and sulfuric acid which indicated that acid leaches were

adequate for most hydroxide sludges while ammonium carbonate would only dissolve copper and nickel. A literature study of several potential recovery methods for copper and nickel was made, but no work was done to verify their efficacy; again, chromium recovery was not considered.

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CHEMICAL DESTRUCTION/DETOXIFICATION OF CHLORINATED DIOXINS IN SOILS

Robert L. Peterson
Edwina Milicic
Galson Research Corporation
East Syracuse, New York 13057

Charles J. Rogers,
U.S. Environmental Protection Agency
Cincinnati, Ohio 45268

ABSTRACT

Laboratory experiments using 1,2,3,4 tetrachlorodibenzo-p-dioxin show that chlorinated dioxins in soil may be chemically reduced to levels below one part per billion. The decontamination processes involve the addition to the soil of a mixture of alkali metal hydroxide, polyethylene glycols or capped polyethylene glycols, dimethyl sulfoxide and water. The reagent is either added directly to the soil with mixing (in-situ process) or mixed 1:1 by volume with soil in an external reactor (slurry process). The dioxin is dechlorinated to a water soluble form, which may be then removed from the soil (slurry process) or allowed to biodegrade (in-situ process).

INTRODUCTION

The contamination of large areas of soil with dioxin have created a need for a cleanup method which is capable of handling large volumes of contaminated soil in a cost effective manner. Proposed treatment methods include incineration, solvent extraction and direct chemical dechlorination. This paper will discuss the successful use of direct chemical dechlorination in decontamination of dioxin contaminated soils on a laboratory scale and the implications of these data for large scale soil treatment.

The basis for use of chemical dechlorination as a decontamination method lies in the relationship between the toxicity of chlorinated dioxins and the number of chlorine atoms on the dioxin molecule. In order for a dioxin isomer to exhibit high toxicity a minimum of three chlorine atoms are required, and these must be in the 2,3, and 7 positions (1). In addition, the lipophilic nature of many chlorinated dioxins contributes to their bioaccumulation activity. The dechlorination processes used in this study reduce the number of chlorine atoms on the dioxin molecule and produce a hydrophilic material which is more easily removed from the soil than the parent dioxin.

PURPOSE

The purpose of this project is to identify and evaluate at the laboratory level an effective chemical process for destruction/detoxification of chlorinated dioxins in soil.

APPROACH

Direct chemical decontamination of soil can be considered to be a two step process;

1. Application of the reagent to the dioxin contaminated soil
2. Reaction of the dioxin and reagent

These two aspects of the process interact. For example, a reagent with high mobility in soil requires a less rigorous application method than a reagent which is highly viscous.

However at a minimum the reagent must be capable of reducing dioxin concentrations to <1 ppb, or favorable mobility and ease of application become irrelevant. For this reason, the reaction system was selected first, with the method of application designed around the reagent system.

Application methods for direct decontamination of soil must be compatible with the reaction system selected. In order for a direct chemical reaction process to be effective, the contaminated soil and reagent must be brought into close contact. The degree of contact between soil and reagent may be increased by mechanical mixing, by addition of diluents and co-solvents to increase the reagent mobility, and by heating the soil/reagent mixture to reduce the viscosity of the reagent. After selection of the reaction system, a variety of application methods were tested under laboratory conditions for use in dioxin soil decontamination.

In order to reduce the costs of handling and analyzing soil samples, a low toxicity dioxin isomer, 1,2,3,4 tetrachloro-p-dibenzo dioxin (TCDD), was used in place of 2,3,7,8 TCDD for all testing. Laboratory tests of 2,3,7,8 TCDD and 1,2,3,4 TCDD indicated that rates of reaction for the two isomers were sufficiently similar to allow generalization of results between isomers.

To insure sample uniformity, all samples for treatment used uncontaminated soil which was spiked with a known amount of dioxin. Each soil sample was spiked individually, with the entire sample used for analysis. Uncontaminated soil samples were obtained from the vicinity of a dioxin site in Mississippi and spiked with 1,2,3,4 TCDD before processing. Soil from an authentic test site was used to avoid the wide variations seen in previous tests of treatability of different PCB contaminated soils. It was anticipated that dioxin contaminated soils would show similar variations.

PROBLEMS ENCOUNTERED

Major problems encountered during this project involved the analytical procedure. Analysis of soil samples by gas chromatography was frustrated by the large number of interferences found in the test site soils. The interference problem was exacerbated by the ability of the reagents used to extract materials from the soil which were not extracted by the analytical solvents used. While this high extraction efficiency for the treatment solvents contributed to the success of the dioxin destruction, it complicated the analysis. The failure of cleanup procedures to produce an acceptable sample necessitated a move to gas chromatography/mass spectroscopy as the primary method of analysis.

An additional problem was caused by the tendency of the test site soil to solidify if exposed to high temperatures (100°C or above) under alkaline conditions. This problem was solved by moving to lower temperatures, which proved adequate for purposes of treatment.

RESULTS AND DISCUSSION

Selection of Reagent System - Of the available reactions, including ultraviolet dechlorination, ruthenium tetroxide oxidation and nucleophilic substitution, nucleophilic substitution using alkali metal hydroxides has given the best results in both literature studies and laboratory trials. The preferred reactions of this type for use with halogenated aromatics involve combination of potassium hydroxide and polyethylene glycols to form an alkoxide, which is the reactive species. The addition of a sulfoxide catalyst/co-solvent, usually dimethyl sulfoxide, greatly enhances the rate and degree of reaction, although it is not known if this is due to the effectiveness of the sulfoxide as an extractant for aromatics or to the catalytic effect of the sulfoxide for substitution reactions. The probable mechanism for this class of reactions follows;

$$ROH + KOH \text{ --------- } > ROK + HOH$$

$$ArCl_n + ROK \xrightarrow{\text{Sulfoxide}} ArCl_{n-1}OR + KCL$$

The partially dechlorinated, water soluble reaction product may continue to undergo dechlorination, depending on the reaction conditions. Several reactions of this type have demonstrated reduction of dioxin concentrations in liquids to <1 ppb.

Selection of Application Method - A wide variety of hydroxide/alcohol/sulfoxide reaction systems will effectively dechlorinate dioxins in liquid solution. However, application of the reagent to the soil in such a manner as to allow these reactions to occur is a significant problem. The necessary degree of contact has been achieved using two different approaches; direct addition of reagent or a reagent/water mixture to the soil with mixing in place (in-situ process) and excavation of the soil followed by mixing equal volumes of soil and reagent in an external reactor (slurry process).

Both the slurry and in-situ processes may be used at elevated temperatures. Heating methods for an in-situ system would use radio frequency (RF) or microwave heating(2). The simplest method of heating for the slurry process is to preheat the reagent prior to mixing of the soil and reagent. Both of these heating methods are applicable to large scale processing.

The two application methods have different areas of application. The in-situ process is limited to areas of shallow contamination and the soil and reagent may be mixed with conventional agricultural equipment. In addition, the degree of contamination must be relatively uniform. If small areas of high concentration or "hot spots", are present, the high local concentration of contaminant might exhaust the amount of reagent which may be economically applied. While the concentrations of dioxin generally observed in the field are not high enough to cause a problem, dioxins are often found in combination with other chlorinated wastes, which may be present in high concentrations. However, in suitable cases, large areas of shallow soil contamination could be treated in a fairly short period of time using the in-situ process. In cases where dioxin has penetrated to depths > 1-2 feet, or where significant areas of high concentrations occur, the slurry process is more suitable. The slurry process, which uses large volumes of reagent followed by reagent recovery, is more suited to treatment of "hot spots" than is the in-situ process.

Results of Combined Application/ Reaction Process - The slurry and in-situ process results will be discussed separately.

Results of In-situ Processing - Two different reagents have been used for in-situ processing in this study; potassium hydroxide/polyethylene glycol 400/ dimethyl sulfoxide (KOH/PEG/DMSO) and potassium hydroxide/2-(2-methoxy ethoxy ethanol)/dimethyl sulfoxide (KOH/MEE/DMSO). Water has been added in some cases as a co-solvent in an attempt to give readier penetration of small amounts of reagent into the soil. Each set of samples had an associated set of spikes and blanks. The spikes used reagent without the addition of KOH and were handled in the same manner as the samples. The blanks were untreated soil. Samples treated at above ambient temperatures were maintained uncovered in a water bath unless otherwise noted. The results of the in-situ processing are summarized in table 1.

Discussion of In-situ Processing

Spike Recovery - The recovery of TCDD from spikes in the in-situ process was extremely variable, ranging from 120% to <4%. In general, the higher the temperature and longer the hold time, the lower the spike recovery. Sealing the top of the spike reduced the loss of TCDD for the 2 day KOH/MEE/DMSO run to less than that for the 1 day run, indicating that the lower spike recoveries are probably due to losses from volatilization and/or extraction into the spike solvent (PEG/DMSO or MEE/DMSO), which is not analyzed. In the slurry tests, where volatilization is not a factor, analysis of the spike reagent showed that some 77% of the original TCDD was present in the spike reagent. The highest spike recovery was from the 20°C run, which is consistent with the volatilization hypothesis. Extraction of the TCDD into a polar solvent would tend

Table 1 - Summary of Results of In-situ Processing - All soils initially at 2000 ppb

	wt% in soil	temp, ^{o}C	time, days	avg ppb TCDD spl	spike
1:1:1 KOH/PEG/DMSO	20	20	7	980	2500
1:1:1 KOH/PEG/DMSO	20	70	7	<1	740
1:1:1 KOH/PEG/DMSO	20	70	1	5.3	730
2:2:2:1 KOH/MEE/DMSO/WATER	20	70	1	3.3	500
2:2:2:1 KOH/MEE/DMSO/WATER	20	70	2	2.8	870*
2:2:2:1 KOH/MEE/DMSO/WATER	20	70	4	2.1	210
2:2:2:1 KOH/MEE/DMSO/WATER	20	70	7	1.2	190
2:2:2:6 KOH/MEE/DMSO/WATER	20	70	7	2.1	140
2:2:2:30 KOH/MEE/DMSO/WATER	50	70	7	18	170
2:2:2:30 KOH/MEE/DMSO/WATER	20	70	7	50	70
BLANKS - ALL				<1	

* SPIKES SEALED

to enhance volatilization, similar to the effects of water on the volatilization of PCBs in soil (3). It is interesting to note that the worst spike recoveries were in the MEE reagents which used water as a co-solvent.

Effects of Temperature - Only two reaction temperatures have been tested to date using the in-situ process. The improvement in reaction efficiency in going from 20°C to 70°C was dramatic, improving reaction efficiency from 50% to > 90%.

Effects of Reagent Formulation - PEG vs. MEE - The test results for the 70°C reactions were slightly better at 1 day for the MEE reagent and slightly better at 7 days for the PEG reagent. This difference does not appear to be significant.

Effects of Water as a Co-Solvent - Four sets of tests were run for 7 days at 70°C using KOH/MEE/DMSO with water as a co-solvent. These data show a good correlation between wt% reagent and TCDD concentration after 7 days, as shown in figure 1. The plot of % active reagent vs. ppb TCDD shows the expected first order relationship. This demonstrates that dilution of the reagent with water to provide more contact, followed by evaporation of the water to encourage reaction, was not effective in reducing the amount of reagent required.

The plot of % reagent vs. ppb TCDD shows the expected first order relationship. This demonstrates that dilution of the reagent with water to provide more contact, followed by evaporation of the water to encourage reaction, was not effective in reducing the amount of reagent required.

Results of Slurry Processing - The slurry process conditions tested and the results of GC/MS analysis are summarized in table 2.

As little as 2 hours at 70°C were adequate to reduce TCDD levels from 2000 ppb to < 1 ppb, for a removal efficiency of > 99.95%. The bulk of this removal occurred in the first 30 minutes, when < 99% of the TCDD had been reacted. The reaction at 25°C was slower, but did remove 98% of the original dioxin after two hours.

Reagent Recovery Efficiency - Reagent recovery of the PEG reagents by distillation was only partially successful (about 50% recovery), due to the poor heat stability and low vapor pressure of the PEG. Reagent recovery by washing has been more successful, with 94-99+% recovery of reagent. The degree of recovery is important

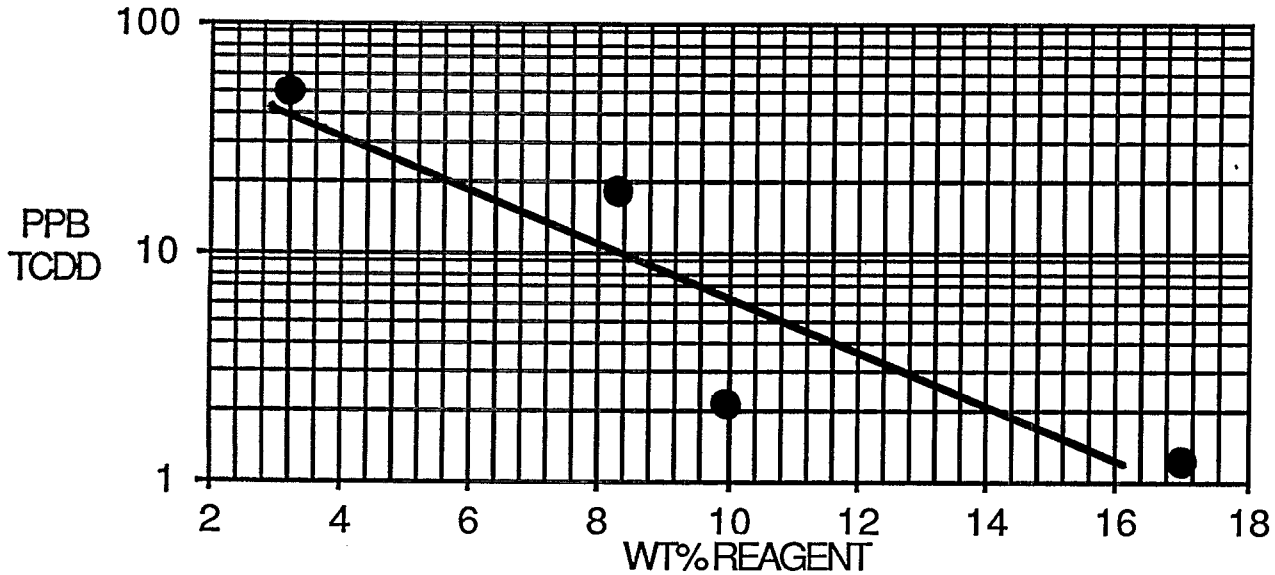

Figure 1 - wt% active reagent vs. ppb TCDD after 7 days

Table 2 - Results of Slurry Processing

Reagent	Temp, ^{o}C	Rxn time, hrs	ppb TCDD
1:1:1 KOH/PEG/DMSO	180-260	4	< 1
1:1:1 KOH/PEG/DMSO	180	2	< 1
1:1:1 KOH/MEE/DMSO	150	2	< 1
1:1:1 KOH/MEE/DMSO	70	2	< 1
1:1:1 KOH/MEE/DMSO	70	0.5	15
1:1:1 KOH/MEE/DMSO	25	2	36

Blanks - all < 1 ppb TCDD

Spikes - % recovery in soil - 0.1-5.9
- % recovery in decanted solvent - 77

to the overall economics of the process.

Dioxin Recovery Efficiency - Analysis of the PEG/DMSO reagent used in the slurry process spikes gave a high recovery of dioxin (77%). As in the case of the in-situ samples, slurry spikes were treated with an alcohol/sulfoxide mixture without the addition of alkali. Additional analysis of both the solvents and the soil (soil extracted with acetone/hexane after decantation of the alcohol/sulfoxide) from the slurry spikes showed the presence of a large variety of halogenated materials which were not originally added to the soil or removed from the soil using the analytical reagents. The amount of additional chlorinated material removed from the untreated soil by the PEG/DMSO was on the order of 140 ppm, calculated as lindane. These materials may be pesticide residues or naturally occurring chlorinated species. Analysis of treated slurry samples also shows these materials, although at much lower levels, indicating that these are some form of aromatic halide. Results of analyses for DDT, DDE and chlorinated dioxin were negative.

These data indicate that conventional methods of extraction may underestimate concentrations of halogenated

organics in soil due to an inability to remove halogenated species from the humics present in the soil, while reagents containing PEG/DMSO are capable of removing these halogenated organices from treated soil.

PRELIMINARY ECONOMIC EVALUATION

In order to provide a rough estimate of relative costs, two scenarios were constructed. In the first case, a 1 acre site 3 feet deep was to be treated using the in-situ process with radio frequency heating. Capital costs for this option are estimated at $2,970,000 for a capacity of 27,600 tons/year of soil (4). In the second case, soil was to be excavated and placed in a 3 reactor slurry process system. Capital costs for this option are $2,350,000 for a 40,000 ton/year capacity. Capital recovery costs for both processes assumed an interest rate of 14% over 5 years. Cost estimates for the two cases are shown in table 3.

Table 3 - Preliminary Economic Analysis of In-situ and Slurry Processes

Cost item	Cost, $/ton soil in-situ	slurry
Capital recovery	31	17
setup and operatin	65	54
reagent	200	20
Total costs	296	91

The major difference in costs between the two processes is in the cost of reagent. In the in-situ process, where reagent is not recovered, this cost is 67% of the total cost. For the slurry process, the operating costs assume a site that is reasonably easy to excavate. For cases where excavation is required to levels below the water table or in very rocky soil, this cost could increase greatly, although this would also be the case for landfill or incineration. In cases where excavation is difficult, the overall costs for the in-situ process may be lower than for the slurry process.

CONCLUSIONS

1. Dioxin concentrations in soil can be reduced from 2000 ppb to <1 ppb by mixing the soil with a combination of alkali metal hydroxide, alcohol and sulfoxide.

2. Mixing of the soil and reagent can be done effectively in two different ways; direct addition of reagent to in-place soil with one time mixing (in-situ process) or combination of soil and reagent in a reaction vessel with continuous mixing (slurry process).

3. Estimated costs for processing are in the range of $100-$300/ton soil.

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GENE ENGINEERING OF YEASTS FOR THE BIODEGRADATION OF HAZARDOUS WASTES

John C. Loper[a,b], Chien Chen[a] and Chitta R. Dey[a]

[a]Department of Microbiology and Molecular Genetics
[b]Department of Environmental Health, College of Medicine
University of Cincinnati
Cincinnati, OH 45267-0524

ABSTRACT

Yeasts are eukaryotic microorganisms whose cytochrome P-450 monooxygenase systems may be amenable to genetic engineering for the hydroxylation and detoxication of polychlorinated aromatic hydrocarbons. We are examining the molecular genetic properties of strains of baker's yeast, Saccharomyces cerevisiae, and an n-alkane utilizing yeast, Candida tropicalis ATCC750. Standard methods were used to purify cytochrome P-450 and NADPH-cytochrome c (P-450) reductase proteins from cells cultured by semi-anaerobic glucose fermentation (S. cerevisiae, C. tropicalis) and by growth on tetradecane (C. tropicalis). Polyvalent antisera prepared in rabbits to some of these proteins were used in tests of immunological relatedness among the purified proteins using sodium dodecyl sulfate-polyacrylamide gel electrophoresis and nitrocellulose filter immunoblots. The results provide evidence for gene relationships which should prove useful in gene isolation and subsequent engineering of P-450 enzyme systems in yeast.

INTRODUCTION

Chemicals entering the environment can be classified into three categories with respect to biotransformation. Those subject to complete biodegradation or mineralization are consumed as organic nutrients and energy sources by the bacteria, yeasts, molds and other microorganisms in the biosphere; the great majority of natural and man-made chemicals are in this category. Certain other compounds undergo limited biotransformation reactions without being degraded for appreciable utilization. Typically these cases involve co-oxidation reactions in which the compound is modified by enzymes normally active with other substrates. Given the diversity of microorganisms in the environment, it is not surprising that some of these altered compounds may then be metabolized further by additional members of the microbial mixtures. In this manner a subset of compounds in the category of co-oxidation occasionally also may become completely mineralized.

The remaining category, relatively small in number, is comprised of environmentally stable compounds. Persistence of these compounds is ascribed to a variety of reasons. Some may be inherently toxic for the available microorganisms. For some the genes for the necessary enzymes might not exist among the members of the available microbial population. For microbes capable of only limited co-oxidative transformation, failure to derive useful energy or building blocks from the compound offers no selective advantage and such organisms may not compete. Alternatively the necessary enzymes may not be induced by the amounts of the compound which enter the cell.

PURPOSE AND APPROACH

Unfortunately among these environmentally stable compounds are several known to be hazardous to human

health. The isolation or development of microbes capable of degrading such stable organic wastes could yield a safe and cost-effective treatment of industrial waste streams and toxic environmental sites. Development of such microorganisms is the purpose of this research.

We anticipate that several of the barriers to biodegradation can be overcome in yeasts using recombinant DNA technology (9). The compounds of interest are all polychlorinated aromatic hydrocarbons having no unsubstituted adjacent carbons, e.g. hexachlorobenzene, and highly chlorinated biphenyls, dibenzodioxins and dibenzofurans. Because of their structure, the initial step in any microbial transformation of these compounds is likely to require hydroxylation by a monooxygenase or a dechlorination step, or both. Fungi and yeasts are eukaryotic microorganisms which are known to catalyze a broad range of monooxygenase reactions using cytochrome P-450 enzymes, (15) and mammalian cytochrome P-450 monooxygenase systems have been implicated in the hydroxylation/dechlorination of such compounds as 2,3,7,8-tetrachlorodibenzo-p-dioxin (3,12,14), 2,3,7,8-tetrachlorodibenzofuran (13), and hexachlorobenzene (19).

Our strategy in using yeasts is based upon the common features of cytochrome P-450 systems among higher and lower eukaryotes (17). These are particulate electron transport systems whose chief components are membrane lipid, NADPH-cytochrome c (P-450) reductase (reductase) and one of several cytochromes P-450. According to the substrate specificity of each cytochrome P-450, the overall reaction results in a mixed distribution of the atoms of O_2 to yield a monooxygenated product and water. By our strategy, we first would isolate a structural cytochrome P-450 gene and its essential regulatory sequences from the yeast Saccharomyces cerevisiae. Molecular genetic techniques are particularly well developed for this eukaryotic microorganism. Next, exogenous cytochrome P-450 genes which encode desired biotransformations would be introduced into this yeast under the control of appropriate regulatory sequences. There is evidence that functional cytochrome P-450 systems can be assembled from yeast and mammalian protein components in vitro (2) and in vivo (H. Ohkawa, personal communication). Thus we expect that the P-450 genes could come from any appropriate source: mammalian, yeast or fungal. Further laboratory experiments would be conducted to express such a system in a yeast variant which could persist in a contaminated medium. A yeast such as a Candida sp. which utilizes n-alkanes in petroleum may be useful for this purpose. The intended product organisms would be able to take up the hazardous organic compound and detoxicate it through co-oxidation, even though the compound were present in low concentrations in the environmental site.

Our implementation of this strategy has included the isolation of major cytochrome P-450 system proteins from S. cerevisiae and Candida tropicalis and the production in rabbits of immune sera to these components. This paper presents our observations of immunological cross-reactivity among these protein isolates.

MATERIALS AND METHODS

Chemicals

Procedures of Guengerich (4) were followed for the recrystallization of cholic acid for use as sodium cholate, and for the synthesis of n-octylamino sepharose 4B. Cytochrome c was horse heart type III obtained from Sigma Chemical Co., St. Louis, MO. Protein molecular weight standards were the low molecular weight standard kit of Bio-Rad Laboratories, Richmond, CA, supplemented by preparations obtained from Sigma of both bovine liver catalase and bovine liver glutamic dehydrogenase, used as molecular weight markers of 58 kd and 53 kd respectively (20). Nitrocellulose filter paper was supplied by Schleicher and Schuell, Keene, NH; hydroxylapatite was Hypatite C of Clarkson Chemical Co., Williamsport, PA. Tetradecane was obtained from Fisher Chemical Co., Cincinnati; all other chemicals were acquired as reagent grade from commercial suppliers.

Cell Culture and Protein Purifications

Sources and relevant properties of

the strains of S. cerevisiae and C. tropicalis used in this study are presented in Table 1. All cultures of S. cerevisiae were carried out at 30°C and C. tropicalis was grown at 24°C. Except where tetradecane was used, all strains were grown semi-anaerobically for glucose fermentation (glucose grown cells) under conditions described by Yoshida et al. (22) using one of two media. Medium for strains JL20 and JL21 consisted of 2% casamino acids, 0.67% yeast nitrogen base without added amino acids, 6% glucose and 0.004% each of L-histidine HCl and adenine HCl. The second medium, used for all other strains, consisted of 1% bactopeptone, 1.7% yeast extract, 0.09% NaCl and 6% glucose, pH 6.7. All glucose grown cells were harvested at mid-log phase.

Growth of C. tropicalis on tetradecane was based upon the media and procedures described by Duppel et al. (2). A New Brunswick fermentor FM-75 was used to maintain 40 liter cultures under aeration of 3 ft^3 min^{-1} with mechanical agitation at 200 rpm. Cells were cultured initially using 0.5% glucose and were then induced for 16 hr in 0.5% tetradecane. Cells were harvested and stored at -80°C in phosphate buffered saline made 20% with respect to glycerol. Cell disruption employed a Biospec Products "Bead-Beater" (Bartlesville, OK) under conditions recommended by the manufacturer. Microsomes were isolated and washed as described by Yoshida et al. (23). For solubilization, microsomes from S. cerevisiae strains were suspended at 15 mg total protein ml^{-1} in solubilization buffer of Yoshida et al. (24) and sodium cholate was added to be 1%. For C. tropicalis, microsomes were suspended at 19 mg total protein ml^{-1} in buffer C of Guengerich (4) and sodium cholate was added to be 1.6%. All preparations were clarified by centrifugation at 100,000 xg for 60 min.

Cytochromes P-450 were partially purified by column chromatography on n-octylamino Sepharose 4B and DEAE Sephacel based upon a procedure of Guengerich (4). Subsequent purification steps utilized CM-Sephadex based upon a method described by Yoshida and Aoyama (25).

Partially purified reductase preparations, obtained by elution from the same columns by Guengerich's procedure (4), were purified by further chromatography. For S. cerevisiae this involved separation on hydroxylapatite according to the method of Bertrand et al., using the detergent Lubrol PX in place of Mulgofen BC-720 (1). This was followed by chromatography on Sephedex G-150. For C. tropicalis, reductase obtained from tetradecane grown cells was chromatographed through a column of Sephadex G-150; reductase from glucose grown cells was passed through Sephadex G-150 and then received a final chromatography on hydroxylapatite as described by Bertrand et al. (1).

Assays

Cytochrome P-450 concentrations were determined as described by Guengerich (10) using a molar extinction coefficient of 91 mM^{-1} cm^{-1} (11). Activity of reductase was determined based upon the assay using horse heart cytochrome c as described by Guengerich (4). Protein determinations were according to Lowry et al. (10) or used the methods and reagent kit of Bio-Rad Laboratories.

Gel Electrophoresis, Transfer and Detection of Antigen Immunoblots

Procedures for sodium dodecyl sulfate polyacrylamide gel electrophoresis (PAGE) were based upon those of Laemmli (8). Protein bands in gels were visualized by the silver staining method of Wray et al. (21). Transfer of proteins from the polyacrylamide gel to nitrocellulose filters was done according to Bio-Rad Laboratories using their product "Trans-blot" cell. Immunological screening of the filters employed the BLOTTO procedure of Johnson et al. (5). Bound antibody was determined by the horse radish peroxidase (HRP) color reaction of Towbin et al. (18) using the reagents obtained from Bio-Rad Laboratories.

Antibody Preparations

Polyclonal antisera to the isolated proteins were prepared in rabbits according to the method described by Kaminsky et al. (6). Control sera were collected from the rabbits prior to their inoculation.

RESULTS

Pioneering work in the laboratories of Yoshida and Aoyama (25), of Wiseman (7), and of Coon (2) among others has defined methods for the isolation from yeasts of the major cytochrome P-450 system proteins. Using minor modifications of their published procedures with our strains, we were able to purify several such proteins to homogeneity as determined by silver staining of proteins bands formed in PAGE. In those cases where impurities appeared likely to be a problem in antibody production, the enzymes were recovered from slices of the polyacrylamide gel.

Five different preparations of antigens were used to produce antisera in rabbits. For S. cerevisiae cytochrome P-450, the antigen was a pair of proteins isolated from glucose grown cells of diploid strain JLD15. These two proteins overlapped extensively through several separation procedures and both gave characteristic CO binding spectra (data not shown). Antisera to reductase of S. cerevisiae was prepared against enzyme purified from the same strain. For C. tropicalis, two cytochrome P-450 proteins were isolated and used separately for antisera production. One of these, of apparent m.w. 59 kd, was purified from glucose grown cells and the other, of apparent m.w. 54 kd, was purified from cells grown on tetradecane. Antisera to the reductase of this organism was prepared against enzyme purified from the tetradecane grown cells.

These and additional isolated cytochrome P-450 system proteins were then characterized as to apparent m.w. and immunological relatedness using PAGE plus immunoblots. Comparable amounts of the proteins being compared were electrophoresed from each well, and the visual intensity of each HRP color reaction was recorded on a scale of 0 to 4^+. Immunoblots run as controls using nonimmune sera were always negative (data not shown). All the data, excluding those using control sera, are summarized for cytochrome P-450 proteins in Table 2A and for reductase in Table 2B.

All the S. cerevisiae cytochrome P-450 proteins tested reacted strongly with the antisera prepared to the two protein mixture isolated from the diploid strain JLD15. This diploid had been formed by crossing JL11 and JL12, two haploid strains which had been shown in previous studies to have relatively high P-450 content among haploid strains (1). More recently we have demonstrated that a 56 kd P-450 protein is formed by one of these haploids and a 57 kd one is formed by the other. Thus the two P-450 proteins isolated from JLD15 appear to have resulted from the expression of two genes provided singly by the haploid progenitors.

This strong immunoreactivity among the S. cerevisiae cytochrome P-450's is of particular interest for the P-450 proteins from strains JL10, JL20 and JL21. Strain JL10 was used in experiments to be described elsewhere for the isolation of plasmids pVK1 and pVK2, plasmids which code for a functional cytochrome P-450 gene (Kalb et al., manuscript in preparation). Examination by PAGE of cytochrome P-450 protein partially purified from JL10 revealed a major band of apparent m.w. 56 kd. Strain JL10 variants containing pVK1, or pVK2, were designated as JL20 or JL21 respectively. Thse strains expressed elevated levels of cellular P-450 (manuscript in preparation); microsomal extracts of these strains also showed elevated P-450 content. For strain JL20 this appeared as an increase in a cytochrome P-450 of apparent m.w. 56 kd, not shown to differ from the protein detected from JL10. Strain JL21 however developed high levels of a cytochrome P-450 with an apparent m.w. 58 kd, a form not detected in our other strains.

By contrast one of the cytochrome P-450 proteins purified from C. tropicalis was immunologically unrelated to two others. Antisera prepared against the form purified from glucose grown cells did not react with either of the two immunologically related forms purified from tetradecane grown cells. Similarly antisera prepared against one of the two latter proteins, the 54 kd form, did not bind to the cytochrome P-450 from glucose grown cells.

However, as recorded in Table 2A, evidence of low level cross-reactivity was observed for cytochrome P-450

proteins isolated from glucose grown cells of S. cerevisiae and C. tropicalis.

Data for the reductases isolated from these yeasts are summarized in Table 2B. For C. tropicalis, reductase purified from glucose grown cells was identical by m.w. and immunological reactivity to reductase purified from cells grown on tetradecane. Although this reductase did differ in m.w. from the form purified from S. cerevisiae, the reductases of these two yeasts were distinctly immuno-cross-reactive.

DISCUSSION

Although the purification of protein components of yeast cytochrome P-450 systems has been published, the isolation of yeast genes for cytochrome P-450 expression has not been described. Elsewhere we present results of a parallel study which has yielded plasmid clones of cytochrome P-450 genes of S. cerevisiae (Kalb et al., manuscript in preparation). In this phase of the work we were interested in these proteins primarily in order to obtain antibodies prepared against them for use in procedures of gene characterization. Access to yeast strains engineered for high level expression of such genes will facilitate the purification of these enzymes in quantity. The enzymes can then be examined as to their possible substrate specificity for compounds of environmental concern and in comparison to activities of yeast cytochrome P-450 system enzymes described in the literature (1,2,7,16,25).

The data in Table 2 provide useful insights as to the probable yeast genes for these systems. For C. tropicalis, identical properties were seen for the NADPH-cytochrome c (P-450) reductase when that organism was cultured by glucose fermentation or by tetradecane oxidation. Thus this enzyme is expressed from a single gene or from nearly identical genes under these two growth conditions. Comparison to the reductase data for S. cerevisiae in Table 2 shows an apparent m.w. difference of 2 kd, but these enzymes of both species react to immunosera prepared using either reductase. This is a strong indication that the corresponding genes will prove to share regions of sequence homology.

By contrast, culture of C. tropicalis on tetradecane resulted in elevated levels of two cytochrome P-450 proteins not detected in extracts of this yeast grown on glucose. These two proteins showed apparent m.w. values of 53 and 54 kd, compared with the 59 kd value obtained for the cytochrome P-450 isolated from glucose grown cells. Both the 53 kd and the 54 kd proteins reacted with antisera elicited to the 54 kd form. However, when these two P-450 proteins were tested in immunoblots using antisera prepared to the 59 kd form, no cross-reactivity was observed. Thus these data suggest that unique P-450 genes are induced under these alternate growth conditions, a conclusion reached earlier by Sanglard et al. on the basis of other criteria (16).

For S. cerevisiae, the data for cytochrome P-450 proteins in Table 2 are particularly interesting as they provide evidence for three proteins, all immunologically related, but of different genetically determined size. Cytochrome P-450 antiserum was prepared using a mixture of two P-450 proteins obtained from a diploid strain. These two proteins, with apparent molecular weights of 56 kd and 57 kd, subsequently were shown to be coded separately, one each in the haploids which were used to derive the diploid. Of the two plasmid clones isolated with cytochrome P-450 structural genes (Kalb et al., in preparation), presence in the cell of one of these, pVK2, results in the accumulation of a protein with an apparent molecular weight of 58 kd, a form not detected in our other S. cerevisiae strains. Gene sequence and enzyme specificity studies will be required to determine whether these three proteins are expressed from alleles of one or more P-450 genes. The gene for the glucose grown P-450 in C. tropicalis may have some sequence homology with these S. cerevisiae gene(s), based upon the low level immuno-cross-reactivity observed for these proteins.

Thus use of these antisera preparations has provided evidence as to possible gene relationships among several cytochrome P-450 monooxygenase systems of these two organisms. The antisera will

be useful in the isolation and characterization of these genes for the subsequent gene engineering of P-450 enzyme systems in yeast.

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Table 1. Strains

Name	Description	Source
S. cerevisiae:		
JL10	local name for BWG2-9A	L. Guarente, Massachusetts Inst. of Technology
JL11	strain D5-1C a, ade2-40 leu	this laboratory
JL12	strain D5-3C α, ade2-40 trp1	this laboratory
JLD15	diploid isolate from mating of JL11 and JL12	this laboratory
JL20	JL10 containing pVK1	this laboratory
JL21	JL10 containing pVK2	this laboratory
C. tropicalis:		
ATCC750	prototroph	American Type Culture Collection

Table 2. Molecular Weights and Immunological Relatedness of Cytochrome *P-450* System Proteins Purified from Strains of Saccharomyces cerevisiae and from Candida tropicalis ATCC 750.

A. Cytochromes P-450

Organism and culture conditions	Apparent m.w. (kd) determined using PAGE[a]	Cross reaction in immunoblots with rabbit antisera prepared to protein (kd) from strain		
		JLD15	ATCC750	
		56,57	59	54
S. cerevisiae, glucose fermentation				
JLD15	56	4+	+	0
	57	4+	+	0
JC11	56	4+	+	0
JC12	57	4+	+	0
JL10	56	4+	+	0
JL20	56	4+	+	0
JL21	56	4+	+	0
	58	4+	+	0
C. tropicalis, glucose fermentation	59	(+)	4+	0
tetradecane oxidation	53	0	0	2+
	54	0	0	4+

B. NADPH-cytochrome c (P-450) reductase

		JLD15	ATCC 750 grown on tetradecane
		72	74
S. cerevisiae JLD15, glucose fermentation	72	4+	2+
C. tropicalis, glucose fermentation	74	3+	4+
tetradecane oxidation	74	3+	4+

[a]PAGE: polyacrylamide gel electrophoresis.

BIODEGRADATION OF ENVIRONMENTAL POLLUTANTS BY THE WHITE ROT FUNGUS PHANEROCHAETE CHRYSOSPORIUM

John A. Bumpus, Ming Tien, David S. Wright, Steven D. Aust
Department of Biochemistry
and
Center for the Study of Active Oxygen in Biology and Medicine
Michigan State University
East Lansing, MI 48824-1319

ABSTRACT

The white rot fungus, Phanerochaete chrysosporium secretes a unique hydrogen peroxide-dependent oxidase capable of degrading lignin, a highly complex, chemically resistant, non-repeating heteropolymer. Due to its ability to generate carbon-centered radicals, this enzyme is able to non-specifically catalyze numerous cleavage reactions producing smaller lignin-derived compounds which may then be metabolized by more conventional enzyme systems. We have proposed that the lignin degrading system of this fungus may also have the ability to degrade environmentally persistent organopollutants. In this study we have shown that P. chrysosporium is able to degrade carbon-14 labeled 1,1'-Bis(4-chlorophenyl)-2,2,2-trichloroethane (DDT), 3,4,3',4'-tetrachlorobiphenyl, 2,4,5,2',4',5'-hexachlorobiphenyl, 2,3,7,8-tetrachlorodibenzo-p-dioxin (TCDD), the gamma isomer of 1,2,3,4,5,6-hexachlorocyclohexane (Lindane) as well as the non-halogenated pollutant benzo[a]pyrene to ^{14}C-carbon dioxide.

INTRODUCTION

Biotreatment systems using microorganisms for the degradation of toxic recalcitrant organopollutants hold the promise of being an efficient and economical means of detoxifying vast quantities of contaminated water, soils and sediments. Unfortunately, few microorganisms possess the ability to degrade recalcitrant organopollutants. Generally these compounds are poorly soluble in water and are adsorbed to particulate matter thus making them even less accessible to microbial attack. Some pollutants of interest are often present in the parts per million range or less. Microbial enzymes which may possess the innate ability to degrade organopollutants rarely possess the very high affinity (low Km) required in order for significant degradation to take place at such low substrate concentrations. Degradation of organopollutants present in low concentrations is also difficult even for microbial strains which have been adapted to grow on these chemicals. When the selective pressures imparted by high concentrations of the chemical are removed, these strains may not be able to compete effectively in biotreatment systems containing other microorganisms. Similar

problems face microbial strains developed using recombinant DNA technology.

Our studies focus on the use of the lignin-degrading white rot fungi as potentially useful organisms in the aerobic biological treatment of hazardous organic wastes. The use of lignin degrading fungi may overcome many of the problems generally associated with the biological degradation of insoluble recalcitrant organic compounds.

In the initial stages of lignin degradation by P. chrysosporium, numerous carbon-carbon and carbon-oxygen bonds in the insoluble lignin polymer are cleaved by a unique non-specific and non-stereoselective H_2O_2-dependent, extracellular oxygenase (1,2). The enzyme catalyzes the formation of carbon-centered radicals which react with oxygen to initiate oxidation (3). This free radical mechanism may be responsible for the lack of specificity and stereoselectivity that is characteristic of this system. Synthesis of this enzyme is promoted by nitrogen starvation (4), not substrate availability, as is the case with many biodegradative systems. The mixture of soluble low molecular weight aromatic compounds thus formed may then undergo further modification or ring cleavage and metabolism via the β-ketoadipate pathway to Krebs cycle intermediates and, hence, to carbon dioxide.

PURPOSE

It was the purpose of this study to determine if a white rot fungus, P. chrysosporium, had the ability to degrade recalcitrant organopollutants.

APPROACH

Cultures of P. chrysosporium (ME-446) were maintained on 2% malt agar slants at room temperature. Experiments were performed in liquid culture at 39°C. For the first 3 days cultures were incubated under air after which the culture atmosphere was changed to 100% oxygen. Cultures (10 ml) were incubated in 250 ml Wheaton media bottles equipped with gas exchange manifolds similar to those described by Marinucci and Bartha (5). The culture medium, consisting of glucose (56 mM), ammonium tartrate (1.2 mM), and dimethylsuccinate buffer, pH 4.2 (100 mM), supplemented with thiamine and trace metals, has been previously described (4). The $^{14}CO_2$ evolved during degradation of ^{14}C-labeled organopollutants was trapped by using oxygen to flush the atmosphere of the incubation flasks through an ethanolamine-containing scintillation cocktail as described (4). Radioactivity was quantitated using a Packard Tri-Carb Liquid Scintillation Spectrometer (Model 3310).

Metabolism of 1,1'-Bis(4-chlorophenyl)-2,2,2-trichloroethane (DDT) was studied by incubating DDT with the fungus and assessed by extracting the cultures with 25 ml of acetonitrile, 2 ml of saturated NaCl and two 50 ml portions of hexane. The hexane extracts were combined and the amount of DDT and metabolites were quantitated using a Varian GLC (Model 3700) equipped with an electron capture detector and a Hewlett Packard Digital Integrator (Model 3390A). The identity of metabolites was confirmed by GC-MS and by comigration of metabolites or their derivatives with authentic standards during GLC.

Experiments were conducted in triplicate or quadruplicate. Data points represent the mean ± 1 standard deviation.

RESULTS

Initial studies using DDT as a model recalcitrant substrate demonstrated that P. chrysosporium degraded DDT. During a thirty day incubation period approximately 53% of the DDT was metabolized (Fig. 1). Synthesis of DDT meta-

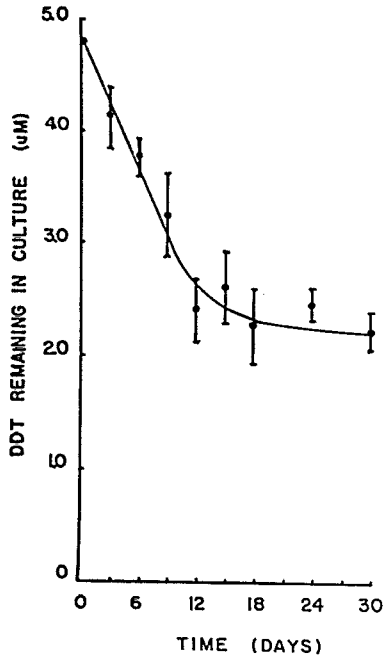

Figure 1. Disappearance of DDT in cultures of P. chrysosporium. The initial concentration of DDT was 4.8 uM.

bolites was also examined. Fig. 2 demonstrates that 1,1'-Bis(4-chlorophenyl)-2,2-dichloroethane (DDD) is the major DDT metabolite synthesized during the first 3 days of incubation. During continued incubation, DDD levels decreased and 4,4'-dichlorobenzophenone (DBP) levels increased to become the major metabolite observed. During GLC, 1,1'-Bis(4-chlorophenyl)-2,2,2-trichloroethanol (Dicofol), and 1,1'-Bis(4-chlorophenyl)-2,2-dichloroethanol (FW-152) decompose, yielding DBP. Thus, in our metabolite studies (Fig. 2) the DBP curve actually represents the total of Dicofol, FW-152 and DBP that is present. Studies aimed at quantifying these metabolites by HPLC are in progress.

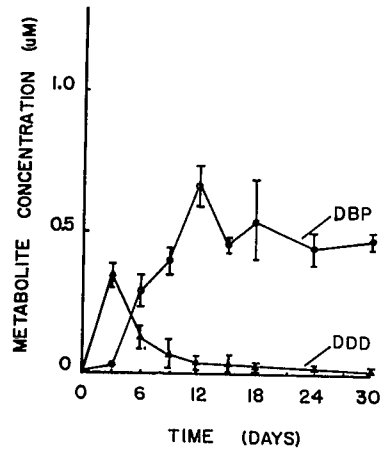

Figure 2. Appearance and disappearance of DDT metabolites in cultures of P. chrysosporium. The initial concentration of DDT was 4.8 uM. The DBP curve represents the total amount of DBP, Dicofol and FW-152 that is found.

In Fig. 1 it was shown that 47% of the DDT still remained after incubation for thirty days. Fortification of cultures with additional glucose (56 mM) at day 31 and day 61 demonstrated that additional degradation occurred under these conditions (Table 1). Less than 1% of the DDT initially present still remained after 75 days of incubation. Neither DDD nor 1,1'-Bis(4-chlorophenyl)-2,2-dichloroethylene (DDE) accumulated, although the DBP peak

TABLE 1. DEGRADATION OF DDT BY P. CHRYSOSPORIUM: EFFECT OF SUPPLEMENTAL GLUCOSE

Days of Incubation	Glucose Addition (56 mM)	DDT Concentration (uM)	Percent Degradation
0	+	4.8	0
30		2.3	48
31	+		
48		0.4	92
61	+		
75		<0.048	>99

accounted for approximately 25% of the DDT initially present. These studies suggest that degradation will continue as long as a suitable carbon source is present.

When the organism was grown in the presence of ^{14}C-DDT, 4% of the original DDT was evolved as $^{14}CO_2$ after 30 days (Fig. 3) when roughly 50% of the DDT was degraded (Fig. 1), indicating that the remaining carbon atoms are either incorporated into the organism or are present as intermediates in the pathway between DDT and CO_2. Unlike DDT disappearance studies (Fig. 1), which demonstrate that substantial degradation occurs during the first three days of incubation, $^{14}CO_2$ evolution did not occur until after 3 days of incubation (Fig. 3). This is the same type of lag as that which is observed for lignin degradation (4) and is consistent with the hypothesis that lignin degradation and DDT degradation are mediated by the same enzyme system.

Table 2 lists six structurally diverse toxic organopollutants that were found to be degraded by P. chrysosporium as assayed by $^{14}CO_2$ evolution. Like DDT, 1,2,3,4,5,6-hexachlorocyclohexane (Lindane), 2,3,7,8-tetrachlorodibenzo-p-dioxin (TCDD), Benzo[a]pyrene, 3,4,3',4'-tetrachlorobiphenyl (3,4,3',4'-TCB) and 2,4,5,2',4',5'-hexachlorobiphenyl (2,4,5,2',4',5'-HCB) are all degraded to CO_2 by this microorganism. In all cases radiolabeled substrates were added to cultures when they were inoculated with fungi at day 0. By day 3 substantial growth was apparent as evidenced by the appearance of a mycelial mat. However, in no case did $^{14}CO_2$ evolution occur. Between day 3 and day 6, $^{14}CO_2$ evolution began in all cultures. It was maximal between day 3 and day 18 and continued at decreasing rates until day 30. After 30 days of incubation, glucose was not detectable in the incubation media. Fortification of the media with additional glucose (56 mM) and continued incubation resulted

in an increased rate of $^{14}CO_2$ evolution for the duration of another 30 days at which time the experiment was terminated.

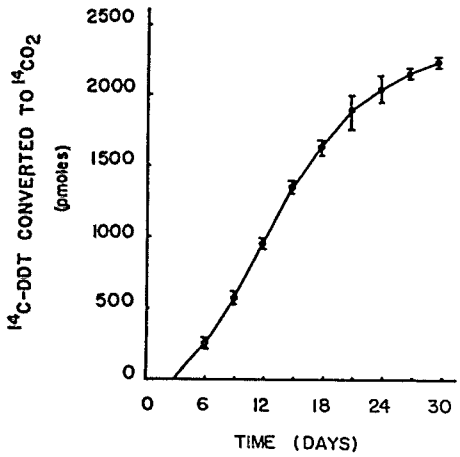

Figure 3. Conversion of ^{14}C-DDT to $^{14}CO_2$ in cultures of P. chrysosporium. Each incubation flask contained 50 uCi of ^{14}C-DDT. The initial concentration of DDT was 4.8 uM. These data represent the minimum amount of DDT converted to CO_2. Some CO_2 may have been incorporated into the organism, in carboxylation reactions, for example.

The lignin degrading system of P. chrysosporium may prove to be ideally suited for use in biotreatment processes for the degradation of recalcitrant organopollutants. First, the enzyme system normally attacks an insoluble recalcitrant substrate. Thus organopollutants which are adsorbed to sediments may actually mimic the lignin molecule. The analogy is even more striking when one considers that many sediments and soils to which organopollutants are adsorbed have high lignin contents. Second, problems associated with substrate specificity appear to be obviated by the non-specific and non-stereoselective carbon-centered free radical mechanism that is characteristic of this system. This lack of specificity has the advantage of allowing the organism to attack and degrade a broad spectrum of structurally diverse recalcitrant compounds as shown in Table 2. Third, P. chrysosporium is a highly successful competitor in nature, especially when the carbon source consists of wood, wood by-products or other lignin containing materials. Thus, if wood chips or sawdust, for example, are used as the carbon source in biotreatment systems, competition by non-lignin degrading organisms is likely to be minimal. Fourth, because degradation is promoted by nitrogen starvation rather than by the presence of substrate, low levels of organopollutants do not repress the biosynthesis of enzymes required for their degradation. Fifth, typically, degradative enzymes must possess very high affinities (low Km) in order for significant degradation to occur. The carbon-centered radical mechanism appears to provide an alternative mechanism which allows degradation of lignin, and possibly other recalcitrant compounds, to proceed to completion.

Of special significance for the degradation of organohalides is the fact that P. chrysosporium has the demonstrated ability to dehalogenate and degrade chlorobenzene derivatives (6) and to cleave aromatic rings (7). Included among the compounds degraded by P. chrysosporium are 4,5,6-trichlorophenol, 3,4,5,6-tetrachloroguaiacol and 2,4,6-trichlorophenol (6). In our studies we have shown that DDD is an intermediary metabolite formed during DDT degradation. We have

TABLE 2. DEGRADATION OF ^{14}C-RADIOLABELED ORGANOPOLLUTANTS TO $^{14}CO_2$ BY P. CHRYSOSPORIUM

	Initial Rate of Degradation to $^{14}CO_2$ (pmoles/day)	Radiolabeled Substrate evolved as $^{14}CO_2$ (pmoles)		% of Radiolabeled substrates evolved as $^{14}CO_2$ in 60 days
		30 days	60 days	
Lindane	11.3	190.8	267.6	21.4
Benzo[a]pyrene	7.5	117.2	171.9	13.8
DDT	2.7	48.0	116.4	9.3
TCDD	1.2	27.9	49.5	4.0
3,4,3',4'-TCB	0.7	13.8	25.1	2.0
2,4,5,2',4',5'-HCB*	2.4	44.2	86.0	1.7

* Substrate concentration was 1.25 nmoles/10 ml for all ^{14}C-radiolabeled compounds except 2,4,5,2',4',5'-HCB. Because of its low specific radioactivity a concentration of 5.0 nmoles/10 ml was used for 2,4,5,2',4',5'-HCB.

also shown that Lindane, a compound that is chlorinated at every carbon atom, is converted to CO_2. These results demonstrate that P. chrysosporium may also dehalogenate alkyl halides.

SUMMARY

The lignin degrading system of P. chrysosporium appears to be ideally suited for the degradation of other recalcitrant organic compounds. The initial stages of lignin degradation are extracellular, non-specific and non-stereoselective. Degradation proceeds all the way to CO_2. Additionally, P. chrysosporium has a constituitive aromatic ring cleavage system as well as a system which can dehalogenate many organohalides.

Under conditions which promote lignin degradation, P. chrysosporium also degraded Lindane, benzo[a]pyrene, DDT, TCDD, 3,4,3',4'-TCB and 2,4,5,2',4',5'-HCB to CO_2. These studies suggest that P. chrysosporium may prove to be an extremely useful microorganism in the biological treatment of hazardous organic waste.

ACKNOWLEDGEMENTS

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BACTERIAL DEGRADATION OF CHLORINATED COMPOUNDS

Paul H. Tomasek and A.M. Chakrabarty
Department of Microbiology and Immunology
University of Illinois at Chicago; Chicago, IL 60680

ABSTRACT

Plasmid gene sequences of the 2,4,5-trichlorophenoxyacetate (2,4,5-T) degrading Pseudomonas cepacia AC1100 strain show strong homology to a cluster of genes present on the 2,4-dichlorophenoxyacetate (2,4-D) degradative plasmid pJP4. There is little AC1100 deoxyribonucleic acid (DNA) homology to the chlorocatechol genes present on the 3-chlorobenzoate (3CBA) degradative plasmid pAC27. The homology to the 2,4-D degradative plasmid pJP4 may therefore be attributed to other genes involved in the degradation of chlorophenoxyacetates. 2,4,5-T grown AC1100 cells seem to lack ring-fission dioxygenase activity for chlorocatechol intermediates of the 3CBA and 2,4-D pathways. These results suggest that a significantly different catabolic pathway may have evolved in P. cepacia AC1100. Transposon mutagenesis has shown that at least some of the 2,4,5-T catabolic genes are chromosomal. A short chromosomal DNA sequence associated with a putative 2,4,5-T gene is repeated many times on both the chromosome and plasmid of strain AC1100. Such a repeated element may have been important in the evolution of the degradative plasmids as well as genetic rearrangements necessary to efficiently degrade novel substrates.

INTRODUCTION

It is generally believed that the complete biodegradation of chlorinated compounds in water and soil is accomplished primarily by microorganisms (1). Failure of microbial populations to degrade some of these compounds can be attributed to the lack of genetic information coding for appropriate degradative enzymes (2). This reflects the relatively short timespan such compounds have been present in the biosphere (several decades) compared to the long evolutionary history of microorganisms in contact with naturally occuring products (3).

It is clear that the biodegradative abilities and limitations of microorganisms must be thoroughly examined if we want to utilize them for degradation of persistent toxic chemicals. It is of equal importance that we understand the genetic organization and regulation of existing biodegradative genes in a variety of organisms if genetic engineering is to play a role in the construction of new microbial strains with enhanced degradative capabilities. The study of gene structure may shed some light on those particular evolutionary mechanisms which allow microorganisms to adapt to novel compounds. This may, in turn, allow for more efficient gene engineering. Studies of the biochemistry and genetic organization of 3-chlorobenzoate (3CBA) and 2,4-dichlorophenoxyacetate (2,4-D) degrading bacteria have contributed most extensively to our knowledge of chlorinated aromatic chemical biodegradation (4). The biochemical pathways of both compounds is shown in Fig. 1.

Genetics of 3CBA-degrading bacteria

The complete degradation of 3CBA has been reported in Pseudomonas putida strain AC858, Pseudomonas sp. B13, and Alcaligenes eutrophus JMP134 (5,6,7). All these independently isolated strains carry plasmids (pAC27, pWR1, and pJP4 respectively)

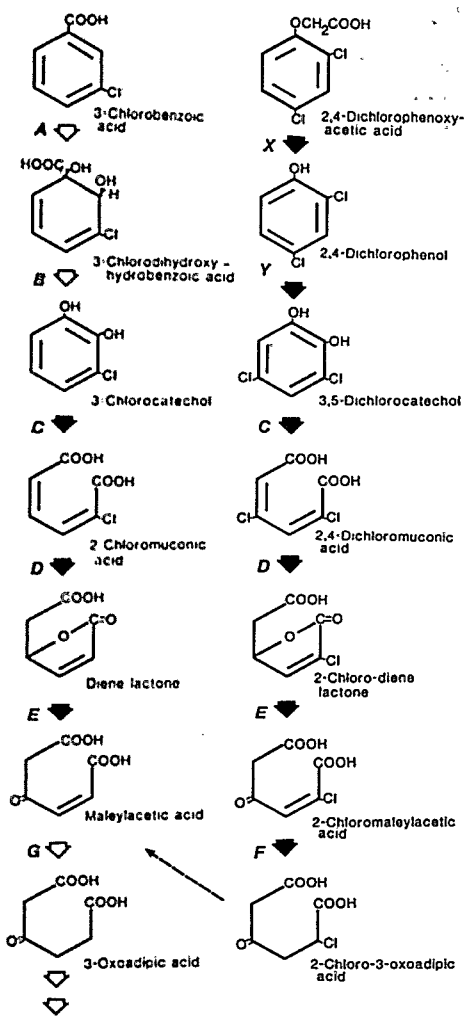


Fig. 1. Proposed pathways for the degradation of 3CBA and 2,4-D. Solid arrows indicate plasmid-encoded enzymes while open arrows represent chromosome-encoded enzymes in an appropriate host. The plasmid-encoded pyrocatechase II, and cycloisomerase II have broader substrate specificities than their chromosomal iso-functional counterparts and thus catalyze reactions with chlorinated substrates. Hydrolase II specifically recognizes chlorinated substrates. Dechlorination of chloromuconates is thought to occur spontaneously as the result of lactonization by cycloisomerase II. A-Benzoate Dioxygenase, B-Dehydrogenase, C-Pyrocatechase II, D-Cycloisomerase II, E-Hydrolase II, F-Chloromaleylacetate Reductase, G-Maleylacetate Reductase, X-2,4-D Monooxygenase, Y-2,4-Dichlorophenol Monooxygenase. (After K.N. Timmis et al., 4).

which code for many of the essential degradative enzymes: pyrocatechase II, cycloisomerase II and hydrolase II genes (C,D, E; Fig.1) (8). The initial degradative enzymes are coded by the host chromosome (9). The plasmids pAC27 and pWR1 are essentially identical (10) whereas pJP4 also carries genes for mercury resistance and additional enzymes necessary for 2,4-D degradation. The structural genes for pyrocatechase II, cycloisomerase II, and hydrolase II have recently been cloned from both pAC27 and pJP4 (8). In both plasmids the genes are clustered: pAC27 genes are localized to the 4.2 kilobase pair (kb) Bgl II E fragment; pJP4 genes are located on the 15 kb Eco R1 B fragment (Fig. 2). These gene clusters show extensive DNA homology with each other. In addition, potential regulatory gene(s) necessary for efficient expression of the 3CBA pathway are located near the structural gene clusters: pAC27 Bgl II C fragment and pJP4 Eco R1 E fragment (Fig. 2).

Genetics of 2,4-D degrading bacteria

A number of different 2,4-D degrading bacterial strains have been isolated (7, 11,12). The genetically best characterized is Alcaligenes eutrophus strain JMP 134, carrying the plasmid pJP4. In addition to carrying the pyrocatechase II, cycloisomerase II, and hydrolase II genes (C,D,E; Fig.1) which allow chlorocatechol metabolism, the pJP4 plasmid also encodes the two initial pathway enzymes, 2,4-D monooxygenase and 2,4-dichlorophenol monooxygenase (X,Y; Fig.1) (9) as well as 2-chloromaleylacetate reductase (F; Fig.1) (13). With the possible exception of the

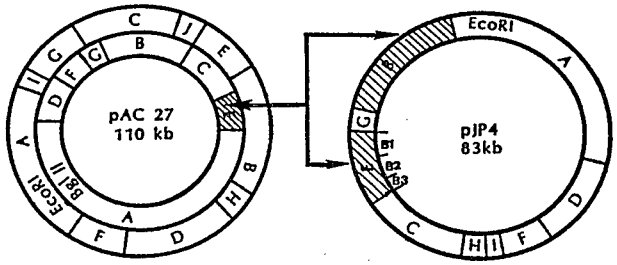


Fig. 2. Physical maps of the plasmid pAC27 with Eco R1 and Bgl II and pJP4 with Eco R1. Fragments B1-B3 were generated by Bam H1 digestion of the pJP4 Eco R1 E fragment. Regions of homology are indicated by shaded areas. (After D. Ghosal et al., 8).

latter enzyme, all 2,4-D catabolic enzymes are coded by the 15 kb Eco R1 B gene cluster of pJP4. This fragment has been cloned (8,9) and transfer of the recombinant plasmid to a plasmid-free A. eutrophus JM134 derivative allowed growth on 2,4-D and 3CBA, provided selection pressure was maintained (4,9). There have been recent attempts to further localize genes within this cluster. Liu and Chapman (13) recently localized the pyrocatechase II (dichlorocatechol dioxygenase) gene to a 4.9 kb Pst I restriction fragment of pJP4. They also reported that the hydrolase II (chloro-diene lactone hydrolase) gene and the chloromaleylacetate reductase were both present on a 3.4 kb PstI fragment of pJP4. The relationship of these fragments to the established physical map (8,14) of pJP4 remains to be reported.

Degradation of 2,4,5-trichlorophenoxyacetic acid

Pseudomonas cepacia AC1100, originally isolated from a chemostat enrichment system, has the ability to completely degrade 2,4,5-trichlorophenoxyacetic acid (2,4,5-T) as it sole source of carbon and energy (15). Although 2,4-D and 2,4,5-T are chemically analogous, it is not known whether the biodegradative pathway of P. cepacia AC1100 is similar to that found in 2,4-D degrading strains. Rosenberg and Alexander (16) proposed a 2,4,5-T catabolic pathway based on gas chromatography-mass spectrometry of accumulated metabolites from a mixed population of soil bacteria . Similar to 2,4-D degradation, they proposed that 3,5-dichlorocatechol was the ring-fission substrate. A variety of metabolites including 3,5-dichlorocatechol are produced when AC1100 cells are grown on 2,4,5-T. Mass spectral evidence indicates that hydroxylation, reductive dechlorination of the aromatic ring, dehalogenation/ hydroxylation of the ring, and cleavage of the acetate side chain are all possible transformations (17,18).

Genetics of the 2,4,5-T degrading strain

Unlike its 3CBA and 2,4-D degrading counterparts, little is known concerning the genetic organization of strain AC1100 for 2,4,5-T biodegradation. Determination of the role of plasmid genes encoding 2,4,5-T biodegradative enzymes has been hampered by the presence of several different plasmids and their low yield from AC1100. Through electron microscopic measurements it has been determined that a 170 kb plasmid (pDG3) comprises about 85% of the total plasmid population. A 40 kb plasmid (pDG4) accounts for 10% of the plasmid population while the remainder is made up of a heterogeneous mixture of plasmids ranging from 3 - 30 kb (18).

In order to learn more about the genetic organization of the 2,4,5-T degrading P. cepacia AC1100, we compared AC1100 chromosomal and plasmid DNAs to sequences known to carry clusters of 3CBA and 2,4-D catabolic genes through DNA-DNA hybridization. To establish whether AC1100 utilized a ring-fission dioxygenase such as pyrocatechase II, we synthesized several chlorocatechols and used them as substrates for dioxygenase assays. We also used transposon mutagenesis to introduce genetic markers for mapping the 2,4,5-T genes and to generate mutants blocked in the catabolic pathway. In the course of these and other studies we obtained evidence of genetic rearrangements affecting the expression of degradative genes. We also identified a DNA sequence from the chromosome of AC1100 which is repeated more than 25 times throughout the chromosome and plasmids of this strain.

METHODS:

Growth of strain AC1100 (15), isolation of plasmid DNA (6), restriction digestion, gel electrophoresis and Southern blotting of DNA fragments to nitrocellulose (19), and DNA electron microscopy (8) have been documented elsewhere. When P. cepacia AC1100 was grown for plasmid DNA isolation, the 2,4,5-T medium was supplemented with 2 g/l glucose. Isolation of individual DNA fragments was done with NA45 DEAE paper (Schleicher and Schuell, Keene, NH) using procedures recommended by the manufacturer. DNA fragment sizes were determined by electrophoresis of standard DNA fragments (1 KB Ladder, BRL, Gaithersburg, MD). Radiolabeling of DNA probes was accomplished using the nick-translation kit and protocols of BRL, and alpha-^{32}P-nucleotides from Amersham, Arlington Heights, IL. In vitro packaging of DNA cloned in the cosmid vector pHC79 and subsequent transfection into E. coli AC80 were performed using reagents and proto-

cols of Amersham. Transposon mutagenesis was performed in a tri-parental mating (20) using E. coli strains carrying ColE1::Tn5 (donor) and pRK2013 (mobilizing functions) and 2,4,5-T-grown AC1100 cells (recipient). Selection of kanamycin-resistant Tn5 mutants was done by plating mating mixtures on Pseudomonas Isolation Agar (Difco,, Detroit, MI) supplemented with 100 ug/ml kanamycin. 2,4,5-T$^-$ mutants were identified by failure to grow on 2,4,5-T agar plates containing 15 ug/ml kanamycin. Preparation of cell extracts and measurement of oxygen consumption in enzymatic analyses were performed essentially as described previously (21). Chlorocatechols were synthesized according to Knuutinen (22).

RESULTS:

AC1100 DNA homology to chlorocatechol degradative genes

To establish whether there was significant homology between the genes of the 2,4,5-T degrading AC1100 strain the 2,4-D plasmid pJP4 originally isolated from A. eutrophus, Eco R1 digested AC1100 chromosome and plasmid DNA were probed with individual radiolabeled pJP4 Eco R1 fragments. There was strong homology between a fragment (about 4 kb) from the AC1100 plasmid digest and the 15 kb EcoR1 B fragment of pJP4 which harbors the structural genes for both 3CBA and 2,4-D metabolism. A similar hybridization experiment with the chlorocatechol genes of the 3CBA plasmid pAC27 (4.2 kb BglII E fragment) recently failed to show any homology to AC1100 plasmid or chromosomal DNA under stringent conditions.

Testing chlorocatechol dioxygenase activity in AC1100

Despite similarities in chemical structure between 2,4-D and 2,4,5-T, P. cepacia AC1100 cannot grow on 2,4-D, unless these genes are deliberately introduced into AC1100 (18). We have been unable to demonstrate any ring-fission dioxygenase activity on 3,5-dichlorocatechol or 4-chlorocatechol in cell extracts of 2,4,5-T grown P. cepacia AC1100. These compounds are substrates for pyrocatechase II described earlier. 4,5-Dichlorocatechol was also not oxidized.

Isolation of 2,4,5-T$^-$ mutants generated by transposon mutagenesis

Transposon insertion mutagenesis with Tn5 was used to generate blocked mutants and introduce convenient genetic markers into the 2,4,5-T degrading P. cepacia strain AC1100. About 100 mutants deficient in 2,4,5-T metabolism were obtained from 1700 putative Tn5 insertion mutants, expressing kanamycin resistance of Tn5. A number of amino acid auxotrophs were also identified. Plasmids and chromosome from five Tn5 mutants (four 2,4,5-T$^-$, one 2,4,5-T$^+$ leu$^-$) were digested with Eco R1 restriction endonuclease. These DNA fragments were immobilized on nitrocellulose and hybridized with radioactively labeled Tn5 DNA. The probe hybridized only to the chromosomal DNAs in all cases. Thus the Tn5 insertion site for the 5 mutants tested is chromosomal. The 2,4,5-T mutants varied in phenotype upon growth on glucose and exposure to 2,4,5-T: different amounts of 2,4,5-trichlorophenol accumulated, varying amounts of chloride were released to the culture medium, and after 2-3 days of culturing the color ranged from colorless to a very dark brown color. One mutant, PT88, was selected for further genetic analysis since it produced a dark brown color when exposed to 2,4,5-T. PT88 was a putative chlorocatechol dioxygenase mutant since such a color is often associated with chlorocatechol formation. The chlorinated metabolite produced by this mutant remains to be adequately characterized.

Identification of a chromosomal repeated DNA sequence specific to strain AC1100

The kanamycin resistance marker of the PT88 Tn5 insertion was used to clone chromosomal DNA sequences flanking the site of insertion. Total genomic DNA was partially digested with Sau3A restriction endonuclease. The large (20 - 40 kb) fragments generated were cloned into the vector pHC79, and the recombinant plasmids introduced into E. coli. Kanamycin-resistant colonies were used to identify clones containing the Tn5 and the flanking chromosomal DNA. Using radiolabeled Tn5 DNA as a probe, two clones were identified which shared a common 6 kb SalI restriction fragment with the original PT88 chromosome. This 6 kb DNA fragment contained approximately half of the Tn5 sequence including

the kanamycin resistance gene. The 6 kb SalI fragment was isolated from one of the clones and used to probe native AC1100 chromosomal digests in an effort to localize the putative 2,4,5-T structural gene. As shown in Fig. 3A, the 6kb probe identified several homologous regions on both the P. cepacia AC1100 chromosomal (lanes 1,4,7) and plasmid (lane 6) digests. It did not hybridize with P. cepacia 383 chromosomal DNA (lane 3) included as a control. The highly repeated sequence present on the 6 kb SalI fragment has been further localized to a 1.4 kb SalI, PvuII restriction fragment. When this fragment was used as a radioactive probe against P. cepacia AC1100, P. aeruginosa, P. putida, and P. mendocina digested chromosomes, only the AC1100 showed homology (Fig.3B).

Genetic rearrangements in pJP4 affecting degradation

Transfer of the intact pJP4 plasmid from A. eutrophus to P. putida and prolonged selection on 3CBA plates (4-5 weeks) eventually allowed the recipients to grow on 3CBA. The restriction profile of the resident plasmid was different from native pJP4 (18). The resulting plasmid (represented by pYG2) was further characterized by Southern hybridization and electron microscopy of heteroduplex structures obtained by DNA denaturation/fast renaturation (Fig.4). These experiments demonstrated that pYG2 was derived from pJP4 which had undergone genetic rearrangements: deletion of about 15 kb, inverted duplication of the chlorocatechol structural gene cluster (Eco R1 B fragment and other fragments), and gene fusion. A. eutrophus carrying pJP4 grows slowly on 3CBA and restriction digestion profiles of plasmids isolated from cells maintained on 3CBA showed a mixture of native pJP4 and altered (pYG2) plasmids. Such 3CBA selected A. eutrophus strains do not readily express 2,4-D phenotype. Transformation of P. putida with intact pJP4 and selection with 2,4-D has not been successful. The transformation did occur using the plasmid-free P. cepacia strain 383 as a recipient and there were no apparent genetic alterations of pJP4 in such 2,4-D degrading strains.

DISCUSSION

Unlike 3CBA and 2,4-D degradative genes which are located on plasmids, the location of the 2,4,5-T biodegradative genes in P. cepacia AC1100 plasmids is still unknown. The chromosomal location of several Tn5 insertion mutations which block 2,4,5-T metabolism suggests that chromosomal genes are essential for catabolism of this substrate. The role of plasmid gene sequences is suggested by the reported homology between a 4 kb region of plasmid DNA (a mixture of at least two plasmids) and the cluster of 2,4-D catabolic genes located on the 15 kb EcoR1 B frag-

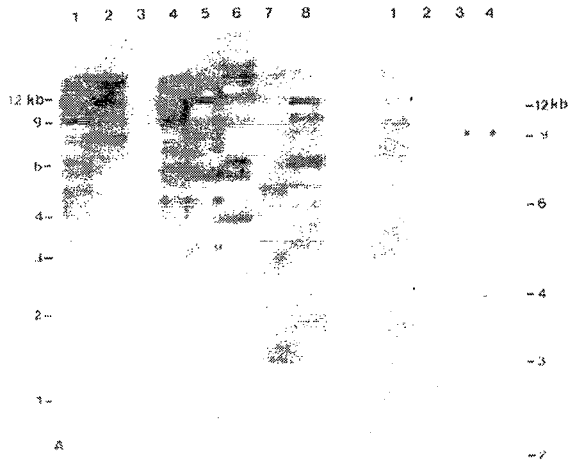
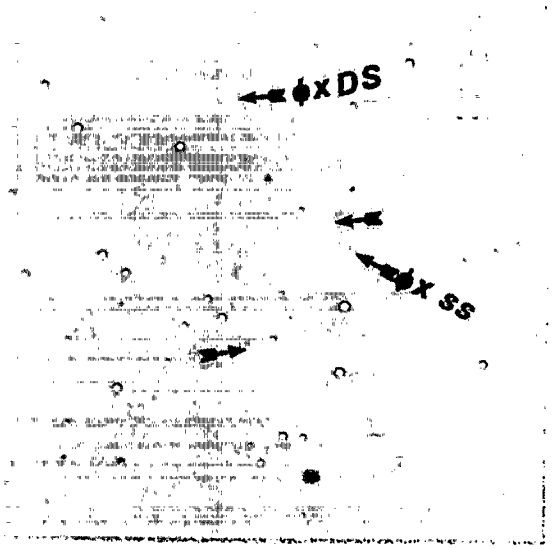


Fig. 3. Hybridization of various chromosome and plasmid restriction fragments probed with radiolabeled DNA fragments containing a repeated sequence from P. cepacia AC1100 chromosome. A. Lanes 1-3: AC1100, PT88, and P. cepacia 383 chromosomal DNAs, respectively, digested with Eco R1; Lanes 4-6: AC1100 and PT88 chromosomal DNAs, and AC1100 plasmid DNA, respectively, digested with Pvu II; Lanes 7-8: AC1100 and PT88 chromosomal DNAs, respectively, digested with Sal I. The hybridization probe was a 6 kb Sal I fragment isolated from the Tn5-generated 2,4,5-T mutant PT88. The 6 kb fragment contains part of Tn5 and flanking chromosomal sequences at the site of Tn5 insertion. B. Lanes 1-4: P. cepacia AC1100, P. aeruginosa, P. putida, and P. mendocina chromosomal DNAs, respectively. digested with Eco R1. The hybridization probe was a 1.4 kb Sal I-Pvu II fragment from the 6 kb Sal I fragment described above.



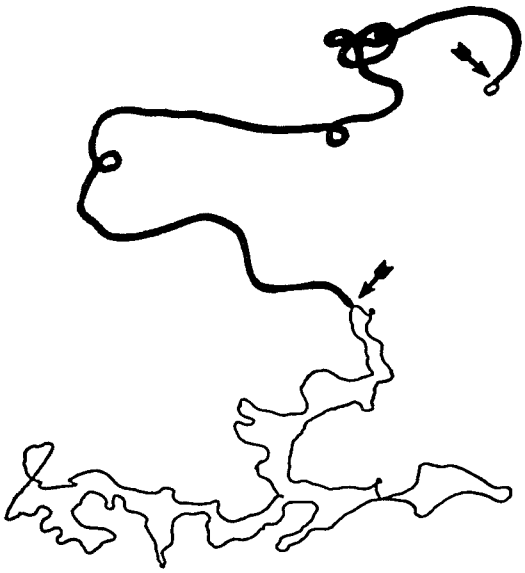


Fig. 4. Electron micrograph and corresponding drawing of an altered pJP4 plasmid (pYG2 form) upon denaturation and fast renaturation. The presence of a 25 kb inverted duplication of pJP4 genes is indicated by the double-stranded DNA "stem" with 1.3 kb and 43 kb single-stranded loops on the ends. Restriction mapping and Southern hybridization analysis reveal that about 15 kb of pJP4 DNA have been deleted from pYG2. pYG2 forms are generated when either P. putida or A. eutrophus hosts carrying pJP4 are subjected to 3CBA selection pressure. ϕX174 single stranded and double stranded DNA standards are indicated. (From Ghosal et al., 18).

ment of pJP4 (17). However, the apparent lack of DNA homology to pAC27 sequences coding for pyrocatechase II, cycloisomerase II, and hydrolase II genes indicates that the homology between AC1100 plasmids and pJP4 may be due to other genes involved in the degradation of chlorophenoxyacetates. Although the putative chlorocatechol dioxygenase genes may be unstable in this strain, the inability of Pseudomonas cepacia AC1100 to utilize 2,4-D or 3CBA as well as chlorocatechol intermediates of these pathways suggests that AC1100 may have evolved a significantly different pathway for 2,4,5-T degradation. Further mapping of Tn5 mutants and additional DNA hybridization studies are required to localize the 2,4,5-T structural and regulatory genes.

Gene rearrangements play an important role in the ability of microorganisms to develop new catabolic pathways (23). This is illustrated by the amplification, deletion, and fusion which occur when pJP4-harboring strains are exposed to strong 3CBA selection pressure. In this case the genetic alterations retard the ability of A. eutrophus JMP134 to degrade 2,4-D, normally a readily metabolized substrate in this strain (8,17). Through such rearrangements the cell is able to express previously existing biodegradative genes with broad substrate specificity for catabolic (3CBA) functions which are normally silent. It is interesting that biodegradative gene sequences from two different catabolic plasmids (pAC27 and pJP4) are amplified 7-10 times (8) when cloned in isolation from the normal regulatory genes and subjected to strong selection pressure. Apparently such an increase in gene dosage is required to produce sufficient quantities of 3CBA degradative enzymes in the absence of genetic regulatory systems that allow efficient enzyme formation.

Repeated sequences in tandem or inverted orientation are often associated with gene amplification and deletion (24, 25). These sequences may be partially or completely homologous. When the plasmid pJP4 is denatured and rapidly reannealed and examined by electron microscopy, Ghosal et al. (17,18) observed many small stem-loop structures (indicating inverted repeats) up to 1.8 kb in length. Several such structures were present in EcoR1 frag-

ments B and E, which contain the structural and putative regulatory gene(s) for chlorocatechol metabolism.

A highly repeated DNA sequence present in both the plasmid and the chromosome of P. cepacia AC1100 has been identified. The repeated element was isolated by its close proximity to a chromosomal Tn5 insertion affecting 2,4,,5-T biodegradation. It is likely that this element is associated with a 2,4,5-T biodegradative or regulatory gene. It is tempting to consider that this or a similar repeated sequence led to the recruitment and rearrangement of various biodegradative genes into an efficiently regulated 2,4,5-T catabolic system. Further efforts are currently underway to establish whether the repeated sequence present in a 1.4 kb segment will enhance genetic recombination given the multiple chromosomal and plasmid sites showing strong homology to the repeat.

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TECHNIQUES FOR MICROSCOPIC STUDIES OF SOLIDIFICATION TECHNOLOGIES

H. C. Eaton, M. E. Tittlebaum and F. K. Cartledge
Colleges of Engineering and Basic Sciences
Louisiana State University
Baton Rouge, LA 70803

ABSTRACT

The mechanism(s) whereby organic hazardous wastes interact with cement matrices is important for characterizing existing and future solidification technologies. Because in the complex chemistry of cement setting reactions there are many microscopic phases formed, it is necessary to use microscopy and microanalytical tools in studies of these systems. Several methods, currently in use by the authors, are discussed. They include scanning electron microscopy, transmission electron microscopy, selected area diffraction, energy dispersive x-ray analysis and electron probe microanalysis. Specimen preparation techniques are discussed. Results from the application of the techniques to studies of cements containing ethylene glycol and para-bromophenol are given.

INTRODUCTION

Although landfilling is not the method of choice for the disposal of some hazardous chemical wastes, it remains an important technology today. Moreover, it is expected to retain its place in the overall waste management scheme of the future. This is true for a number of reasons. First, there are, and will be, equally hazardous residues from environmentally and socially more acceptable processes, such as incineration. These residues cannot be ignored. Secondly, there are a number of hazardous wastes which are not amenable to such disposal techniques as incineration, physical/chemical or biological treatment. The disposal of these wastes may still require land disposal techniques. Thirdly, land treatment and disposal will remain an important HW management technique with regard to abandoned sites where economics prohibit other alternatives.

For these reasons, it is important to increase the scientific base of information about the nature of the solidified/stabilized complexes that are currently being produced. It must be understood, for example, precisely how the waste is contained in the solidified product.

It has not been the accepted practice for the waste disposal vendors to provide information about the mechanism(s) whereby their product entraps the waste. Instead, they are required to show that there is an acceptably low level of leaching of the waste from the landfill site. Although this provides a practical database for "prediction by extrapolation" of the long-term stability of the site, it does not provide a sound scientific basis for this kind of prediction. The real need is for a complete elucidation of the mechanisms of chemical waste entrapment and a description of the kinetic processes which govern the leaching behavior.

PURPOSE

The present communication describes the approach used in the authors' laboratory where there is an attempt to answer these basic and important questions about a variety of solidified waste systems. To date, the primary focus has been on systems which utilize Type I Portland cement as the matrix. This commonly used base material has been widely assumed to provide a product with good longterm

stability. It is important to recognize, however, that the chemical processes involved in the setting of hydrated Portland cement are many and complex. There is a multiplicity of mineral phases formed and the formation of this composite of minerals can be further complicated by the presence of organic and inorganic additions.

APPROACH

In the sections which follow, several microscopic and microanalytical techniques are described. Each of these are currently being used to determine the way in which two different model wastes are entrapped. The specific model wastes were chosen because (1) they are chemically different, (2) one of them is on the list of hazardous materials, and (3) one of them is amenable to analysis by one of the important microanalytical tools to be described in the text. Organic chemicals were chosen because they represent a special problem to the solidification industry relating to the well documented "interference" with the hydration processes occurring in the setting of Portland cement. The two organics were ethylene glycol (EG) and para-bromophenol (PBP).

RESULTS

Material Preparation

As discussed, the objective of the study is to identify the kinds of bonding present in stabilized organics. An additional goal is to quantify the bonding potential of stabilizing agents towards organics using extraction procedures. Type I Portland cement was solidified with pure EG, a water soluble organic, and water. Samples were prepared by weighing EG into a 20 mL borosilicate glass, screw cap scintillator vial. Portland cement and water were added and the mixture was stirred to homogeniety with a glass stirring rod. Samples were prepared by mixing 0.4, 1 or 2 gm of EG with 10 gm of cement and 4 mL of water. They were allowed to cure for variable lengths of time. Extractions were carried out with solvents of varying polarity. They included dichloromethane (DCM) with a polarity index of 3.1, dimethyl sulfoxide (DMSO) with a polarity index of 7.2, and water with a polarity index of 10.2. After the appropriate curing time had elapsed, the sample vials were broken and the contents were ground to pass a 100 mesh sieve. The powder was transferred to a 125 mL Erlenmeyer flask, mixed with 120 mL of solvent and shaken for 0.5 hour. The mixture was filtered under suction and analyzed by gas chromotography using an HP 5790A Gas Chromatograph coupled to an HP 3390A Integrator. The results of a one month old EG sample is shown in Table 1.

A similar method was used to prepare samples containing PBP and to extract using the same solvents.

The extractions provide information about the percent recovery of EG as a

Table 1. THE CONCENTRATION DEPENDENCE IN THE EXTRACTION OF ETHYLENE GLYCOL

Grams of EG per 10.0 Grams of Cement	Percent Recovery in a Single Extraction		
	DCM	DMSO	H_2O (pH=9.9)
0.4	3.4	11.0	78.9
1.0	6.8	15.3	83.3
2.0	7.1	43.4	83.4

function of solvent polarity, hydrogen bonding ability, concentration of organic in the curing cement and the characterization of the entrapment mechanics once the particular phases are identified. In addition, the data provides a macroscopic clue to the concentrations where important chemical processes may be occurring. This is a valuable aid to selecting a time of cure. The data is very important in the selection of specimens which should be examined by the microscopic and microanalytical methods.

Scanning Electron Microscopy

The scanning electron microscope has become one of the most valuable microscopic tools for the characterization of engineering materials. It reveals the microscopic details of the specimen surface with magnifications easily up to several tens of thousands of diameters. In addition, the large depth of field allows an image of the surface which displays the large excursions that are often possible in fractured surfaces. The electron beam that is rastered over the specimen surface is usually produced by thermionic emission of electrons from a heated tungsten filament. These electrons are focused and then rastered by electromagnetic lenses that are central to the image formation system. When these primary electrons strike the specimen, secondary electrons are emitted and then detected by a scintillator within the vacuum chamber. The light from the scintillator is detected by a photomultiplier tube mounted on the air side of the chamber but in communication with the scintillator by means of a light tube. These signals are used to modulate the raster of a cathode ray tube monitor. Since the raster of the monitor is synchronized with the raster of the primary electron beam, the image displayed on the monitor contains information about the microscopic point-to-point differences in the secondary electron emission from the specimen surface. These differences are a function of the topography largely and to a minor extent on other things, e.g. atomic number. Therefore, the image reveals the desired information about the microscopic variations in the surface topography.

Fracture Surfaces

Samples of the solidified waste systems were fractured at liquid nitrogen temperatures in order to reveal the nature of the interior. Liquid nitrogen temperatures were chosen because of the plastic deformation and tearing that has been observed to occur in these materials at room temperature (2).

A small cube of material, approximately 1-3 mm on edge, was selected and then mounted on an aluminum specimen holder with double-sided conducting tape. The entire assembly was then coated with AuPd in a sputter coater or with carbon in a vacuum evaporator. The specimen was then examined in an ISI 60-A Scanning Electron Microscope operated at no more than 15 keV. These low operating voltages were preferred in order to avoid extensive surface penetration. Previous studies of cement structure (1) have failed to realize the importance of this parameter, however. Figures 1 and 2 illustrate well that at the lower voltages more surface detail is revealed.

An important observation of the authors' studies is that the structure of the cement/waste system remains similar to that of the pure cement (2). This discovery greatly aids our investigation since there is a large amount of literature about the structure of hydrated Portland cement. It should be noted, however, that micrographs should be interpreted with extreme caution because of the widespread controversy over the structure of the pure cement itself.

Polished Surfaces

The examination of polished surfaces allows yet another type of information about the nature of the microstructure to be obtained. Studies of polished surfaces allow the potential use of energy dispersive x-ray analysis for the determination of the microchemistry of the waste containing solids. In addition, the polished surfaces appeared to provide views of the material that are much easier to interpret than the fractured surfaces.

Each specimen was impregnated with a low viscosity, hard grade acrylic resin in order to increase the mechanical integrity and stability of the sample prior to

grinding and polishing. Polymerization of the resin was carried out in vacuo. When polishing and grinding was not preceeded by acrylic impregnation, a grossly distorted specimen surface resulted, therefore it was concluded that there is some degree of acrylic penetration into the specimen pore spaces. Grinding was performed with sandpaper using grit sizes 250, 340, 400, and 600, followed by polishing on a rotating wheel which was impregnated with 6 micron diamond paste. This was followed by a 0.5 micron diamond wheel, and finally on a wheel containing 0.05 micron alumina. In all of the grinding and polishing operations isopropanol was used, rather than water, in order to cool and lubricate without the removal of microphases. Previously, methanol and dichloromethane were used but with less desirable results. A carbon coating was applied to the polished surfaces and they were then examined in the SEM and some analyzed by EDX. Figure 3 is an example of a micrograph of a polished specimen surface. Our preliminary analyses suggest that the matrix phase consists of CSH (calcium silicate hydrate) gel phase and that the large inclusions (indicated by the arrow) are calcium aluminosilicates.

Electron Microprobe Microanalysis

The cement samples were analyzed using an ARL-EMX electron probe microanalyzer (EPMA). The probe is equipped with three wavelength dispersive spectrometers and a Tracor-Northern Energy Dispersive Spectrometer system. It is partially automated and simultaneous analysis of several major and trace elements is possible. The electron gun is operated at 15 keV at 150 microamperes current. The vacuum is maintained in the 10^{-6} torr range. Detection and measurement of x-rays follows Bragg's law. The sample surface is highly polished and carbon coated to make it conductive. The take-off angle of the x-rays is 52.5°, where take-off angle is defined as the angle that the detector crystal makes with the horizontal surface of the specimen. Different crystals having different d-spacings allow the analysis of elements ranging from C to U and most elements can be analyzed with concentrations in the parts per million (ppm) level.

The EPMA method is a comparative method, like many other spectroscopies, therefore its accuracy is only as good as the purity of the standards used. The ratio of the x-ray intensity generated for any element in the unknown sample compared to the intensity of the element in the known is called the k-ratio and, to a first approximation, is equivalent to the concentration of the element in the unknown. It is not exactly equal to the concentration because the x-ray intensity is modified by its interaction with the atoms in the sample. The theory of microprobe analysis is quite well developed now and basically two methods of correction of data are used to obtain accurate concentration information. One is an empirical method and the other theoretical. The theoretical procedure requires the calculation of concentration from first principles and is known as the ZAF method ("Z" is from atomic number, "A" from adsorption, and "F" from fluorescence).

The specimen current, the current which flows during analysis when the specimen is earthed, for the analyses was set to 10 nA for Bentonite. All analyses, including standardization, were carried out under identical conditions. Seven elements were analyzed using mixed standards, e.g. SiO_2 for Si. Oxygen was calculated by difference assuming that the components should sum to 100%. Figure 4 is an example of the form of the data obtained from EDX and Table II illustrates the quantitative information that can be obtained using EPMA.

Energy dispersive x-ray analysis can also be performed in the SEM. The advantage of this type analysis is the ability to image very small objects prior to their analysis by EDX. The EPMA, on the other hand, is not a high spatial resolution instrument (an optical microscope is used to locate the region on the specimen surface which is to be analyzed). Therefore, there are times when very small phases cannot be chemically analyzed in the EPMA but can be analyzed in the SEM.

Transmission Electron Microscopy

The transmission electron microscope (TEM) has been an effective tool in the study of the microstructure of ceramic and composite materials. The main advantage of the TEM is the high spatial resolution that is possible in modern instruments ($\sim$ 0.5 nm). In addition, the selected area

Table 2. Cement Analysis by EPMA

Element	Standard	Matrix Phase (%)	Large Inclusion (%)	Spectrometer Used
Si	Quartz (SiO_2)	5.6	8.9	ED
Ca	Diopside ($CaMgSi_2O_6$)	33.1	38.4	ED
Al	Corundum (Al_2O_3)	1.8	2.8	ED
Fe	Fayalite ($(Fe,Mg)_2SiO_4$)	1.0	2.0	WD
K	Microcline ($(K,Na)AlSi_3O_8$)	0.3	0.1	ED
Mg	Periclase (MgO)	0.7	2.2	WD
S	Barite ($BaSO_4$)	0.5	0.4	WD
O	By difference	57.0	45.2	

WD = wavelength dispersive
ED = energy dispersive

diffraction (SAD) pattern can be used to determine crystal structure and orientation of the crystalline materials imaged in the instrument.

The specimen which is suitable for TEM analysis must be thin (∿ 100 nm thick for analysis at 100 keV) in order to allow for electron penetration. Specimen preparation can be accomplished by either the replica method or by ion thinning. A replica is prepared by impressing a plastic (which is premoistened with acetone) onto the specimen surface. After drying, the plastic can be easily removed retaining a detailed impression of the specimen surface topography. A thin coating (∿ 30 nm) of amorphous carbon is evaporated onto the replica and then a heavy metal is used to shadow the surface from an angle and thereby provide contrast. This process is illustrated in Figure 5. The ion thinning method is used to thin an actual specimen by bombarding it with inert gas ions in vacuo. The present authors have used the replica method in the present study, because of its relative ease, and because in the replication process some of the actual specimen material is removed and can therefore be analyzed in the SAD mode. This procedure is similar to extraction replication which has been used in precipitate analysis of two phase metal alloys (3). Figure 6 is a transmission electron micrograph of a waste containing cement and the SAD pattern obtained from it.

This technique can be developed to provide the definitive analysis of the microscopic phases that are formed due to the addition of organic and/or organic wastes to cement and other binder systems.

SUMMARY

Several techniques have been described. These advanced techniques can be used to characterize the microcrystalline and amorphous phases that are formed during the processes attendant to the solidification/stabilization of organic hazardous wastes. The methods can be used for a host of other environmental studies where it is important to understand the mechanisms whereby complex materials systems are formed, e.g. in the formation of incineration residues.

The application of these methods to the solidification of organic wastes has indicated that the waste is not contained in the solidified mass in a homogeneous way, even when the constituents are mixed thoroughly during the preparation process. The inhomogenities consist of microscopically concentrated regions of waste. Since cements, and other setting materials, undergo complex chemical changes over rather long periods of time (sometimes months) it will be important to determine the time dependent transport paths of the wastes as the system ages.

ACKNOWLEDGEMENTS

The authors would like to acknowledge support for this work from the United States Environmental Protection Agency through the Hazardous Waste Research Center at Louisiana State University, Environment Canada and Ontario Environment. In addition, many individuals have contributed to the work and our understanding of cement and waste solidification. They include M. B. Walsh, D. Chalasani, D. Skipper, A. C. Chou, A. Roy, P. Malone, T. Bridle and C. Wiles.

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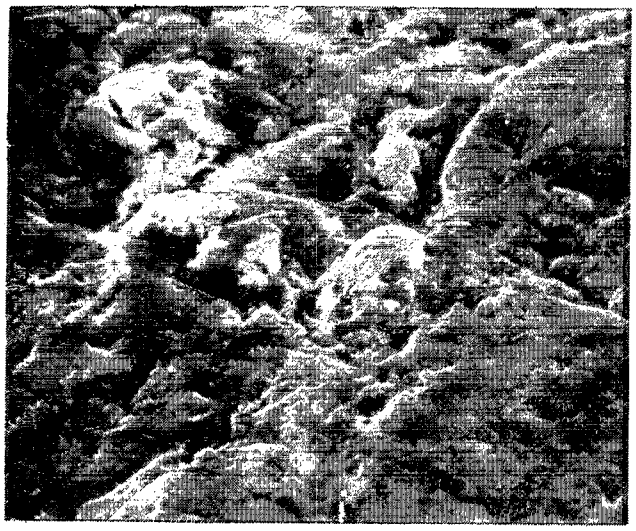


Figure 1. A scanning electron micrograph of a pure cement sample aged for six months. The electron accelerating voltage was 15 keV.

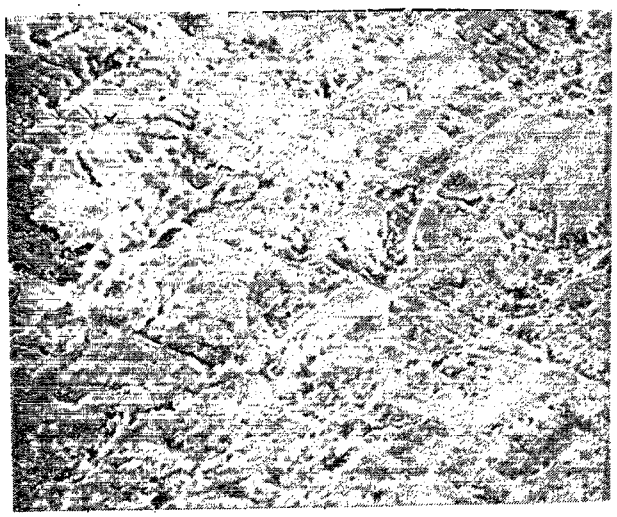


Figure 2. A scanning electron micrograph of the same specimen and region shown in Figure 1. The accelerating voltage was 5 keV and less penetration is evident.

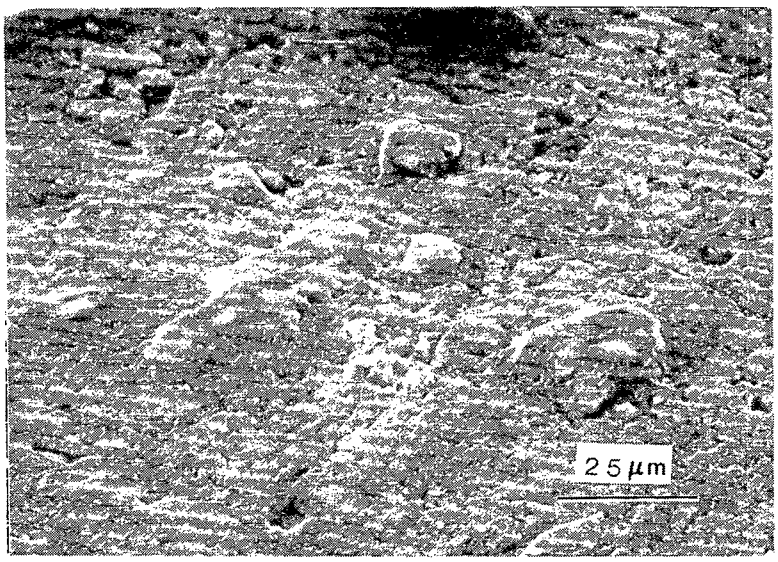


Figure 3. A scanning electron micrograph of a six month old, pure cement sample.

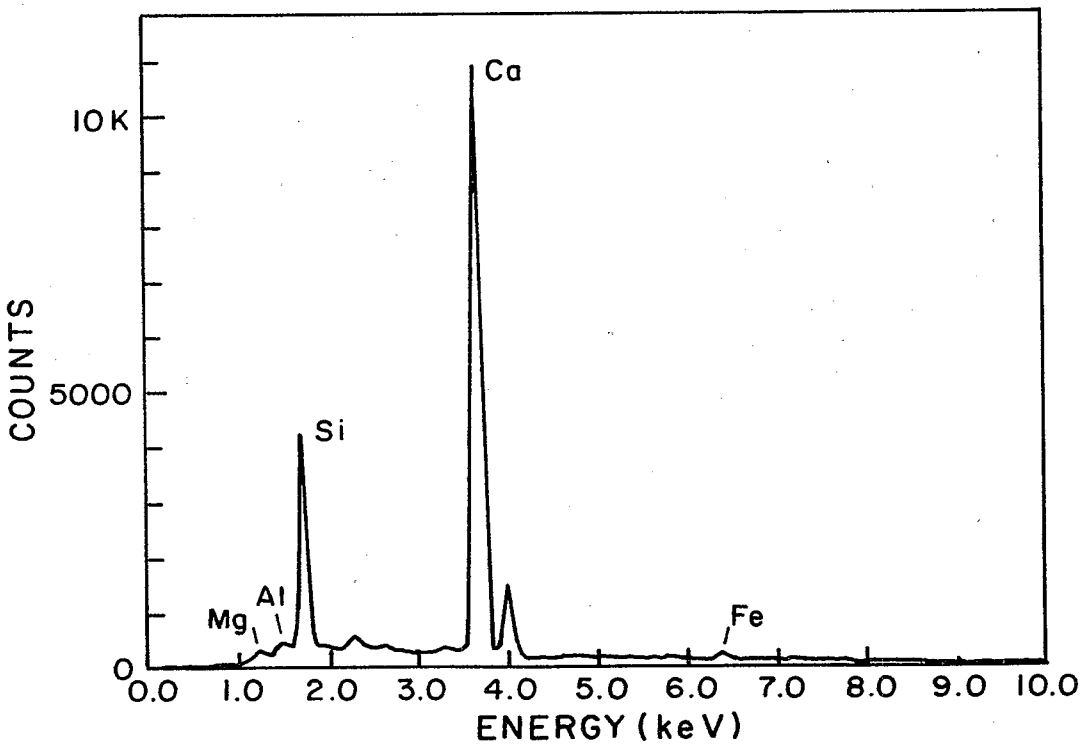


Figure 4. An EDX spectrum from an ethylene glycol specimen.

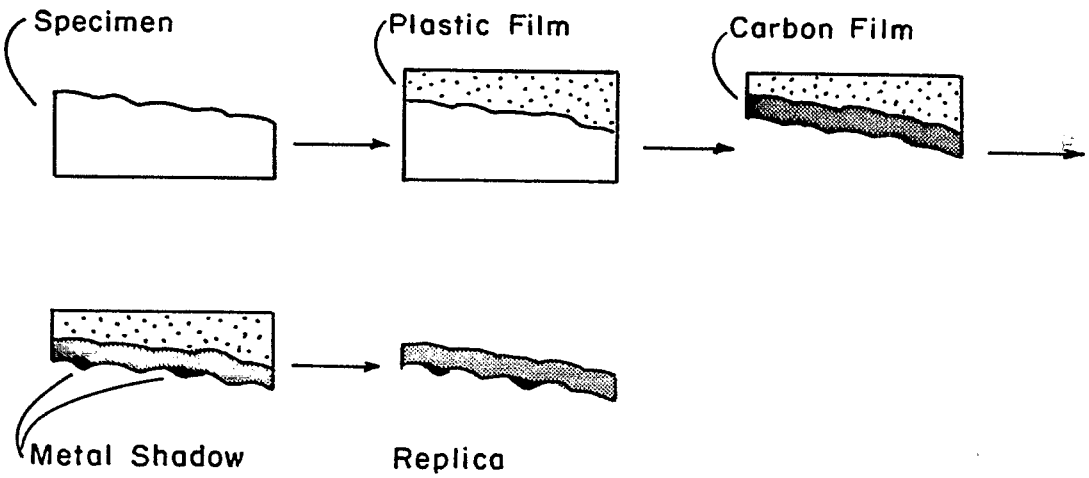
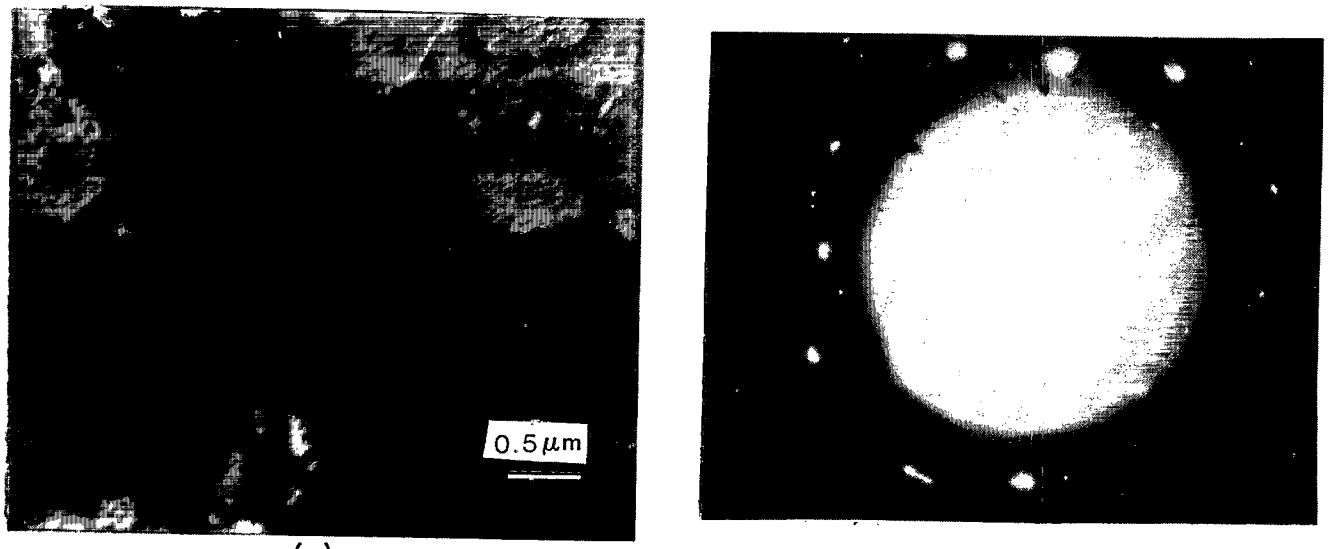


Figure 5. A schematic representation of the procedure used to produce TEM replicas.



(a) (b)

Figure 6. (a) A transmission electron micrograph of a replica containing material removed from a polished surface of a cement containing PBP. (b) The diffraction pattern produced by the material shown in (a).

USEPA COMBUSTION RESEARCH FACILITY PERMIT COMPLIANCE TEST BURN

Richard A. Carnes
USEPA CombustionResearch Facility
Jefferson, Arkansas 72079

INTRODUCTION

In August of 1982, when the USEPA officially accepted title to the Combustion Research Facility (CRF) it was unclear as to the exact permit structure that would be required. At that time it was proposed that the existing air permit, issued by the State of Arkansas Pollution Control Commission, would be sufficient for research purposes. The concept being that the CRF was not a commercial operation, it was not a 24 hour a day operation, it would conduct experiments on controlled volumes of waste material.

USEPA Region VI officials finally decided that in order to conduct research on Resource Conservation and Recovery Act (RCRA) Appendix VIII listed material the CRF would have to have a complete Part B incinerator permit. The final decision was made in early 1983 and set in motion the preparation of the necessary documents for a State Hazardous Waste Permit as authorized by the USEPA under RCRA regulations.

The completed application was officially received by the Arkansas Department of Pollution Control and Ecology on August 8, 1983, and set in motion the following prescribed schedule for processing it:

	TASK	DATE
1.	Completeness Determination	9-8-83
2.	Technical Review	2-7-84
3.	Preparation of Draft Permit	2-7-84
4.	Public Notice Issuance	2-14-84
5.	Public Hearing	3-29-84
6.	End of Public Comment Period	4-11-84
7.	Final Permit Prepared	5-11-84
8.	Final Permit Presented to Commission	5-25-84

Following several short delays, the final Part B permit was officially issued on July 27, 1984, by the State of Arkansas Commission on Pollution Control and Ecology. A specified requirement of the permit is that a compliance test burn, using prescribed chemicals, be conducted to determine system efficiency.

COMPLIANCE TEST BURN PROTOCOL

A major element of the Combustion Research Facility (CRF) incineration system is the newly installed carbon bed/HEPA filter system. The carbon (some 4500 lbs) is reclaimed charcoal and so must be described as "dirty" from the point of view of the sampling and analytical procedures to be employed in the compliance tests. In addition, the installation now includes a considerable run of new fiber reinforced plastic pipe (FRP) that is also expected to be a copious source of background organics (for example, the methyl ethyl ketone used

as a solvent in cementing sections of the FRP). These reasons make the cleanup or removal of these background materials a first requirement of the compliance test.

The synthetic "waste" that was used to challenge the incinerator is a mixture of carbon tetrachloride, monochlorobenzene, trichloroethylene and toluene. This mixture, characterized as EPA Soup One, has been the subject of a rather extensive series of incineration tests at the CRF during the period 1 February, 1984 through 15 June, 1984. These tests were conducted using very small feed rates and a conservative research approach so that no discharge to the environment occurred. To that end the experiments with "Soup 1" were a success, but as we shall see the compliance test burn used much larger feed rates and was designed to study breakthrough of the existing scrubber but not the redundant device.

The compounds that make up the Soup are all low-boiling point materials which are therefore suitable candidates for the use of the volatile organic sampling train (VOST) and for subsequent analysis by thermal-desportion/purge and trap analysis. The procedures are in place and the QA/QC Program at the CRF has been reviewed and accepted by independant audit groups.

Test Materials

The composition of Soup One chemicals are tabulated in Table 1.

Sampling and Analysis

The sampling procedures, using VOST techniques, are essentially those used by others in the field. Analyses of the exposed Tenax Cartridges was carried out using established purge and trap techniques. Each cartridge was spiked prior to sampling; failure to recover the spike at better than 70% resulted in rejection of the sample. The analyses was conducted under the QA/QC procedures established for the CRF.

Sampling of the blowdown water and discharge consideration was conducted for POHC analysis.

Particulate emission, using the full EPA method five train with isokinetic sampling was conducted during experiment #2 (Table 2).

A sheet outlining a summary of the compliance test burn follows and shows pictorially the sampling points and the parameters that were analyzed.

Source of POHC

The chemicals for the feed stock were obtained from the Aldrich Chemical Company from the same batches that were used in the work previously conducted at the CRF. These compounds have been shown to be void of impurities that interfere with quantitation of the primary compounds.

TABLE 1. SOUP COMPOSITION

COMPOUND	FEED RATE (kg/hr)	FEED RATE (gm/hr)	CHLORINE FEED (gm/hr)
CCl_4	3.84	64.0	3.54×10^3
C_2HCl_3	3.49	58.2	2.83×10^3
C_7H_8	1.05	17.5	...
C_6H_5Cl	1.69	28.2	5.33×10^2
TOTALS	10.07	167.8	6.90×10^3

Feed Stocks

Since the purpose of the trial burn was to determine that the carbon bed can insure compliance even when the incinerator might itself be seriously out of compliance, it was proposed that the test burn be limited to a test at a high feed rate and at minimal temperature. Hence, the feed stock will be made up as follows: to one liter of C_7H_8 will be added 1.56 l of C_6H_5CL plus 2.75 l of CCl_4 plus 2.95 l of C_2HCl_3. The resulting solutions should have a heating value of 14.7 KBtu/l, a density of 1.37 kg/l and contain approximately 71% of chlorine. This solution was feed at the rate of 10 kg/hr resulting in a heat release of 107 KBtu/hr.

Test Schedule

The experimental schedule is outlined in Table 2.

conducted as indicated in the Protocol with several operational changes. The preburn, background, and the post burn samples were taken at the same temperatures as for the actual Soup challenge. In place of the proposed three sets of VOST samples, a total of six sets , one in the prefeed interval, were taken for the input/output of the carbon bed filter during the trial burn.

One additional change was made in the Protocol: namely, the THC measurements were not made. The fact that the combustion gases were saturated (relative humidity of 100%) at the required sampling sites required excessive pre-conditioning. This has not yet been successfully accomplished.

The results of this test series showed that the CRF rotary kiln incinerator meets or exceeds the permit requirements on all counts:

TABLE 2. TRIAL BURN SEQUENCE

Experiment	Feed Stock	Feed Rate (kg/hr)	T_K (°F)	T_A (°F)	Sampling Point*	Note
1	Blank	0	995	1400	2+3	(a)
2	Soup	10.07	1150	1400	2+3	(b)
3	Blank	0	995	1400	2+3	

Notes from Table 2 are designed to give considerably more information as follows:

Note (a): sample background run to establish baseline.

Note (b): feed to begin one (1) hour after temperature steady state is established. One (1) hour after feed start, VOST samples at 2 and 3. This will be repeated for a total of six (6) complete samples. After samples taken - shutdown.

RESULTS AND DISCUSSION

During the week of 7 January, 1985 the test burn required by RCRA was conducted at the USEPA Combustion Research Facility. The tests were

- the DRE exceeded 99.99% for all POHC's
- the HCl removal resulted in emissions of less than 0.5 kg/hr.
- the residual particulate matter was significantly below that required by the regulations.

The only unsatisfactory aspect of the Trial Burn was the behavior of the pH control system. The design was supposed to be capable of sustained control at chlorine levels up to 100 lb/hr. Actually, the system experienced wild swings from high to very low pH within periods of a few seconds even though the chlorine feed was of the order of only 20% of the design maximum. Careful checks of the elements of the control system was operating properly. With the given chlorine feed, there is no way for the pH of no less than 120 gallons of water to experience a change of from 10 to less than 1 in a few seconds. The clear indication of these observations was a failure of the mixing action. Examination of the recycle system showed that the downer fromthe tower extended into the recycle reservoir to a position near the intake port for the recycle pump. This arrangement, shown schematically in Figure 1, apparently resulted in short circuiting the intended mixing action. The water returned to the reservoir was, at least partly, derived from the venturi return. This latter solution can be expected to be strongly acid so that the resulting short circuited fluid would, itself, be of very low pH. Since the pH sensor was installed in a by-pass immediately adjacent to the recycle pump output, the wild swings of pH observed simply reflected those of the short circuited solution.

This situation has been corrected by shortening that portion of the downer to approximately 8 inches below the cover of the reservoir. The open end has been fitted with a diffuser plate to markedly increase mixing within the reservoir. The modified system has been challenged with the injection of HCl solution into caustic feed pump, the pH sensor and the controller indicated that each of the

SUMMARY OF EXPERIMENTS

EXPERIMENT: RCRA Trial Burn

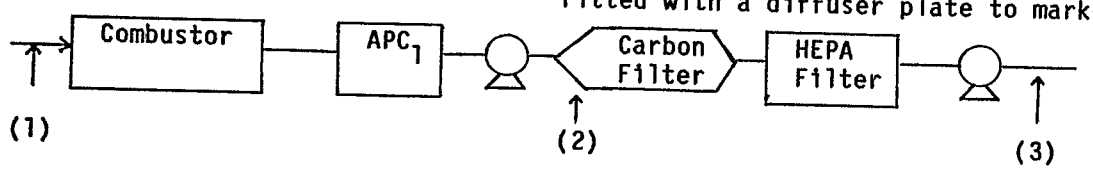
OBJECTIVE: To Demonstrate Compliance of CRF Incinerator System

DURATION: One Week

EXPERIMENTAL MATRIX:

Feed: CCl_4; C_6H_5Cl; C_2HCl_3 and C_7H_8 [70% chlorine]
Feed Rate: 10 kg/hr
T_{kiln}: 1000°F
T_{AB}: 1400°F

EXPERIMENTAL SYSTEM



SAMPLING & ANALYSIS

Sampling Point	Parameter	POHC Feed (CONC)	Fuel Feed	Air Feed	Temp.	O_2	CO	CO_2	Vol flow	HCl	THC	p*	RH+
(1)		✓	✓	✓									
(2)		✓			✓	✓	✓	✓	✓	✓	✓	✓	✓
(3)		✓			✓	✓	✓	✓	✓	✓	✓	✓	✓

* p = pressure
\+ RH = relative humidity

the kiln with the chambers operating at the temperatures used during the test burn. The changes have been shown to markedly increase the pH control so that the operation is now acceptable and a Removal Efficiency (RE) in excess of the required 99.5% was achieved.

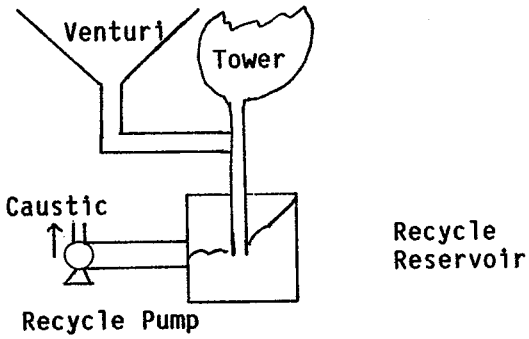


FIGURE 1. SCHEMATIC OF RECYCLE RESERVOIR

As will be shown below, in spite of the control problems, the HCl emissions were, in fact, adequately controlled.

Two measurements were made of the HCl emission rate at the input to the carbon bed; one of 60 minutes duration, the other of 326 minutes duration. The resulting data are shown in Table 3.

At the feed rate indicated in Table 1, the chlorine feed was 6.90×10^3 gm/hr which, on conversion to HCl, represented an HCl feed rate to the scrubber of 7.094×10^3 gm/hr. Thus, the removal efficiency was, in the two cases found to be

RE = 99.45%
RE = 99.34%

and the total emission rate was found to be well below the permissible 500 gm/hr.

Particulate Loading at the Stack

The results of three Method 5 scans of the stack during the Test Burn are summarized in Table 4.

The measured partriculate loading is well within the compliance requirements, the latter being a particle loading of not more than 180 mg/DSCM.

POHC Emission Levels and DRE

The measured emission rates for the four POHCs along with the corresponding

TABLE 3. IONIC CHLORINE OUTPUT RATE

SAMPLE	Sample Flow Rate (l/min)	Sample Time (min)	Sample Total (l)	Chloride Total (mg)	Gas Conc. (mg/l)	Duct Flow Rate (DSCMM)	HCl Emission Rate (gm/hr)
E01091144⊕	1.2	60	72	2.04	0.028	23.3	39.1
E01091254	0.96	326	313	10.55	0.0337	23.3	47.1

TABLE 4. PARTICULATE LOADING OF STACK

Sample	Degree of Isokineticity (%)	Total Particulate Collected (mg)	Sample Vol DSCM	Particulate* Loading (mg/DSCM)	(grains/DSCF)
S01091221#	84.39	25.9	1.127	50.14	0.022
S01091532	102.28	29.9	1.042	62.61	0.027
S01091737	89.54	13.7	0.894	33.44	0.046

* corrected to 12% CO_2. The regulatory maximum for particle loading is 180 mg/DSCM = 0.08 grains/DSCF

⊕ Sample taken at entrace to carbon bed, point number 2 on Summary Sheet.

\# Sample taken at the stack, point number 3 on Summary Sheet.

DRE's are tabulated in Tables 5 through 8 which follow. It is noted that in all cases the required DRE of 99.99% was attained.

TABLE 5. EXPERIMENTAL MEASUREMENTS OF POHC's - CARBON TETRACHLORIDE
[Feed Rate of 64.0 gm/min]

Sample Number	Sample Vol (DSL)	Sample Collected (μg)	Duct Flow Rate (DSMM)	Emission Rate (μg/min)	DRE* (%)
E01091102	21.57	0.354	25.75	419	99.999
S01091102	20.83	0.334	25.06	404	99.999
E01091203	22.91	0.151	23.34	154	99.999
S01091205	21.89	0.032	24.19	35.3	99.9999
E01091300	22.29	0.133	23.34	139	99.999
S01091300	20.93	0.050	23.85	57	99.9999
E01091400	20.48	0.131	24.16	154	99.999
S01091400	21.09	--	23.85	--	LOST SAMPLE
E01091500	23.96	0.133	23.79	132	99.999
S01091500	21.95	0.055	24.81	62.	99.9999

* The values reported for the E samples are strictly speaking DRE since they include the effects of the Anderson scrubber. Those for the S samples are more difficult to identify as DRE's.

TABLE 6: EXPERIMENTAL MEASUREMENTS OF POHC's - TRICHLORETHYLENE
[Feed Rate of 58.2 gm/min]

Sample Number	Sample Vol. (DSL)	Sample Collected (μg)	Duct Flow Rate (DSMM)	Emission Rate (μg/min)	DRE (%)
E01091102	21.57	0.015	25.75	17.8	99.9999
S01091102	20.83	0.074	25.06	89.5	99.9998
E01091203	22.91	0.20	23.34	20.4	99.9999
S01091205	21.89	0.067	24.19	74.0	99.9998
E01091300	72.29	0.014	23.34	14.7	99.9999
S01091300	20.93	0.065	23.85	74.2	99.9998
E01091400	20.48	0.018	24.16	21.2	99.9999
S01091400	21.09	..	23.85	Lost	Sample
E01091500	23.96	0.020	23.79	19.8	99.9999
S01091500	21.95	0.067	24.81	75.6	99.9998

TABLE 7. EXPERIMENTAL MEASUREMENTS OF POHC's - TOLUENE
[Feed Rate = 17.5 gm/min]

Sample Number	Sample Vol. (DSL)	Sample Collected (μg)	Duct Flow Rate (DSMM)	Emission Rate (μg/min)	DRE (%)
E01091102	21.57	0.108	25.75	128	99.999
S01091102	20.83	0.409	25.06	494.5	99.997
E01091203	22.91	0.081	23.34	82.5	99.999
S01091205	21.89	0.328	24.19	362.2	99.998
E01091300	22.29	0.078	23.34	81.6	99.999
S01091300	20.93	0.337	23.85	384.5	99.997
E01091400	20.48	0.074	24.16	87.2	99.999
S01090400	21.09	0.332	23.85	377	99.997
E01091500	23.96	0.056	23.79	55.5	99.999
S01091500	21.95	0.327	24.81	369	99.997

TABLE 8. EXPERIMENTAL MEASUREMENTS OF POHC's - MONOCHLOROBENZENE
[Feed Rate = 28.2 gm/min]

Sample Number	Sample Vol. (DSL)	Sample Collected (μg)	Duct Flow Rate (DSMM)	Emission Rate (μg/min)	DRE (%)
E01091102	21.57	.002	25.75	2.4	99.99999
S01091102	20.83	0.011	25.06	13.3	99.9999
E01091203	22.91	0.010	23.34	10.2	99.9999
S01091205	21.89	0.010	24.19	11.0	99.9999
E01091300	22.29	0.017	23.34	17.8	99.9999
S01091300	20.93	0.017	23.85	19.4	99.9999
E01091400	20.48	0.0009	24.16	10.6	99.9999
S01091400	21.09	0.013	23.85	14.8	99.9999
E01091500	23.96	0.010	23.79	9.9	99.9999
S01091500	21.95	0.008	24.81	9.0	99.9999

Discussion of Effects of Redundant Scrubber

A comparison of the E and S samples shows that, except for CCl_4, the S emission rates are either the same as the E rates or represent greater rates. It appears that the bed has only minimal effect on this group of compounds. It is known that high temperature and water adversely affect the carbon adsorption isotherms so that perhaps this effect is the origin of the observation. In addition the differences are very small and might simply be the result of statistical sampling and analytical errors.

In conclusion the results show that based on an input/output model the CRF rotary kiln system achieved the required 99.99% DRE for all of the target POHCs. After minor modifications to the pH control recycle reservoir system the removal in excess of the required 99.5% HCl was achieved.

The detailed technical report, including appendices, is in the final stages of review in preparation for the required submission to Arkansas permit officials as part of the compliance test requirements.

ACKNOWLEDGEMENT

The author wishes to acknowledge the dedicated engineers, chemists, technicians and secretaries of Versar for their contributions during the trial burn.

ENGINEERING ANALYSIS OF HAZARDOUS WASTE INCINERATION; FAILURE MODE ANALYSIS FOR TWO PILOT SCALE INCINERATORS

W. D. Clark, J. F. La Fond, D. K. Moyeda, W. F. Richter, W. R. Seeker
Energy and Environmental Research Corporation
Irvine, California 92718

and C.C. Lee
EPA Hazardous Waste Engineering Research Laboratory
Cincinnati, Ohio 45268

ABSTRACT

An engineering analysis procedure for prediction of hazardous waste destruction has been applied to two pilot scale incinerators: the Control Temperature Tower (CTT) and the Combustion Research Facility (CRF). The CTT was analyzed in backheated, insulated, and cooled configurations using two dimensional heat transfer and flow models under plug flow conditions with a turbulent core and boundary layers along the wall. First order global kinetic rates were utilized to calculate waste destruction efficiencies. For the CRF kiln and afterburner, residence time distributions were obtained from tracer gas measurements taken on an isothermal flow model; and temperatures were obtained from a single zone heat transfer model of each component. Potential failure modes were investigated including: cooling, change of waste type, poor atomization, low load, high excess air and flameout.

INTRODUCTION

There is increased public awareness and concern associated with the disposal of hazardous waste materials. When operated properly, incineration is the quickest and most effective method for destroying hazardous wastes (7). However, there are a number of risks associated with incineration which must be addressed before an incinerator can be put into operation. The public must be assured that the facility can be operated safely. The incinerator must be designed and built to meet government regulations requiring that hazardous compounds be destroyed and removed with an efficiency greater than 99.99 percent and must prove that these regulations can be met based on costly trial burns or other appropriate data. An envelope of safe operating conditions must be defined, and the impact of equipment failure or operator error must be assessed to determine what precautions are necessary to avoid incinerator failure.

A reliable assessment methodology allowing scaling and extrapolation of pilot scale and trial burn data could substantially decrease the expense and risk of defining the limits of safe operation for a particular incinerator. Such a methodology is under development at Energy and Environmental Research (EER). The state of the art of combustion modeling with respect to hazardous waste incineration has been reviewed (1) and six critical modeling areas have been identified: flow, heat transfer, mixing, injection, tracking, and kinetics. A composite engineering analysis procedure, described in detail by Clark, et al. (1), has been developed incorporating submodels for each of the six critical areas, although some of the submodels are quite simplistic in their current, preliminary form. The procedure has been demonstrated to successfully predict trends of hazardous waste destruction in a pilot scale incinerator (2).

This paper describes the application of the engineering analysis procedure to assist in the planning and interpretation of experiments and to identify potential failure modes for two EPA pilot scale incinerators, the Control Temperature Tower (CTT) and the Combustion Research Facility (CRF).

CTT

The CTT, built by EER, described by Overmoe, et al. (4), and operated by the Hazardous Waste Engineering Research Laboratory of EPA, is shown schematically in Figure 1. The downfired pilot scale incinerator is designed to operate in backfired, insulated, or cooled modes or in combinations of the three. The incinerator has an inside diameter (ID) of 0.254 m and a total length of 2.08 m. It is insulated to an outside diameter (OD) of 1.02 m with layers of refractory designed to withstand high temperatures and provide maximum insulation. The CTT is divided into three sections. The top section includes a 45 degree transition from an ID of 0.048 m at the burner to 0.254 m. The middle section has a slightly enlarged ID to make room for cooling coils which are inserted in the cooled mode of operation. The bottom section has channels in the refractory to allow auxiliary backheating without contact between the main flow and the auxiliary flame.

The engineering analysis procedure was applied to the CTT to analyze and extrapolate the results of the first test burn in late 1983. Data and operating conditions were reported by L. Staley of EPA in personal communication with the authors. The main burner was operated with 16,500 J/s (56,300 Btu/hr) propane at 140 percent theoretical air. The flame swirl number of 1.13 resulted in a short, squat flame which completely filled the cavity. Each of the two backfired channels was operated with a heat input of 10,100 J/s (34,500 Btu/hr). Gas temperature was measured with a thermocouple at a single axial position near the end of the backheated zone.

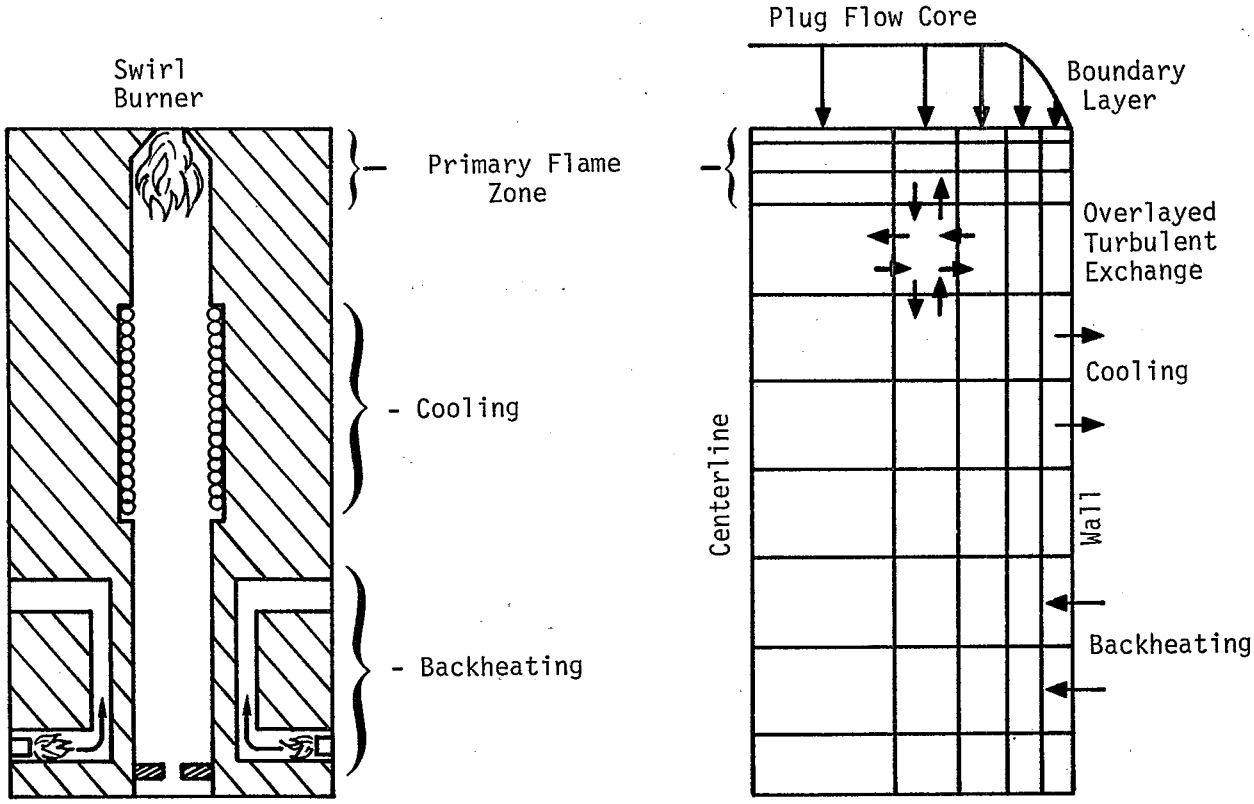


Figure 1. Schematics of CTT reactor and model.

Centerline temperature was measured to be 1161°K and the temperature did not change with radial position until within the boundary layer beginning 0.0254 to 0.0508 m (1 to 2 in) from the wall where the temperature dropped from 1161°K at the edge of the boundary layer to 1126°K at the wall. The true centerline temperature was estimated to be 1307°K from a heat balance on the thermocouple equating heat gained from convection between the gas and the thermocouple to heat lost from radiation between the thermocouple and the wall. This temperature correction was approximate at best due to uncertainties in the thermocouple emissivity and in the wall temperature.

To simplify the modeling effort, the incinerator was approximated as a cylinder with a constant ID of 0.254 m. Ten axial by five radial zones were used in the two dimensional model as shown in Figure 1. Plug flow with overlayed turbulence was assumed for the 0.203 m diameter core of the incinerator, modeled as three radial zones. The outer two zones were modeled as a laminar boundary layer with lower velocities and lower interzonal exchange based on diffusion rather than turbulence. Recirculation was not included because the flame was observed to fill the entire burner cone. Heat release was calculated to coincide with visual estimates of the flame length. Gas temperatures in each zone were calculated using a two-dimensional version of Richter's semistochastic zone model described in detail in references 2 and 5. For backheated sections, effective wall temperatures were calculated based on heat balance averages of the insulated wall temperature and the hot wall temperature. The conductivity of the insulation was calculated from manufacturer specifications.

Results of the heat transfer calculations are shown in Figure 2. No adjustments from the design specifications were necessary to achieve excellent agreement between predicted and measured temperature for the backheated case; however, since corroboration data were available at only a single axial position, predicted temperatures (especially flame temperatures) should be considered only approximate. Nevertheless, estimation of the relative effects

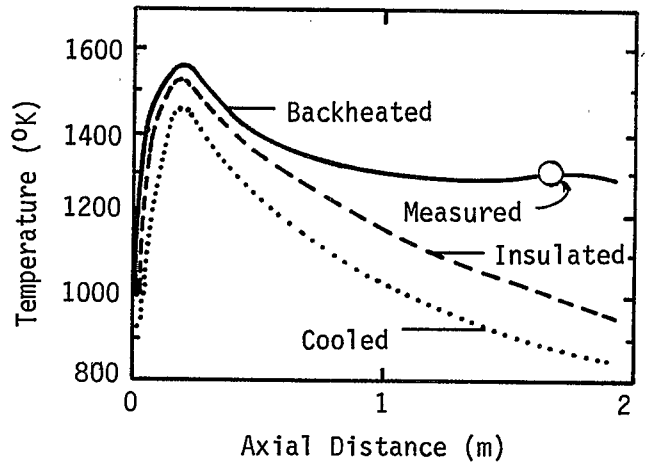


Figure 2. CTT centerline temperature predictions for three modes of operation.

of changing operating conditions should be accurate.

The heat transfer model was used to estimate the effects of changing the the heating/cooling configuration of the CTT. Three modes of operation were investigated: the previously described backheated case, an insulated case under the same operating conditions except that no backheating was used, and a cooled case where under the same operating conditions except that no backheating was used and 0.55 m^2 of the inside wall was covered with cooling coils removing about 1180 J/s (4020 Btu/hr) or seven percent of the heat input. Only the backheated case was run in the actual experiment. Due to the short flame, temperatures were predicted to peak close to the burner and decline rapidly early in the post-flame zone. For the backheated case, the predicted temperature leveled off around 1300°K as heat loss to the walls was balanced by heat addition from the auxiliary flame. Predictions for the insulated case were similar to the backheated case close to the burner (far from the backheating) where there was a difference of only about 30°K in the peak temperatures. However, unlike the backheated case, predicted temperatures for the insulated case continued to decline throughout the incinerator, exiting almost 350°K cooler than the backheated exit temperature. Temperature predictions for the cooled case fairly closely paralleled those for the

insulated case: peak temperature was 75°K cooler and exit temperature was 115°K cooler.

Waste destruction was calculated using first order global post flame kinetic rates reported by the University of Dayton Research Institute (UDRI) (6) according the the equation:

$$d[C]/dt = -[C]A \exp(-E/RT)$$

where [C] is the concentration of the waste compound, t is time, A and E are the frequency factor and the activation energy, R is the universal gas constant, and T is temperature. The kinetic rates were applied to a statistically large number of representative temperature histories obtained from a Lagrangian Monte Carlo tracking model. Temperature histories were the result of particular paths through the incinerator, chosen at random, but weighted by probabilities associated with the flow field. Figure 3 shows predictions of the undestroyed waste fraction (one minus the destruction efficiency) for a number of compounds ranked according to the isothermal temperature required to achieve 99.99 percent destruction in 1 second ($T_{99.99, 1\ sec}$) as calculated from the UDRI rates. Waste was not burned in the actual experiment, so no measurements are available for comparison. For the backheated case, better than 99.9999 percent destruction efficiency (10^{-6} fraction undestroyed)

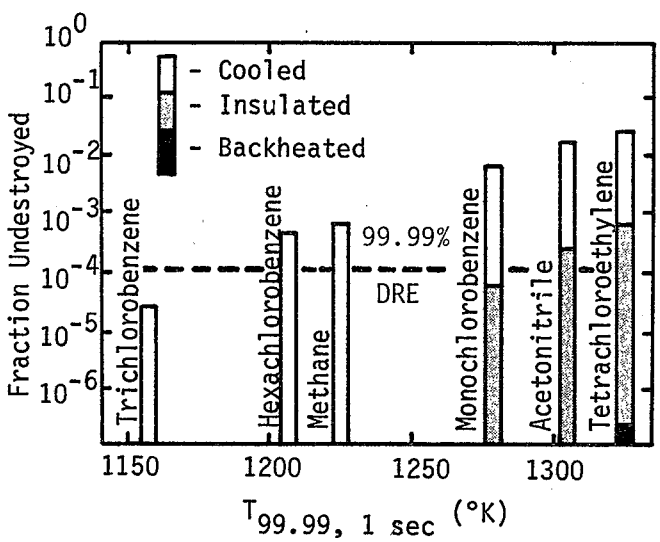


Figure 3. CTT waste destruction predictions for three modes of operation.

was predicted for every compound in the UDRI data set; for the insulated case, a few of the harder to destroy compounds were predicted to fail to achieve 99.99 percent destruction; and for the cooled case, several compounds had predicted destruction efficiencies lower than 99.99 percent. From these results, it is evident that cooling configuration can have a dramatic effect on hazardous waste destruction in the CTT, and that failure conditions can be achieved for some compounds in insulated or cooled operation.

Fast quenching is a potential mode of failure for an incinerator. Quenching can occur due to a massive water leak at a specific point in the incinerator. Effects of quench were investigated by artificially freezing reactions downstream of the flame. Figure 4 shows that most, but not all, of the predicted destruction for the cooled case was achieved within the flame zone. It should be noted here that the UDRI kinetic set was developed under non-flame oxidizing conditions and is expected to provide conservative results when applied to a flame zone where large concentrations of free radicals are present. A comprehensive set of flame-mode global kinetic rates is not presently available.

Effects of poor atomization were investigated for the cooled case by simulating evaporation of all of the waste-containing droplets at one of three locations: instantaneous evaporation at the burner (the standard assumption used in the previous calculations), evaporation at the wall near the end of the flame, and delayed evaporation downstream of the flame. Figure 5 shows that downstream evaporation had the lowest destruction efficiency due to the short residence time and the bypassing of the flame zone; evaporation at the wall yielded the next lowest destruction efficiency due to the probable bypassing of the flame zone; and instantaneous evaporation at the burner yielded the highest predicted destruction efficiency due to the probability that most of the waste passed through the flame. These results suggest that improper spray nozzle operation can be a significant failure mode if large high-velocity droplets are produced which emerge from the flame unevaporated.

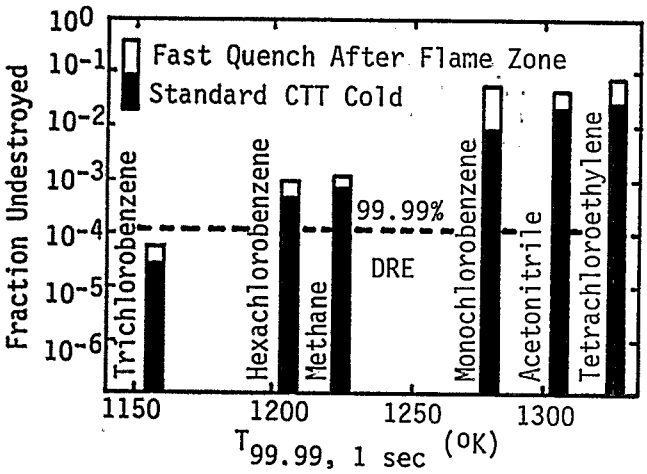


Figure 4. CTT waste destruction predictions with and without quench.

CRF

The CRF, sponsored by the EPA, described by Versar (8), and operated by Versar, is shown schematically in Figure 6. The facility has a 1.07 m ID by 2.34 m long rotary kiln insulated with 0.127 m of refractory. The kiln is connected to a 0.97 m ID by 2.82 m long afterburner insulated with 0.152 m of refractory by means of a 0.305 m by 0.559 m rectangular transfer duct approximately 0.838 m long insulated with 0.127 m refractory. Liquid waste is injected into the kiln in a steady stream on the opposite end from the transfer duct. The kiln is equipped with two burners: the original burner, a low-swirl propane burner rated at 527,000 J/sec (1.8 MM Btu/hr), is located on the same end as the transfer duct and is fired against the waste flow at an off-center skewed angle. The newer, smaller, modified, oil burner is located on the same end as the waste feed and is cofired with the waste flow also at an off-center skewed angle. The kiln products enter the afterburner tangentially close to the end opposite the afterburner exit. The burner in the afterburner, the same model as the original kiln burner, is fired tangentially against the flow of the kiln products to promote rapid mixing but angled slightly downstream.

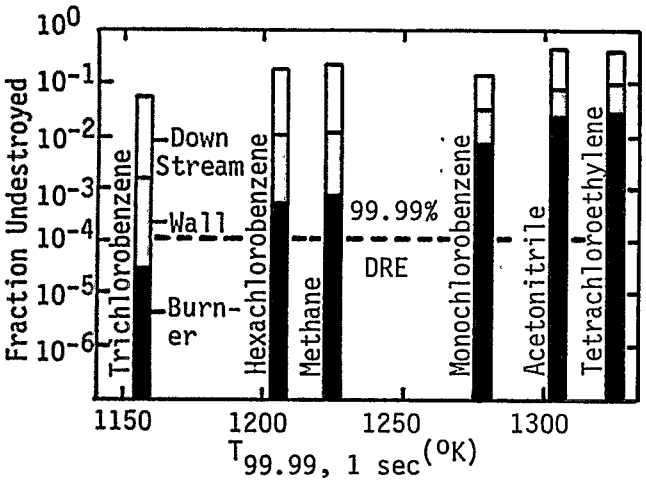


Figure 5. CTT waste destruction predictions for three points of droplet evaporation.

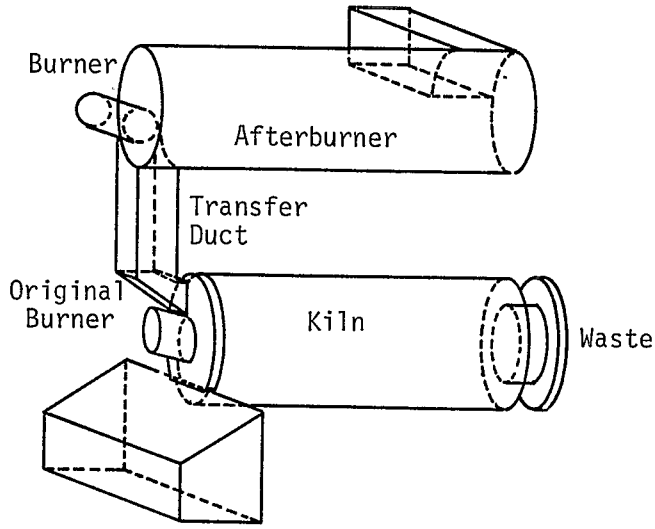


Figure 6. Schematic of CRF.

The engineering analysis procedure was applied to the CRF to simulate a test performed on January 26, 1984. Data from the test were reported in Reference 8 or were collected by personal communications between the authors and Versar. In the test, 100 g/hr hexachlorobenzene were fed in solution with toluene in a continuous flow at 2.84 liters of solution per hour. Propane, the auxiliary fuel, was counter-fired through the original kiln burner at a rate of 0.141 standard cubic meters per minute providing about 90 percent of the 260,000 J/sec gross heat input to the kiln. The kiln was operated at 216 percent theoretical air. Approximately 80 percent of the kiln air was supplied through the burner, with the remainder leaking into the sub-atmospheric pressure kiln around the seals and through the ash bin. Kiln exit temperature was measured at 833°K in the transfer duct with a

thermocouple sheathed in 0.95 cm diameter mullite; however, due to uncertainties in the emissivity of the partially dirty sheath, the wall temperatures and the view factors, the actual gas temperature was unknown. A heat balance on the thermocouple sheath indicated that the gas could easily have been 300°K hotter than the thermocouple. An additional 290,000 J/sec propane was fired in the afterburner with enough additional air added to bring the overall stoichiometry to 201 percent theoretical air. Afterburner exit temperature was measured at 1088°K in the exit duct, also with a 0.95 cm diameter mullite sheathed thermocouple.

An isothermal flow model of the CRF kiln/afterburner system was built to a 1:3 linear scale at EER to investigate the effects of the recent burner modification on kiln flow patterns. La Fond and Moyeda (3) observed that the modified kiln exhibited a markedly different flow pattern from the original. Both had highly three-dimensional swirling flows with large recirculating eddies. But in the original kiln, waste was injected into a dead zone on the opposite end from the burner and took a relatively long time to exit; whereas, in the modified kiln, waste was injected on the same side of the kiln as the burner and was quickly entrained into the main flow leading to a relatively rapid exit.

Complete analysis of the CRF requires utilization of the isothermal flow model results with three dimensional versions of the heat transfer and tracking models described in the previous section. However, for the preliminary analysis reported in this paper, the kiln and the afterburner were each modeled using Richter's semistochastic heat transfer model (5) with a single zone. This simplistic approach, ignoring temperature variations within the kiln or afterburner, is certainly inadequate to predict absolute levels of waste destruction, but should give fairly accurate predictions of relative destruction, allowing trends to be investigated and failure modes to be identified. Residence time distributions were obtained from tracer gas measurements on the isothermal flow model. To allow scaling and extrapolation, the residence times were nondimensionalized, dividing by the ratio of the reactor volume to the total volumetric flow. Waste destruction was calculated by averaging the results obtained from applying UDRI rates (6) at the temperature predicted by the heat transfer model for a number of residence times representative of the residence time distribution.

Residence time distributions of tracer gas injected into the waste end of the kiln for the original and the modified burner configurations are compared in Figure 7. The curves represent the best fits to isothermal model measurements, assuming the kiln could be represented by the combination of a plug flow reactor and a stirred reactor in series which would respond to a step change in tracer gas concentration according to the following equation:

$$\frac{C}{C_o} = 1-\exp -\left[\frac{t-\tau_{plug}}{\tau_{stirred}}\right]$$

where C/C_o is the ratio of the transient to the steady state tracer gas concentration, t is time, and is the plug flow or stirred reactor time constant. Response times for the injection system and the sampling system were taken into account using the same assumptions, and a correction factor was applied to the resulting time constants to account for the slight difference in the volumetric flow to volume ratio between the model and the incinerator as operated on 1/26/84. For the identical operating

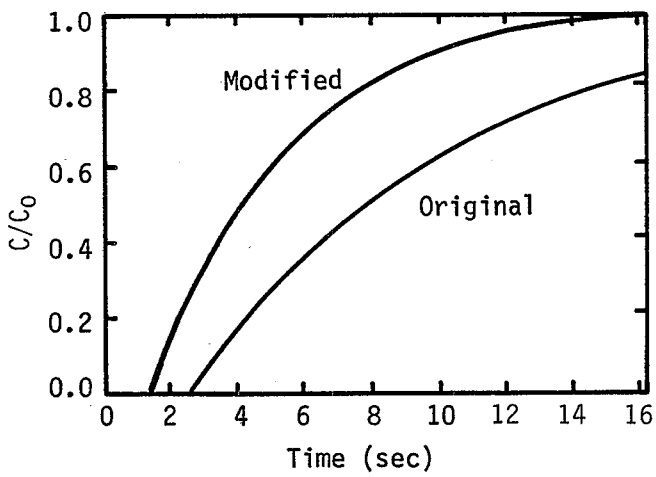


Figure 7. Kiln residence time distributions for original and modified CRF configurations.

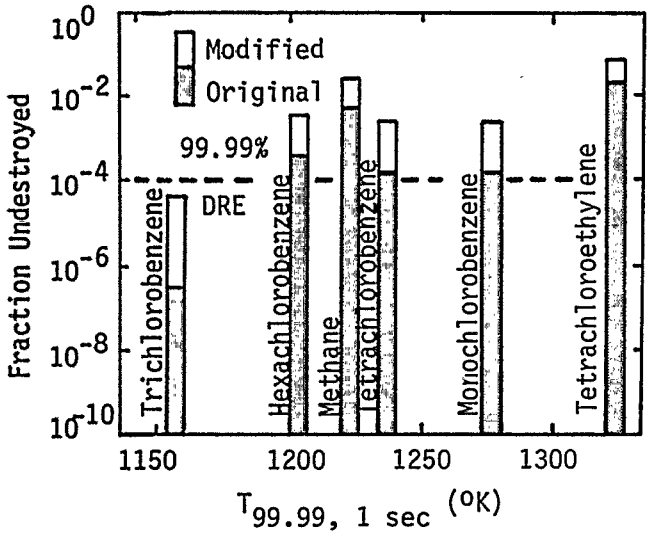


Figure 8. Effect of burner configuration on waste destruction in the CRF kiln.

point, assuming the burner modification did not affect gas temperature, the original kiln had a plug flow residence time of 2.63 sec and a stirred reactor time constant of 7.48 sec, whereas the modified kiln had a much faster plug flow residence time of 1.63 sec and a stirred reactor time constant of 3.672 sec.

Destruction efficiencies were calculated by applying UDRI kinetic rates (6) to the measured residence time distributions at isothermal temperatures. Kiln gas temperature was set at 1107°K so that predicted hexachlorobenzene destruction for the original kiln matched the measured destruction efficiency of 99.97 percent. Because of the faster residence time distribution, destruction efficiencies for the modified kiln were predicted to be lower than those for the original kiln. Figure 8 shows predictions of the undestroyed fraction (one minus the destruction efficiency) for several compounds for the 1/26/84 data point. These predictions suggest that incinerator modifications which shorten the waste residence time may cause the incinerator to fail. The figure also demonstrates that an incinerator which performs well for one waste (trichlorobenzene, for example) may fail for another (tetrachloroethylene). Finally, it illustrates that $T_{99.99,\ 1\ sec}$ is not always a perfect indicator of a compound's relative destruction efficiency.

The heat transfer model was applied to estimate the effects of changing operating conditions. Side wall refractory conductivities were calculated from manufacturer specifications. End wall conductivity was used as a tuning parameter to achieve the desired kiln gas temperature of 1107°K for the 1/26/84 operating conditions. This was the temperature necessary to achieve agreement between the predicted and the measured 99.97 percent hexachlorobenzene destruction for the original burner configuration. An effective end wall conductivity nine times greater than that of the side wall yielded the desired temperature prediction. This was not unreasonable due to the irregularities (burner, waste injector, ash bin, etc.) on the end walls. Measured hexachlorobenzene emissions from the afterburner were so low that they appeared to be in the noise so similar tuning of the afterburner was impossible. For this reason, it was assumed that the same factor of nine applied to the afterburner end wall to side wall conductivity ratio. The residence time distribution for the original kiln configuration was used, modified to account for the changing volumetric flow.

Figure 9 shows the effect of load on predicted temperatures for the CRF kiln and afterburner. In this context, load means the fuel and waste chemical heat input. Afterburner load was maintained at 112 percent of kiln load as in the 1/26/84 data point. Predicted afterburner temperatures were about 100°K hotter than kiln temperatures due to the

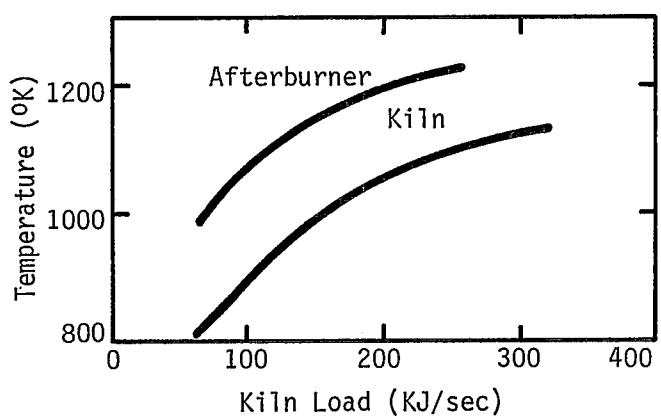


Figure 9. Effect of load on predicted temperatures in the CRF.

lower excess air ratio in the afterburner, the better insulating refractory used in the afterburner, and the high preheat temperature of the kiln exit gas. Predicted temperatures decreased with decreasing load resulting in decreasing predicted hexachlorobenzene destruction efficiency (increasing fraction undestroyed) as shown in Figure 10. Failure conditions (99.99 percent destruction or 10^{-4} fraction undestroyed) were predicted at loads less than 300 KJ/sec (1.02 MM Btu/hr) for the kiln alone, and 120 KJ/sec for the afterburner alone, and at 100 KJ/sec for the system comprising the kiln and the afterburner in series.

Effects of excess air on predicted temperatures are shown in Figure 11. Afterburner air flow was maintained proportional to kiln air flow. Increasing excess air resulted in decreasing temperatures due to the dilution effect. These decreasing temperatures coupled with decreasing residence times due to increased total flow resulted in decreasing predicted destruction efficiencies as shown in Figure 12. Failure conditions for hexachlorobenzene destruction were

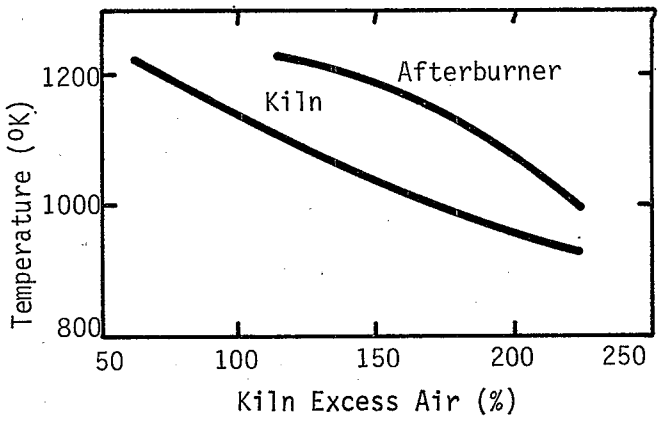


Figure 11. Effect of excess air on predicted temperatures in the CRF.

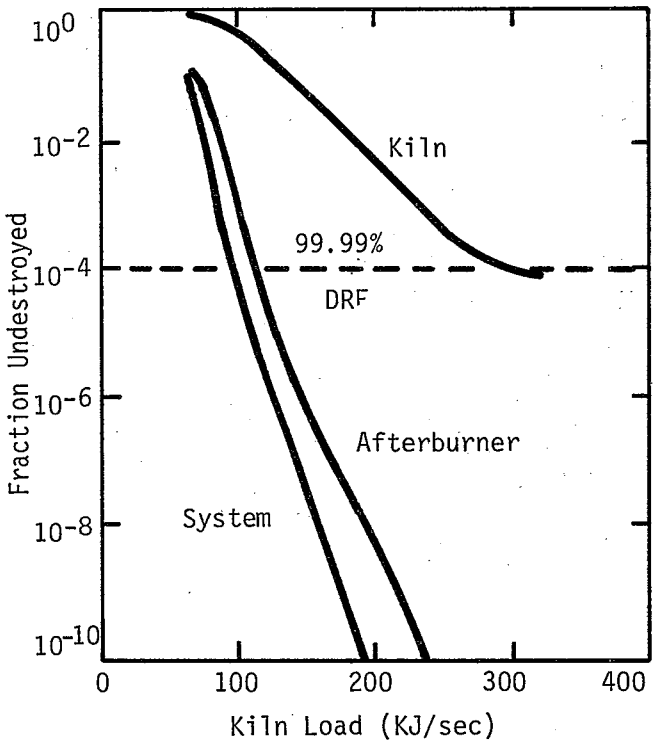


Figure 10. Effect of load on predicted hexachlorobenzene destruction in the CRF.

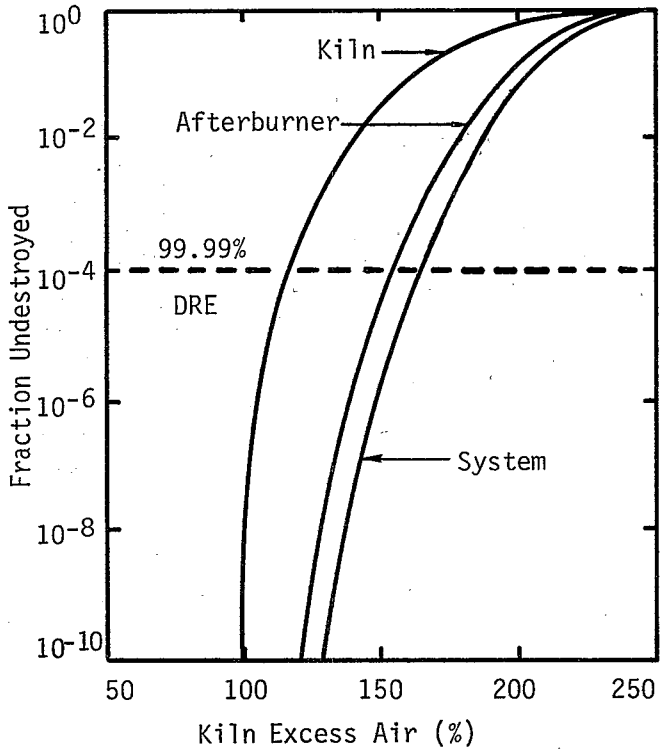


Figure 12. Effect of excess air on predicted hexachlorobenzene destruction in the CRF.

predicted to occur for kiln excess air levels above 113 percent for the kiln alone, 154 percent for the afterburner alone and 163 percent for the system as a whole.

Effects of momentary flameout were investigated by turning off the fuel to the kiln or the afterburner, but maintaining the wall temperatures unchanged from the 1/26/84 data point. Such a condition would only last for a short time before the wall began to lose its residual heat and the wall temperatures began to fall. Figure 13 shows that kiln flameout resulted in a sharp decrease in predicted kiln temperature, but a relatively small decrease in the afterburner temperature. Kiln temperature was, of course, unaffected by afterburner flameout, and afterburner temperature dropped sharply. Figure 14 shows that kiln flameout was predicted to cause a total failure in hexachlorobenzene destruction; however, the afterburner alone was predicted to be sufficient to cause the system to pass the 99.99 percent destruction efficiency criterion. For afterburner flameout, the afterburner alone was predicted to fail, but the combination of the kiln and the afterburner together was sufficient to marginally pass. From these predictions, it is evident that afterburner flameout has the greater effect on the performance of the system as a whole, but afterburner flameout alone is not sufficient to cause the system to fail at the 1/26/84 operating point.

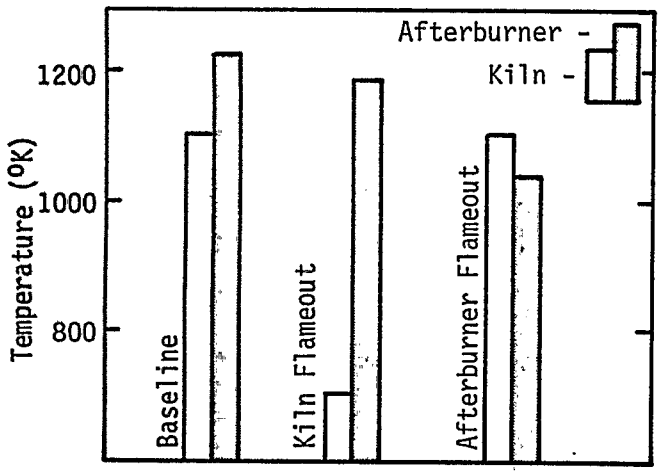


Figure 13. Effect of flameout on predicted temperatures in the CRF.

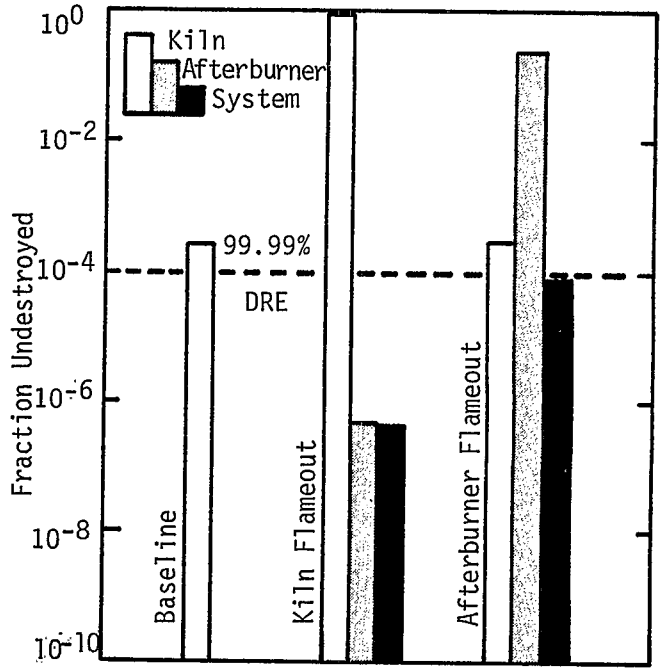


Figure 14. Effect of flameout on predicted hexachlorbenzene destruction in the CRF.

CONCLUSIONS, RECOMMENDATIONS, AND PLANS

The engineering analysis procedure can be an effective tool to assist in the planning and interpretation of experiments and to identify potential failure modes in incinerators. The current state of the art is not capable of predicting absolute levels of waste destruction, but trends can be investigated, and extrapolations from measured data points are possible. Accurate and complete measurements are required for these kinds of extrapolations. It is recommended that experimenters attempt to completely characterize their systems, particularly with respect to gas temperatures by making extensive suction pyrometer measurements.

Both of the pilot-scale incinerators investigated are predicted to be capable of destroying hazardous waste materials when operated properly. The CTT can be pushed to failure by excessive cooling or possibly by poor atomization of waste droplets. The CRF can be pushed to failure by low load or by high excess air conditions. Momentary flameout of the CRF afterburner can cause the system to nearly fail.

In the future it is planned to apply Richter's three dimensional heat transfer model (5) to the CRF. This, coupled with the isothermal flow model, should give a more accurate estimation of possible temperature histories within the incinerator resulting in better predictions of waste destruction. Model development efforts are presently concentrating on the areas of mixing, to identify flame and post flame zones allowing the appropriate kinetic rates (if available) to be applied to each, and liquid injection to determine where droplets evaporate and waste enters the gas stream.

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EXAMINATION OF FUNDAMENTAL INCINERABILITY INDICES FOR HAZARDOUS WASTE DESTRUCTION

Barry Dellinger, John L. Graham, Douglas L. Hall, and Wayne A. Rubey
University of Dayton Research Institute
300 College Park
Dayton, Ohio 45469

ABSTRACT

Rankings of POHCs by the various proposed indices of hazardous waste "incinerability" have been compared to observed incinerability for ten pilot or full scale hazardous waste thermal destruction devices. Each index failed to predict field results except for the method based on laboratory determined thermal stability for hazardous waste mixtures under oxygen deficient conditions. Most importantly, it was found that thermal reaction products (which were also POHCs), could be formed in sufficient yield to dominate the apparent POHC DRE. It is concluded that product formation is the most important factor in determining observed DREs for all but the most stable or difficult to form POHCs. Laboratory thermal decomposition testing of actual waste streams is useful to predict results of full scale incineration.

Current incinerator performance standards require that the principal hazardous organic constituents (POHCs) of each waste be destroyed or removed to an efficiency of 99.99%. Compliance with this standard is usually established through a trial burn. Since the demonstration of 99.99% destruction and removal efficiency (DRE) for every listed organic compound in any waste that may be fed to a given incinerator is prohibitively expensive and difficult, only selected compounds are tested during a trial burn. In order to be certain that the trial burn ensures that all listed compounds are efficiently incinerated, various hierarchies of "incinerabilty" of hazardous organics have been developed. The selected compounds should in general, be more difficult to incinerate (higher of the incinerability hierarchy) than other listed compounds to be fed to the incinerator. Clearly, an accurate prediction of the relative DRE is of critical importance to the current regulatory approach.

In this manuscript, we compare the results of field tests at various facilities with the results predicted by the proposed hierarchies. It appears that sufficient laboratory and field results are now available to make some generalizations concerning predicted field results and to establish guidelines for further trial burn testing.

INCINERABILITY INDICES

Six methods of ranking the relative incinerability of hazardous organic compounds have been previously proposed [1-9].

- Heat of Combustion
- Auto-Ignition Temperature
- Theoretical Flame Mode Kinetics
- Experimental Flame Failure Modes
- Ignition Delay Time
- Gas Phase Thermal Stability

The heat of combustion of a substance is defined as the enthalpy change for a

reaction in which one mole is completely reacted with oxygen [1]. The hypothesis behind this hierarchy is that those compounds with a large heat of combustion per gram molecular weight ($\Delta Hc/g$) will produce a higher flame temperature due to the exothermicity of combustion reaction. Presumably, the higher the flame temperature, the greater the destruction efficiency of the compound. Conversely, those compounds with low $\Delta Hc/g$ will be poorly destroyed due to low flame temperature. A ranking of $\Delta Hc/g$ for listed compounds is presented in the US-EPA Guidance Manual for Hazardous Waste Incineration Permits.

Autoignition temperature (AIT) is the lowest temperature at which a combustible material in the presence of air begins to self-heat at sufficient rate to produce combustion without any other source of ignition [2]. Laboratory studies have shown a correlation between gas phase thermal stability and autoignition temperature [7]. As a result AIT has been suggested as a possible ranking scheme. The lower the AIT, the easier the substance is to decompose. The basis for its applicability would appear to be related to the self heating properties of the waste, and its to sustain radical chain reactions.

Theoretical flame mode kinetics (TFMK) focuses on estimation and extrapolation of elementary reaction rate data that is available from experiment and theory [3]. Only a small number of compounds may be ranked using this approach due to limited data. The approach is based on calculations that predict thermodynamically complete oxidation of most POHCs below 500C. In contrast, field and laboratory results show incomplete oxidation at temperatures greater than 700C for most substances. This implies that kinetics and not thermodynamics is controlling the rate of destruction of the compounds.

The experimental flame failure mode (EFFM) approach is generally based on experimental determination of destruction efficiencies in bench scale flame systems [4]. However, under this approach as originally proposed, the compound ranking may vary depending on the "failure mode" or upset conditions of the flame. Four failure modes have been identified: poor atomization of the waste feed, poor mixing of waste and air, low flame temperature, and quenching of the reactant waste by contact with cool surfaces or makeup air. Only five compounds were originally ranked, but recent laboratory studies have generated additional data and rankings based on flame speed in a flat flame burner [5].

The ignition delay time (IDT) of a hazardous organic compound or mixture is defined as the interval between an initial exposure to a step function change in temperature and the principal exothermicity of the reaction as indicated by a rapid increase in temperature and pressure of the mixture [6]. These times may be measured in shock tube experiments. The basis of this approach is that ignition delay is controlled by, and inversely proportional to, the reaction kinetic rate. Thus, the smaller the IDT of a substance, the greater the ease with which it may be incinerated.

A ranking has been previously proposed based on laboratory determined thermal stability specified by the temperature required for 99% or 99.99% destruction at 2.0 seconds reactor residence time in an atmosphere of flowing air [$T_{99}(2)$ and $T_{99.99}(2)$], [7,8]. The basis for this approach is that any undestroyed material escaping the flame, must eventually be dealt with by thermal oxidation in the post-flame zone. It is proposed that the destruction of POHCs in the fraction of the waste feed experiencing the flame environment is essentially the same for all organic compounds, i.e., greater than 99.999%. Thus, the differences in their measured DRE must be due to differences in their rate of destruction for the fraction of the waste escaping the rigors of the flame.

This scale was originally developed for pure compounds in flowing air. However, recently generated data has shown that relative stability varies as a function of the composition of the waste feed and oxygen concentration [9]. This has led to modification of the rankings to account for the thermal stability of individual POHCs fed as a mixture in both an oxygen rich ($TSHiO_2$) and an oxygen deficient ($TSLoO_2$) environment. These hierarchies have been applied to predicting the results of studies described in the following paragraphs.

COMPARISON OF FIELD RESULTS AND PREDICTIVE METHODS

Intercomparison of field and laboratory data should be conducted with extreme caution. While lab studies are usually conducted under precisely controlled well-defined conditions, field studies are generally not [4,7,9,10]. Upon examination of field study reports, it is obvious that the quantitative intercomparison of the performance of the facilities with respect to operational parameters is not viable. However, relative DRE data for POHCs within a waste feed at a given facility can be analyzed with proper data validation guidelines. To ensure a valid comparison of predicted and observed results, the following data validation and reduction criteria were used:

- only compare POHC DREs for a given incinerator
- only compare POHC DREs when they are fed to the system at a common point
- use averages of DREs when no significant run to run variation in relative POHC DRE is observed
- only use data where the majority of the POHC DREs are less than 99.995%
- include data from non-concurrently fed POHCs if other key parameters are held constant
- conduct the correlation of observed field vs. predicted results on a rank/order basis with a minimum of four data points

The observed incinerability ranking of the test compounds at each source were compared with the prediction of each proposed hierarchy using a rank/order correlation approach [11]. This method was judged to be superior to a linear regression analysis since the latter judges the agreement of the data with a best-fit straight line while the former simply determines if a statistically significant relationship exists between the observed and predicted rankings. The rank-correlation coefficient, r_s, was used to judge if a correlation existed at the 90% confidence level for a number of test compounds, N.

Results of this analysis are summarized in Table I for the ten studies judged to meet the data validation criteria [8-10,12-17]. Of the eight proposed ranking methods, only Hc/g, AIT, $T_{99}(2)$, $TSHiO_2$, and $TSLoO_2$ had a sufficient data base to make predictions for a significant number of sources. Of these, only the experimentally predicted order under low oxygen conditions, $TSLoO_2$ met with a reasonable success, i.e., 70%. The other four methods only correlated with field observations 10-20% of the time. More importantly, it was apparent after detailed examination of the individual data plots that certain trends were occurring that could not be explained by simple application of the ranking methods. In particular, the compounds that deviated in stability from predictions of the $TSLoO_2$ hierarchy were often the same for the various studies. In many cases, this deviation could be explained using other available information.

The paragraphs that follow discuss the data from the specific sources in a manner that demonstrates how the field scale observations can be reliably predicted with modifications of the $TSLoO_2$ hierarchy.

Study A. The test compounds follow the order of stability toluene methyl ethyl ketone 1,1,1-trichloroethane Freon 113. The observed order was the same as predicted by $TSLoO_2$ except for reversal of 1,1,1-trichloroethane and Freon 113. In actuality, both of these compounds are predicted to be relatively very fragile under low O_2 conditions, and the predicted rankings could have been easily reversed. The predicted rankings as pure compounds in flowing air or in a mixture with high O_2 were quite different and did not correlate with the observations. This is consistent with the low O_2 levels noted in the field study reports.

Study B. The predictions of the $TSLoO_2$ method and the observed stabilities agree quite well with only a few exceptions. Chlorobenzene and dichlorobenzene were observed to be reversed from the predicted order. This is readily explained by the observation that significant levels of chlorobenzene were detected in the scrubber makeup waste and could be stripped out and into the stack gases. This would result in an apparent chlorobenzene DRE lower than that actually achieved by thermal destructionand account for the disparity with the $TSLoO_2$.

TABLE 1
RESULTS OF STATISTICAL ANALYSES
OF OBSERVED VERSUS PREDICTED THERMAL
STABILITIES RANKINGS

Study	Hierarchy							
	H_c/g	AIT	TFMK	EFFM	IDT	$T_{99}(2)$	$TSHiO_2$	$TSLoO_2$
A	-0.300/5[1]	-0.200/4	--	--	--	--	0.000/5	0.900/5*
B	-0.190/8	0.200/4	--	--	--	-0.057/6	0.533/10*	0.529/10*
C	-0.500/5	--	--	--	--	0.500/5	0.400/5	0.600/5
D	-0.100/9	-0.060/	--	--	--	-0.800/4	0.386/9	0.493/9*
E	0.589/7*	0.428/6	--	--	--	-0.300/5	0.425/8	0.429/8
F	0.343/15	0.571/7*	-0.100/5	--	--	-0.425/9	0.041/15	0.073/15
G	0.400/4	--	--	--	--	0.800/4*	0.800/4*	0.900/4*
H	-0.333/7	0.457/6	--	--	-0.300/4	-0.161/7	-0.036	0.655/8*
I	-0.077/10	-0.262/8	0.600/4	0.600/4	-0.100/5	-0.217/9	-0.318/11	0.536/11*
J	-0.291/10	0.147/8	0.800/4*	0.600/4	-0.100/5	-0.202/9	-0.114/11	0.523/11*
# Of Success*	1	1	1	0	0	1	2	7
# Of Failure	9	8	2	2	3	8	8	3
% Success*	10	11	33	0	0	11	20	70

[1] r_s/N

*correlation was statistically significant at the 90% confidence level

A major deviation was observed for bis-2-ethyl-hexylphthalate which appeared more stable than predicted. Although the predicted stability for phthalate is questionable due to lack of laboratory data, phthalates are ubiquitous and detected levels may be due to outgassing of plastics in the system and not from undecomposed feed. High levels of phthalates are commonly found in ambient environments and for this reason, should probably be excluded from all data sets [18]. Bis-2-ethyl hexyl phthalate was found at high levels in the scrubber water. Stripping from the water by the effluent gas could account for its observed emissions.

Two other major outliers were aniline and trichloroethylene. These compounds were significantly more fragile than predicted. Neither aniline nor trichloroethylene would be expected to be a major thermal reaction product from this test sample. This is in contrast to chloroform, carbon tetrachloride, and phosgene which unexpectedly surpassed aniline and trichloroethylene in apparent stability. The apparent thermal stability of carbon tetrachloride, chloroform, and phosgene may be due to their formation as products from other components of the waste as opposed to their stability as POHCs. Furthermore, these compounds are quite volatile and could be present in the ambient air in the form of fugitive emissions. Either formation as a product or as an ambient air contaminant could explain the unexpected reversal in thermal stability.

Study C. The waste was spiked with theoretically stable POHCs which had an observed order of stability: acetonitrile benzene trichloroethylene chlorobenzene carbon tetachloride. This was as expected except for benzene which was considerably more stable than predicted based purely on thermal stability. It is possible that benzene was formed as a product from chlorobenzene (or the auxiliary fuel). This hypothesis is supported by two independent observations. First, a simulated waste stream very close in composition to the actual waste was subjected to thermal decomposition in the laboratory. Under low O_2 conditions, benzene would actually have been predicted as a reaction product resulting in a low apparent DRE for benzene as a POHC. Furthermore, the waste stream was fed to the full scale incinerator without benzene in the feed. Roughly equivalent levels of benzene were found in the stack effluent confirming the hypothesis that its emission was due to sources other than residual POHC from the waste feed.

Study D. Field test results were in basic agreement with prediction for low oxygen conditions. The exceptions were phthalates, which were previously discussed, and tetrachlorethylene which was predicted to be the most stable component but was observed to be less stable than benzene, toluene, naphthalene, carbon tetrachloride, and methyl ethyl ketone. Laboratory studies have demonstrated or strongly suggested that each of these compounds can be a significant reaction product from various precursors [9,12,19]. Dichloromethane and chloroform were also found in the source emissions, suggesting the formation of chlorinated methanes as thermal reaction products. Thus, the apparently greater stability of these compounds than tetrachloroethylene may be due to their formation as products in the incineration process.

Study E. A correlation was observed between predicted and observed rankings but there was significant scatter. The fragile nature of 1,1,2-trichloroethane, 1,1,1-trichloroethane, and methyl ethyl ketone were correctly predicted (DREs all at 99.999% or greater). The observed stability of these three compounds were permuted from their predicted value contributing to the poor correlation coefficient.

Methylene chloride and to some extent, carbon tetrachloride appeared more stable than predicted. It should be noted that high levels of other halogenated methanes were found in the stack effluent indicating a source of carbon tetrachloride and methylene chloride emissions other than residual POHC (i.e., either incomplete combustion products or a result of stripping of these volatiles from the scrubber water).

The most unexpected behavior was exhibited by tetrachloroethylene, which was predicted to be the most stable POHC but was observed to be very fragile.

Study F. Although this facility exhibited the lowest correlation of predicted and observed emissions, the

results are extremely informative. Two distinct groups were evident, one consisting of primarily chlorinated aromatics and olefins; and a second consisting of primarily halogenated aliphatics along with bis-2-ethyl hexyl phthalate and hexachlorocyclobutadiene.

Methylene chloride and chloroform were found in the scrubber makeup water which could readily account for their observed emission levels. The other halogenated compounds (in the second group) are also very volatile and have been found in the ambient air surrounding such facilities (presumably due to fugitive emissions) [10]. As previously discussed, phthalate emissions are consistently high at most sources. Finally, there is some question concerning the accuracy of the predicted ranking for hexachlorocyclopentadiene due to lack of lab data. Its low stability prediction was based on possible strain of the five membered ring structure, but could well be in error. If the six compounds in question are eliminated from the data set and a correlation is performed with the remaining nine compounds, a statistically significant rank correlation coefficient of 0.89 is obtained.

Study G. The observed stability is as predicted under low O_2 conditions except for carbon tetrachloride which appeared more stable than chlorobenzene. This is not surprising since chloroform was also present in the mixture and carbon tetrachloride has been established as a thermal reaction product of chloroform by lab studies.

Study H. The POHCs in this test essentially followed the predicted order except for tetrachloroethylene and trichloroethylene which appeared less stable than benzene and toluene, contrary to predictions. This type of result has been observed in other studies and is ascribed to the propensity for formation of toluene and benzene as reaction products. It is also interesting to note that carbon tetrachloride emissions were also quite high (average of 173 g/s) which tends to confirm its prevalence as a reaction product from incineration of chlorinated wastes.

Study I. The observed POHC stabilities followed predicted trends except for benzene, carbon tetrachloride, and 1,2-dichloroethane. Benzene and carbon tetrachloride are again expected to be products of thermal degradation (primarily from chlorobenzene/toluene and methylene chloride respectively). The 1,2-dichloroethane is a volatile compound that is commonly found in scrubber water or in the ambient air as a fugitive emission, factors which could account for its elevated emissions level [10]. The emission level of 1,1,1-trichloroethane, also sometimes found as a fugitive emission or in scrubber makeup water, was also slightly elevated.

Study J. The observed deviations from the predicted rankings were similar to those observed for the previous nine cases. Benzene, toluene, and carbon tetrachloride emissions were higher than expected, an observation which is attributed primarily to product formation.

DISCUSSION

The degree of success, as indicated by the results reported in Table 1 and the subsequent discussions of predicting the relative thermal stabilities of hazardous organics through laboratory flow reactor studies may appear somewhat surprising considering the complexity of the incineration process. However, when one breaks down the overall process into more fundamental phenomena, the degree of success of the predictions is understandable.

In determining the destruction efficiency of hazardous organic materials by incineration, chemical reactions occurring in condensed phases may effectively be neglected. This is true due to mass and heat transfer considerations. Thus, we may primarily concern ourselves with gas-phase chemistry although the nature of the passage of material from condensed phase into the gas-phase by physical processes may be important.

Once in the gas phase, there exist more than one mode of destruction of the material and it is necessary to address the factors affecting these destruction modes. Two modes are clearly evident and they may be designated as direct flame and thermal (non-flame).

Either flame mode or thermal destruction studies indicate that any known organic waste can be destroyed in an

incinerator to greater than 99.99% DE if it is operating under theoretically optimum conditions [4,8,20]. Thermal destruction can be expected at less than 1000C in flowing air at a mean residence time of 2.0 seconds. Flame destruction of waste droplets may occur in flames operating in excess of 850C. The fact that these theoretical optimum conditions roughly correspond to the mean conditions experienced in an incinerator has caused much confusion. The observation of organic emissions from incinerators (sometimes in large quantities) is proof that frequent excursions from the optimum or even the mean conditions are occurring.

Excursions, or fault modes, are probably the controlling phenomena for incineration efficiency. Four parameters; atomization in efficiency, mixing in efficiency, thermal failure, and quenching, have been identified as failure modes in flames [4]. Laboratory studies have shown that relatively small excursions from ideality for these parameters can easily drop measured flame destruction efficiencies from greater than 99.99% to 99% or even less than 90% (three orders of magnitude).

Non-flame upset parameters can be conveniently classified in terms of distributions of oxygen, residence time, and temperature [8,9].

The key to understanding the significance of upset conditions is that only a very small fraction of the total volume of the waste needs to experience these less than optimum conditions to result in significant deviations from the targeted destruction efficiencies.

POHC Destruction Model

To illustrate how laboratory thermal decomposition testing relates to upset modes and can be used to predict observed emissions from full scale facilities, let us examine a specific example.

Previous research has shown that the destruction kinetics of typical hazardous organic compounds can be described satisfactorily using simple pseudo-first order kinetics [9]. Although different or more complex models may be used, the actual model used is not important for the scope of this discussion.

We will first examine the case of a simple one stage combustor where a waste feed mixture is fed directly into a turbulent flame and the hot gases evolving from the flame pass on through a relatively long, high temperature holdup zone prior to exiting the system.

Representative reaction conditions for the flame can be chosen as an average residence time of 0.1s and a bulk flame temperature of 1700K. For the post-flame zone, we may choose a mean residence time of 2.0 s and a bulk gas phase temperature of 1100K. Although a range of residence times and temperatures are actually experienced by the individual molecules, the values chosen are typical effective residence times and temperatures.

As discussed in the previous sections, several destruction failure modes have been identified for the flame. In this model, we will assume that only 1% of the waste feed avoids experiencing the bulk reaction conditions in the flame. This might be caused by a reduced gas phase residence time from an improperly operating nozzle or from experiencing a reduced temperature as a result of being sealed in particulate matter. A third cause might be reduced time at temperature from quenching by cold gases or poor mixing with oxygen.

This one percent of the waste feed must then enters the post-flame zone. The overall measured destruction efficiency at the stack is the weighted average of the destruction efficiencies of the flame and post-flame zones. The results of these calculations for hazardous waste of a range of thermal stabilities are shown in Table 2. From examination of the table, it is apparent that each of the compounds are destroyed to essentially the same efficiency in the flame, i.e., greater than 99.99%. In the post-flame region, significant differences in thermal stability are observed.

From examination of the last column of the table, it is apparent that the overall destruction efficiency parallels the destruction efficiency in the post-flame region. The principle value of the overall DE is 99% in all cases, with the variations in DE occurring to the right of the decimal. The destruction achieved in the flame determines the principle value, while the non-flame destruction efficiency determines the approach to four nines.

TABLE 2

CALCULATED DESTRUCTION EFFICIENCIES FOR REPRESENTATIVE HAZARDOUS ORGANICS

COMPOUND	A (S^{-1})	E_a (kcal/mole)	CALCULATED DESTRUCTION EFFICIENCIES DE (Flame)	DE (Post-Flame)	DE (Overall)
Acetonitrile	4.7×10^{7}	40	99.999+	66.357	99.664
Benzene	2.8×10^{8}	38	99.999+	99.999+	99.999+
Chloroform	2.9×10^{12}	49	99.999+	99.999+	99.999+
Tetrachlorobenzene	1.9×10^{6}	30	99.999+	98.566	99.986
Tetrachloroethylene	2.6×10^{6}	33	99.999+	77.127	99.771
Trichlorobenzene	2.2×10^{8}	38	99.999+	99.968	99.999+

The overall destruction efficiencies quoted in the table are typical of preliminary results reported for studies on full-scale incinerators. The measured destruction efficiencies for essentially all full scale systems have exceeded or approached 99.99% for most compounds. Variations have been in the third, second, or in some cases, the first decimal place.

A further observation has been that most incinerators can achieve a DE of 99.99% for essentially all waste feeds when operating optimally. However, optimum operation cannot be attained on a continuous basis. If an incinerator could be sampled on a continuous basis, one would probably find that at least 90% of the hazardous organic emissions occur in the fraction of time when the incinerator experiences an upset. Such upsets could be loss of flame, an overload of waste feed, or a failure of a spray nozzle. It is during these system upsets that a large percentage of the feed material can escape flame mode destruction and the reaction conditions in the post-flame zones can be degraded from their steady state operating values. Under upset conditions, the differences in waste incinerability may be magnified, the non-flame zone destruction comes to even greater prominence, and the performance of the incinerator fails to achieve four nines for greater number of components of the waste feed.

As indicated in Table 1, laboratory results obtained under high oxygen conditions were not successful in predicting relative POHC stabilities while predictions under low oxygen were very successful. The reason for this relates again to the concept of failure modes.

Poor mixing of waste and oxygen in the afterburner gives rise to a certain fraction of the waste being subjected only to low oxygen conditions. Numerous laboratory studies have shown that destruction of the feed material is much slower under these conditions and product formation is enhanced. We again have the case where although most of the waste experiences oxidizing conditions and is destroyed, the small fraction of the feed experiencing the pyrolytic conditions may be responsible for the emission. The observation in field and lab studies that most reaction products are pyrolysis type products (e.g., benzene, toluene, naphthalene) tends to confirm this hypothesis.

Although the conclusion that a subfraction of a fraction of the waste feed is responsible for most hazardous organic emissions may be surprising at first, the same process is generally responsible for emission of most air pollutants. One is not really concerned with the major chemistry (for example, in a power plant) which forms carbon dioxide and water, but instead the minor reaction pathways which

form sulfur dioxide, sulfuric acid, and nitrogen oxides. These pathways are responsible for less than 0.1-1% of the stack emissions but are the reactions of interest in pollutant formation.

Impact of Thermal Reaction Products

Products of incomplete combustion (PICs) resulting from the incineration of hazardous waste are not currently regulated by the US-EPA. However, the previously discussed field data and results of other laboratory, pilot, and full-scale testing programs have shown that toxic products can be formed and are emitted from incinerators [9,10,12-21].

The previously presented incinerability hierarchies do not directly address the issue of PIC emissions as they are only concerned with thermal stability of the POHCs in the feed material. Many observed PICs are also potential POHCs, consequently, it is entirely possible that a PIC may also be a POHC in the original mixture. Three documented examples are: the formation of carbon tetrachloride from chloroform, hexachlorobenzene from pentachloronitrobenzene, and benzene from chlorobenzene or toluene [9,12,19].

In the previous discussion of field results many such cases were identified. This gives rise to a low apparent DRE for the POHC. Since this effect would be more important when the input concentration of the POHC is low, the result would be an apparent dependence of DRE on input POHC concentration (i.e., the higher the input concentration, the greater the apparent DRE). The true effect, however, is that the emission concentration is constant, since the emissions are probably due to product formation from other waste components.

The observation of an apparent DRE dependence on concentration has been made for hazardous waste incinerators and attributed to greater than first order kinetics for individual POHCs [10]. While such an effect could be possible for combustion of a pure compound, it is highly improbable when the POHC is only a small portion of a complex waste. The reaction chemistry is determined by the overall waste and fuel composition as opposed to pure compound kinetics.

Volatile POHCs in the ambient air as a result of fugitive emissions, volatile POHCs stripped from scrubber waters, and outgassing of phthalate containing materials would also give rise to apparent concentration dependencies since their emissions levels would be constant while the POHC input rate varies. Specifically, it has been shown in the results section that most of the observed deviations from laboratory predicted rankings of incinerability may be attributed to product formation or "contamination" of the stack effluent by volatile POHCs that did not pass through the destruction zones of the incinerator.

As if predicting POHC stability were not difficult enough, we must now predict product formation. This is best accomplished by laboratory thermal decomposition testing of the actual waste stream to be incinerated, or a very close simulation. As indicated by the agreement of lab predictions based on low O_2 conditions, these studies should be conducted under pyrolytic conditions.

An excellent example of this approach is study C. The incinerability ranking based purely on POHC DRE was successful for four out of the five constituents of the waste, only benzene being apparently more stable than the other components. However, lab testing was performed on a very similar waste stream and under pyrolytic conditions, significant levels of benzene were observed. Thus, when product formation is included, lab testing of a simulated waste stream would correctly predict the observed field results.

SUMMARY AND CONCLUSIONS

The results of comparison of ten field studies with thermal stability predictions indicates that no ranking based on pure compound properties can provide an appropriate scale of incinerability. However, a ranking based on predicted POHC stability in complex mixtures under low oxygen conditions gave a statistically significant correlation with field results in seven of ten cases. More importantly, analysis of results gives strong reason to believe that formation of POHCs in the incineration process, may be responsible for their observed DREs.

Pending further confirmatory comparisons with field results, the following conclusions are proposed.

- Measured POHC DREs and relative stabilities of all but the most stable compounds are due to formation as products from other components of the waste or fuel feed.
- Only DREs for very stable POHCs or POHCs difficult to form as reaction products (e.g., acetonitrile) are expected to be unaffected by PIC formation and these stabilities are predictable from pure compound thermal decomposition kinetics.
- The stack emissions and observed DREs of very volatile compounds (e.g., methylene chloride, chloroform, di-and trichloroethanes) may be dominated by fugitive emissions in the ambient air or stripping of these compounds from contaminated scrubber water.
- Thermal destruction, not in-flame destruction determines relative POHC DREs and the identity and yield of products of incomplete combustion.
- Pyrolytic conditions in the incinerator are responsible for most emissons and control the relative DREs of POHCs and the formation of products.
- Predictions of laboratory thermal decomposition testing of pure compounds and mixtures can be effectively used to predict relative POHC DREs.
- Laboratory testing under pyrolytic conditions on actual waste streams or closely simulated waste streams is the most effective and reliable method for predictng relative POHC stabilities and PIC emissions.

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AN OVERVIEW OF LABORATORY- AND BENCH-SCALE RESEARCH IN HAZARDOUS WASTE THERMAL DESTRUCTION

George L. Huffman, Chun Cheng Lee, Ph.D. U.S. Environmental Protection Agency
Cincinnati, Ohio 45268

ABSTRACT

This paper describes some of the past and current efforts in the area of small-scale research that has come about due to the passage of RCRA (the Resource Conservation and Recovery Act). The purpose of this paper is to indicate "who is doing what" in the area of hazardous waste thermal destruction research. This paper covers the following research activities in brief outline form (these activities are synopsized from Reference 9) (9):

▲ Past Research Activities Including:

- Non-flame Thermal Decomposition Research by the University of Dayton Research Institute (UDRI) [though some of this research is still continuing --- see below]
- Non-flame Thermal Decomposition Research by the Union Carbide Corporation (UCC)
- Laminar Flame Combustion of Chlorinated Hydrocarbons by the Illinois Institute of Technology (IIT)
- Flame-Mode Hazardous Waste Thermal Destruction Research by the Energy and Environmental Research Corporation (EERC)
- Thermal Destruction of Chlorophenol Residues by Environment-Canada

▲ Current Research Activities Including:

- Hazardous Waste Incineration Engineering Analysis (by EERC)
- EPA In-House Research (by the Hazardous Waste Engineering Research Laboratory, HWERL)
- Investigation of Gas-Phase Thermal Decomposition Properties of Hazardous Organic Compounds by UDRI
- The Incineration Characteristics of Selected Chlorinated Hydrocarbons by the Louisiana State University (LSU)
- Non-Flame Waste Decomposition of Hazardous Waste by the Midwest Research Institute (MRI)
- Heterogeneous Catalytic Oxidation of Model Chlorinated Hydrocarbons by the Massachusetts Institute of Technology (MIT)
- Oxidation of Model Waste Components in Supercritical Water by the Massachusetts Institute of Technology (MIT)
- Molecular Beam Mass Spectroscopic Study of Chlorinated Hydrocarbon Flames by the Illinois Institute of Technology (IIT).

PAST RESEARCH ACTIVITIES

Non-flame Thermal Decomposition Research (by UDRI)

Under a series of contracts and grants with EPA's Hazardous Waste Engineering Research Laboratory, the University of Dayton Research Institute (UDRI) has been performing laboratory-scale studies of waste thermal oxidation characteristics in a non-flame environment since 1974 (4, 15, 5, 6, 2, 7, 3).

During their studies for EPA from 1974 to 1984, UDRI developed four thermal instrumentation systems and tested numerous compounds. The four instrumentation systems are:

- Discontinuous Thermal Systems (DTS)
- Thermal Decomposition Analytical System (TDAS)
- Thermal Decomposition Unit-Gas Chromatographic (TDU-GC) System
- Packaged Thermal Reactor System (PTRS)

Compounds tested on these four systems have the following general attributes in common:

- Microgram quantities of test compounds investigated
- Non-flame environment
- Pure compounds premixed with air and some actual waste streams and mixtures tested
- Plug flow assumption.

For purposes of illustration, Figure 1 represents a typical thermal decomposition profile (here for chloroform and its associated Products of Incomplete Combustion, PICs) routinely available from the TDU-GC system.

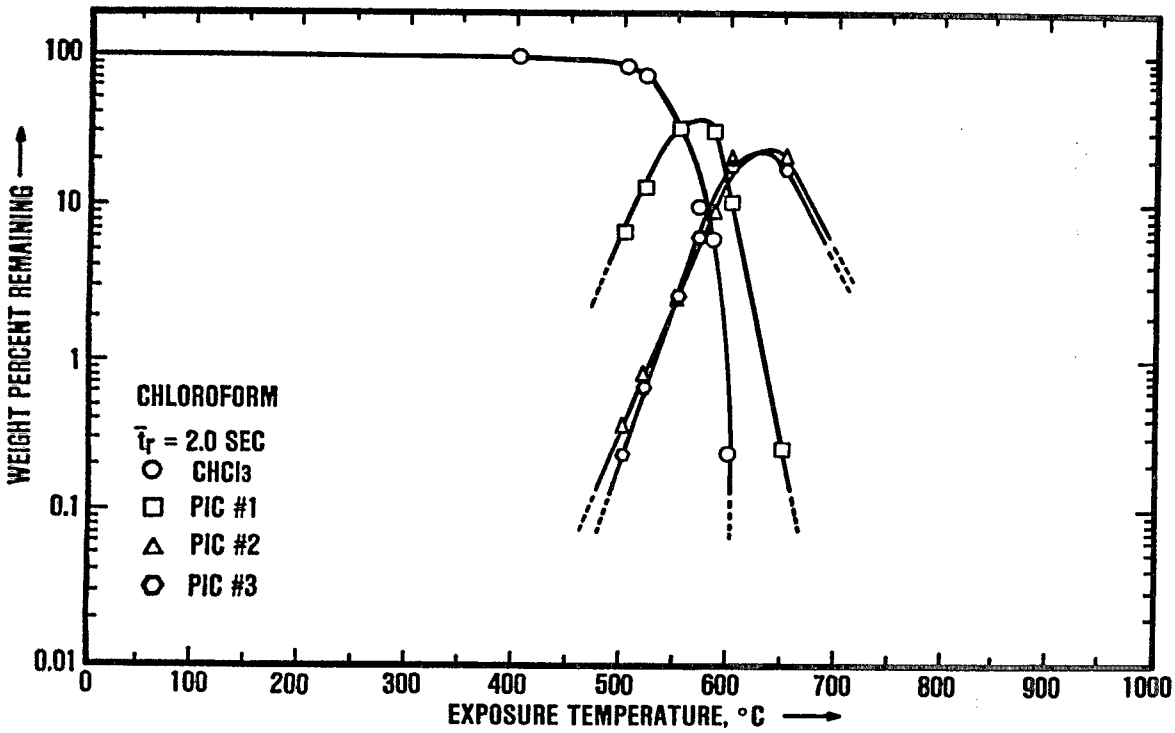


FIGURE 1. THERMAL DECOMPOSITION PROFILE OF CHLOROFORM

Non-flame Thermal Decomposition Research by Union Carbide Corporation (UCC)

This research featured a modification of the system used by the University of Dayton Research Institute (4). The major modification was the manner in which the mixtures of experimental gases (test compounds) were inserted. UCC pre-mixed the test compound with air and contained the mixtures in a cylinder, while UDRI mixed the test compound with air when air was used as carrier gas to bring the test compound into the reactor. UCC claimed that their test set-up had better mixing than that of UDRI's.

In general, the test set-up used a 0.9mm bore quartz tube. The quartz tube was twice folded at twelve-inch intervals so that 75 percent of its length of 130 centimeters could be located within the central portion of the furnace and within the limits of the flat temperature profile. The radial and longitudinal velocity and temperature gradients were minimized by the narrow bore, which allowed conditions approaching a plug flow.

As a result of the research, UCC published two papers. The first paper (10) discussed thermal oxidation kinetics of four chemicals: vinyl chloride, benzene, ethyl acrylate, and acrolein. The thermal oxidation data for all four chemicals was shown to fit a first-order kinetic rate model. The kinetic-rate model was then used to develop predictive equations for oxidation temperature and residence time requirements for a 99.9 percent destruction efficiency under different flow conditions. During the experiments, all compounds were run at 1000 ppm_v. Some of the compounds were run at 100 and 500 ppm_v and these runs gave a good agreement with the 1000 ppm_v runs. The temperatures studied ranged from 800 to 1500°F and residence times from 0.1 to 2 seconds. Analyses were done for both specific chemicals and total hydrocarbons.

The second paper (11) discussed thermal oxidation kinetic data for 15 chemicals and also presented equations for predicting thermal oxidation destruction efficiencies based on molecular structure, residence time and autoignition temperature. The two most important variables in the predictive equations were found to be autoignition temperature and residence time.

Laminar Flame Combustion of Chlorinated Hydrocarbons by MIT/IIT

Under an EPA Grant, Professor S.M. Senkan studied this subject first at the Massachusetts Institute of Technology and then at the Illinois Institute of Technology (22, 16, 18).

Flame velocities were measured by using a quartz Bunsen burner with a diameter of 1.0 centimeters. Liquid chlorinated hydrocarbons (all of which were with at least 99.9% purity) were injected into metered and heated air/methane mixtures. When the desired flow-rates were set, and a stable, laminar flame was obtained, pictures were taken using an Olympus OM I camera and high-speed black and white film. Flame-front areas were then determined from the enlarged picture of the Bunsen cone using the cone-angle method (22). Burning (flame) velocity is important because the square of it is proportional to the overall rate of combustion of the mixture.

Figure 2 shows that the flame velocities of chlorinated hydrocarbon systems decrease as the chlorine substitution of the molecule is increased.

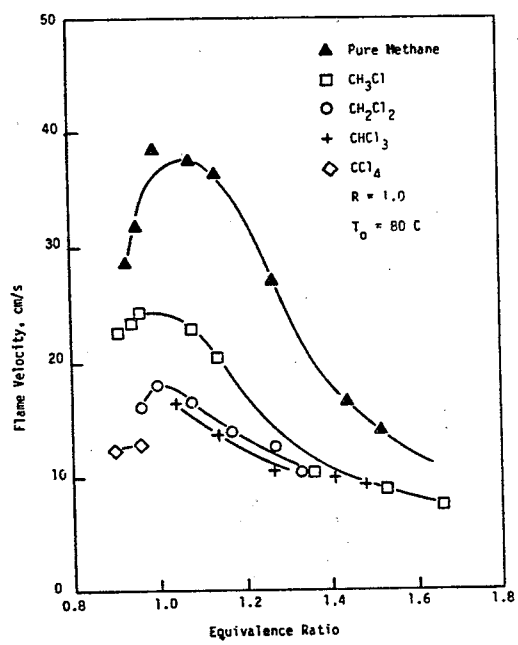


FIGURE 2. FLAME VELOCITIES OF CHLORINATED METHANE-METHANE-AIR MIXTURES

Dr. Senkan also carried out a Carbon Formation Study (17). Carbon formation limits were determined visually, and were identified as the combustible mixture equivalence ratio at which the carbon luminosity was just suppressed. Dr. Senkan found that, in actual flames, carbon formation occurs more readily than might be expected and varies from fuel to fuel.

Furthermore, Senkan's data suggested that the measurements of the CO concentration levels in the incinerator flue gases may be quite suitable as an indicator of PIC and CHC emissions. That is, if significant CO emissions are not present, the presence of the other carbon-based pollutants would be highly unlikely. Conversely, the presence of significant levels of CO in the combustion products would indicate that the conditions in the incinerator are improper and may result in CHC and other PIC emissions.

Flame-Mode Hazardous Waste Thermal Destruction Research by EERC

Under an EPA contract, the Energy and Environmental Research Corporation (EERC) conducted a laboratory-scale study of flame-mode hazardous waste thermal destruction during 1981-1982 (8).

A Microspray Reactor was employed by EERC to investigate single droplet thermal reactions without limitations associated with atomization, mixing, quenching or turbulent mixing. In this flame reactor, particles or droplets of the material to be studied were injected through a laminar, premixed, hydrocarbon flat flame and thermal decomposition of the material took place in a flame environment.

Also, a Turbulent Flame Reactor was used to provide a turbulent liquid spray flame, including swirl, recirculation, broad droplet size distribution, and high variation in droplet number density. The reactor was capable of simulating the compound escape mechanisms that could occur in flame zones of liquid injection incinerators. Very high heat removal rates were utilized to quench post-flame reactions. Thus, the destruction which occurred in the turbulent diffusion flame was exaggerated over any non-flame decomposition which could occur in the post-flame region.

Some of the more important conclusions of this study were:

(1) Under optimum conditions, flames are capable of destroying hazardous waste compounds with very high efficiencies (greater than 99.995 percent) without the need for long residence time, high-temperature post-flame zones or after-burners;

(2) Reduced flame destruction efficiencies are the result of operation under some failure mode such as poor atomization, poor mixing, or flame quenching; and

(3) Optimum conditions for destruction of hazardous waste compounds in turbulent diffusion spray flames correspond to minimal concentrations of CO and total hydrocarbons in the exhaust.

Thermal Destruction of Chlorophenol Residues (by Environment-Canada)

Environment-Canada conducted this research (20) to study the thermal decomposition phenomena of chlorophenol which the Canadian wood industry is using for wood protection/preservation. The experimental reactor used was similar to what was used earlier by UDRI and the Union Carbide Corporation. The compounds were evaluated in order of increasing complexity of thermal destruction, beginning with pure compounds and then continuing with wood preserving mixtures and contaminated sludges. During the work with pure compounds, the thermal destruction characteristics including destruction efficiency and PICs were determined as a function of temperature and retention time. Testing was done in a non-flame mode oxidative environment in two steps: the compound was gradually vaporized and then passed through a high temperature zone with an excess of oxygen in order to avoid the possibility of pyrolytic reactions.

Pure compounds of pentachlorophenol (PCP), 2,3,4,5 tetrachlorophenol, 2,4,6 trichlorophenol and 2,4,5 trichlorophenol (TCP) were tested and the decomposition thermograms of PCP and 2,4,5 TCP are given in Figure 3. Based on the pure chlorophenol destruction data, Environment Canada estimated that at 900°C a gas residence time not exceeding 2.9 seconds is needed to ensure complete (>99.99 percent) destruction of both tetrachlorophenol and PCP whereas extrapolated data for 2,4,5 TCP show a residence time in excess of 5 seconds would be required.

CURRENT RESEARCH ACTIVITIES

Hazardous Waste Incineration (HWI) Engineering Analysis (by EERC)

Under contract to EPA, the Energy and Environmental Research Corporation (EERC) is carrying out a "paper study" to: (1) Predict the impact of changes in waste compositions and operating conditions on incinerator performance parameters such as destruction efficiency and PIC formation; (2) Extrapolate performance data from trial burns or field tests to predict the performance of similarly designed units; (3) Extrapolate performance data from smaller scale to larger scale thermal destruction devices; and (4) Analyze the susceptibility of a design to different failure modes and to predict their impact on incinerator performance.

The research approach is to integrate both theoretical analysis and experimental results into predictive models so that the performance of incinerators can be estimated. The approach for the theoretical analysis part is to use existing models (kinetic, fluid dynamics, heat transfer, etc.) to develop predictive equations that govern incinerator performance. These models/equations will also be useful in generating hypotheses for performing future experimental work. The experimental part is to monitor the conduct of laboratory-, pilot- and full-scale testing to verify the applicability of the predictive hypotheses assumed. Results of all of EPA experimental projects will be analyzed for achieving this project goal.

EPA In-House Thermal Destruction Research (by HWERL)

To supplement its extramural research, EPA has constructed both bench- and pilot-scale combustors at the Center Hill Facility of EPA's Hazardous Waste Engineering Research Laboratory in Cincinnati, Ohio (HWERL). The primary focus of this in-house research is to: (1) Establish how combustion parameters and variables affect failure of a simulated hazardous waste incinerator or an industrial boiler that co-fires hazardous waste with conventional fuel to achieve 99.99% DRE (Destruction and Removal Efficiency); and (2) Determine how, when and why PICs are formed (e.g., too low an oxygen concentration or too low an operating temperature) and to determine how or whether they can be subsequently destroyed or removed (e.g., by secondary combustion or scrubbing/adsorption techniques).

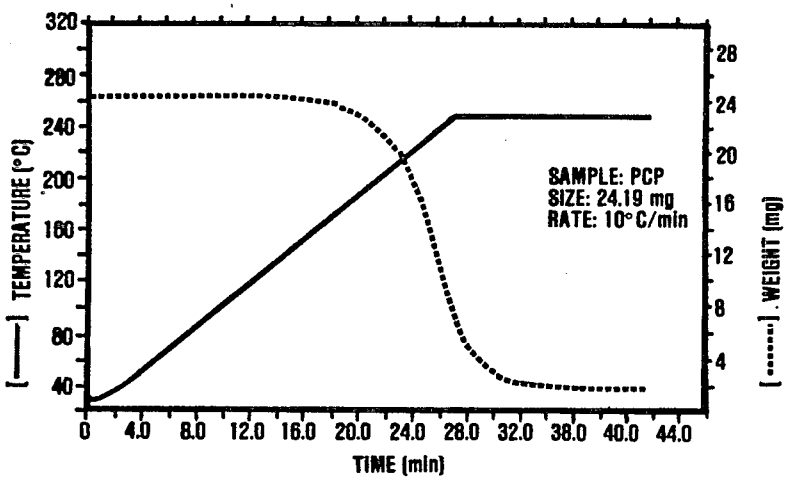
Four experimental systems will be utilized; they are:

- Thermal Destruction Unit-Gas Chromatographic (TDU-GC) System --- A non-flame unit akin to what UDRI used previously.
- Microspray Reactor --- A flame-mode reactor similar to what EERC used in their previous study.
- Turbulent Flame Reactor --- A flame-mode reactor similar to what EERC used in their previous study.
- Controlled Temperature Tower (CTT) --- A pilot-scale (150,000 Btu/hr), flame-mode, refractory-lined unit.

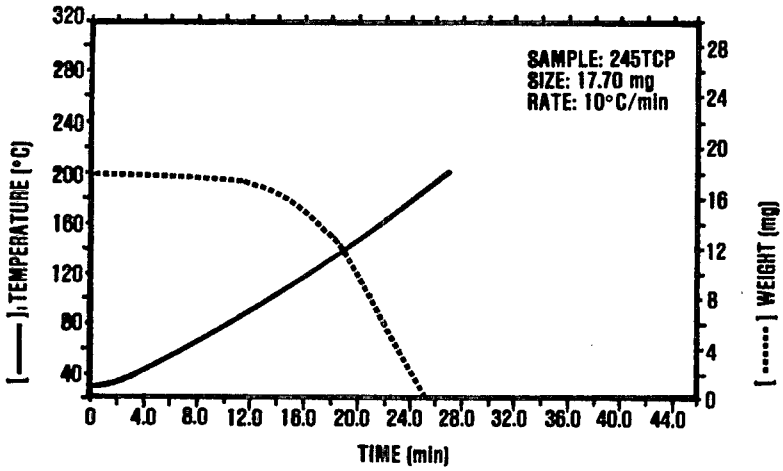
All four experimental systems described above and a scrubber system have been installed and all but the Microspray Reactor have undergone shakedown testing.

Investigation of Gas-Phase Thermal Decomposition Properties of Hazardous Organic Compounds (by UDRI)

Under EPA's support, the University of Dayton Research Institute (UDRI) is continuing their investigation of non-flame thermal decomposition



PCP DECOMPOSITION THERMOGRAM



2,4,5 TCP DECOMPOSITION THERMOGRAM

FIGURE 3 . PCP DECOMPOSITION THERMOGRAM AND 2,4,5 TCP DECOMPOSITION THERMOGRAM

phenomena. Their previous studies are described herein under Past Research Activities. UDRI's current research objectives are to study the: (1) Kinetics of Radical Attack; (2) Factors Affecting High Temperature Gas-Phase Thermal Decomposition; and (3) Measurement of the Thermal Stability of Principal Organic Hazardous Constituents (POHCs) and the Formation of Products of Incomplete Combustion (PICs).

The Incineration Characteristics of Selected Chlorinated Hydrocarbons (by LSU)

As an EPA Center of Excellence, the Louisiana State University (LSU) at Baton Rouge has been conducting fundamental studies relative to the incineration characteristics of selected chlorinated hydrocarbons (CHC) since 1982 (14, 19).

A stainless steel shock tube was employed to study the ignition delay time for measuring the incinerability of CHC. The ignition delay time was defined as the time interval from the arrival of the shock at the end of the tube until the sudden rise in pressure due to the onset of the principal reaction exothermicity.

In the operation of a shock tube, a one-dimensional shock wave is caused to propagate within a tube filled with a potentially reactive gas sample. This shock wave compresses the gas sample, thereby, heating the sample to a temperature high enough to initiate reactions.

Compounds/mixtures tested in the shock tube were: (1) methane and its chlorinated derivatives; (2) ethane, 1,1,1-trichloroethane, and 1,2-dichloroethane; (3) ethane and trichloroethane, and (4) benzene and monochlorobenzene.

Current efforts are focussed on the spectroscopic study of the apparent inhibition of the carbon monoxide conversion to carbon dioxide during the oxidation of CHCs. Future research direction will include the use of a single pulse shock tube to study the product distributions from the pyrolysis, oxidation and reduction of selected CHCs.

In a companion study at LSU, a "laminar-flow flat-flame" burner is also being tested. It is similar to the EERC and HWERL units described earlier. The burner has a 6.0 cm diameter, sintered, porous stainless steel plug with heating/cooling coils embedded in it. The flames are shrouded from possible entrainment effect by passing a concentric nitrogen (N_2) shield gas around the flame holder through a bronze porous plug of 6.6 cm diameter. A 75 micro mesh screen is placed 6.2 cm above the burner to improve flame stability. The burner assembly which is housed within a 15.2 cm Pyrex tube is supported by a 28.6 cm diameter Teflon® rod.

Compounds tested on this unit were CH_3Cl, CH_2Cl_2 and CCl_4. Both CH_2Cl_2 and CCl_4 are liquid at standard conditions. Major results, so far, are the findings of stable, hazardous intermediate compounds such as vinyl chloride (C_2H_3Cl) and dichloroethene ($C_2H_2Cl_2$) during the flame-mode decomposition of CH_3Cl, CH_2Cl_2 and CCl_4.

Non-Flame Waste Decomposition of Hazardous Waste (by MRI)

The Midwest Research Institute (MRI) has built a laboratory-scale unit to test gram quantities of hazardous waste in liquid, semi-liquid, or solid forms. The MRI system consists of a volatilizing/pyrolysis heater containing the liquid or solid sample, and a second-stage incineration heater. In this system, a sample of the waste material is inserted into a sample "boat" (in a hood) and pushed into the sample heater. Alternately, liquid can be continuously fed into the sample heater. The sample in that heater is volatilized or pyrolyzed, with the gaseous products being transported by a heated carrier gas (e.g., N_2). This gas then combines with heated flue gas, containing excess oxygen, after which it enters an incineration section (heater). Gas exiting the incineration heater passes through a sampling train for full-flow collection of samples for analysis.

Hexachlorobenzene (HCB) tests have been conducted because HCB is a solid and also a surrogate for PCBs. A liquid waste (containing trichloroethane, tetrachloroethane, bromochloromethane, pentachloroethane, hexachloro-

ethane and dichlorobenzene) is being used because MRI feels that its constituents may be difficult to incinerate since they have low heats of combustion.

Heterogeneous Catalytic Oxidation of Model Chlorinated Hydrocarbons (by MIT)

Under an EPA Grant, Professor Michael P. Manning of the Massachusetts Institute of Technology is currently conducting research to investigate the catalytic oxidation of selected chlorinated hydrocarbons.

The first catalyst tested was a commercial supported V_2O_5 sulfuric acid oxidation catalyst. Preliminary experiments were carried out at temperatures of 360 and 412°C using inlet concentrations of 5% (mol) CH_3Cl in air. CH_3Cl and air were passed over the fresh catalyst for several hours before data was taken to allow the reaction and catalyst activity to reach steady state.

Visual inspection of the used catalyst showed a pronounced color change: the yellow-brown fresh catalyst had turned blue-green after exposure to CH_3Cl.

Preliminary study results included: (1) A commercially available, promoted V_2O_5 oxidation catalyst has been found to be inactive for the oxidation of methyl chloride below 420°C [this inactivity is most probably due to the temperature involved rather than halogen poisoning (12)]; and (2) Chromia-based catalysts, Cr_2O_3 supported on Al_2O_3, have been found to be effective for the oxidation of several chlorocarbons such as di, tri, and perchloroethylene (13).

Oxidation of Model Waste Components In Supercritical Water (by MIT)

Supported by NASA, Professor Jefferson W. Tester of the Massachusetts Institute of Technology is conducting research relative to the reaction rates and mechanisms of waste destruction in the supercritical water environment.

The overall goal of this research program is to understand the oxidation kinetics of model waste components in supercritical water. Reaction mechanisms in supercritical water are different from those in either low-pressure flame oxidation (combustion) or wet oxidation. Rate expressions from these other processes cannot be extrapolated a priori to conditions in supercritical water, because the supercritical water environment is much different than combustion or wet oxidation environments.

Oxidation in supercritical water is a new process for wastewater treatment, capable of almost complete conversion of toxic organics to carbon dioxide and water. Supercritical water, which is water above both its critical temperature of 374°C and critical pressure of 27.6 MPa (3200 psia), has much different physical properties than room temperature and pressure water and is an excellent media for oxidative reactions for several reasons. The high temperature of supercritical water promotes rapid reaction rates. Supercritical water also forms a miscible solution with air or oxygen, which eliminates the interphase mass-transport limitations that exist in a two-phase oxidation process (21). The high solubility of organics in supercritical water promotes complete oxidation by preventing char formation from oxidation or decomposition by-products (1).

Currently, this research is investigating the oxidation of carbon monoxide and ammonia in supercritical water, as these steps may be the last and rate-limiting steps in the conversion of organic carbon to carbon dioxide and of organic nitrogen to molecular nitrogen. The reactor utilized is operated isothermally in plug flow, both of which are important to simplify the rate expression calculation. The reactor is constructed of Inconel 625, which can withstand the high temperatures and pressures of the experiments. The reactor can be operated over a wide range of conditions, between 400 and 600°C and between 24 and 34 MPa (3500-5000 psia).

By the end of the current phase of the project, the experimental investigation of the oxidation of ammonia and carbon monoxide in supercritical water will be completed. Consequently, the orders of reaction for carbon monoxide,

ammonia and oxygen, along with the activation energy and preexponential constant will then be able to be determined.

Molecular Beam Mass Spectroscopic Study of Chlorinated Hydrocarbon Flames (by IIT)

Under an EPA grant, Professor S. Senkan of the Illinois Institute of Technology is continuing his studies on the laminar flames of chlorinated hydrocarbons CHC). Present research is aimed at developing a more detailed understanding of the chemistry of such flames, more comprehensive models describing the CHC oxidation process, and at assessing the formation and emission of pollutants from practical combustion incineration systems.

Experiments are being carried out in a laminar flat flame burner similar in design to the systems described earlier. The flames are probed for the determination of species profiles using molecular beam sampling coupled with on-line mass spectroscopy (MBMS). The MBMS is a highly versatile method for studying reactive gaseous mixtures, because of its ability to furnish information on the presence of all stable and radical species in flames.

In parallel with the experiments, detailed chemical kinetic modeling of the flames is also being pursued.

RECOMMENDATIONS

- Information on PICs (Products of Incomplete Combustion) is very limited. Because PICs could be more hazardous than compounds in the original waste, studying PIC formation and control should be one of the most important and focal research areas for EPA.

- Much of limited amount of data shown in this paper were obtained from non-flame and microgram-quantity testing environments. The credibility of these data for actual thermal destruction under flame conditions remains to be demonstrated. Therefore, research is needed to determine the applicability of non-flame, and microgram-testing, results to the full-scale realities of actual incinerators and other types of combustors.

- Although there is a significant amount of experimental data now available in the literature, no calculational methods have been developed to predict what DRE or PICs would result if incinerator conditions change. Research is needed to fill that void.

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A LABORATORY STUDY ON THE EFFECT OF ATOMIZATION ON DESTRUCTION AND REMOVAL EFFICIENCY FOR LIQUID HAZARDOUS WASTES

John C. Kramlich
Elizabeth M. Poncelet
Wm. Randall Seeker
Gary S. Samuelsen

Energy and Environmental Research Corporation
18 Mason
Irvine, California 92718-2798

ABSTRACT

The results of a laboratory-scale experimental program on the effects of spray atomization quality on waste destruction efficiency in incineration processes are presented. The hypothesis considered is that spray atomization quality can, under some circumstances, be the dominant cause of a unit's failure to achieve high efficiency destruction. The waste destruction efficiency measurements were performed in a laboratory scale turbulent spray flame reactor. The measurements were obtained under correct atomizer operation and under degraded operation. These measurements were compared with direct measurements of droplet size distribution from the nozzles by laser diffraction. The results indicated that the penetration of oversized droplets through the flame zone or to the wall was the principal cause of reduction in waste destruction efficiency. In addition, the potential of a phenomena known as "secondary atomization" as a means of improving efficiency was examined. (Secondary atomization is a phenomena in which a volatile component is introduced into the fuel; during heating the volatile component vaporizes and fractures the droplet, thereby improving atomization quality. The occurrence of secondary atomization due to the inclusion of volatile wastes in No. 2 fuel oil was demonstrated and was shown to markedly improve efficiency.

INTRODUCTION

Incineration is an attractive alternative native for the disposal of organic hazardous wastes. As opposed to landfilling or deep well injection, it effects a permanent solution. However, incineration is attractive only if the waste is destroyed to an acceptable efficiency and if harmful emissions of hazardous byproducts are avoided. The Federal government has recognized that the public welfare requires government regulation of waste disposal through the Resources Conservation and Recovery Act (RCRA)(10). Through RCRA Congress has

charged the Environmental Protection Agency (EPA) with the development of regulations and the enforcement of these regulations. The EPA has identified over 300 compounds as hazardous (2,3) and has established licensing and operating regulations for devices destroying these compounds (4). These regulations recognize the fact that thermal destruction devices cannot operate to 100 percent efficiency. Therefore, some emission level must be defined as a minimum standard for safety. Presently, 99.99 percent destruction and removal efficiency (DRE) of the principal organic hazardous constituents (POHCs) is the standard.

Field testing of full-scale waste destruction facilities (11) and testing of subscale flames (8) has shown that well designed systems have little trouble meeting the performance standard. Indeed, the evidence suggests that a substantial perturbation of design or operational parameters are necessary for substantial emissions to occur (8). These perturbations have been termed "failure modes" because the perturbation has caused some fundamental rate limiting step to fail to completely destroy the waste (7). Thus, the key questions with respect to DRE are:

1. What are the mechanisms that permit the small amount of waste to escape during high efficiency operation?

2. What different mechanisms are responsible for waste release during a failure mode?

In this paper we address failure modes associated with the atomization of liquid fuel or waste.

Considerable work has been directed toward characterizing the effect of atomization quality on the combustion efficiency of liquid fuels. Edwards (1) describes two ways in which atomization influences efficiency. First, the spray must be sufficiently fine to allow complete evaporation within the flame. Secondly, the spray must be injected into the correct portion of the flow field to ensure stability. Organic hazardous waste can be viewed as simply another fuel constituent. A high DRE of the hazardous component can be viewed as its high "combustion" efficiency. Thus, the same atomization factors that influence fuel consumption efficiency would also be expected to influence waste DRE.

In practical units, atomization failure modes can be associated with worn or plugged nozzles. Previous results from our laboratory (8) have shown that atomization characteristics representative of worn or plugged nozzles can result in DRE failure. The objective of the work reported here was to characterize the link between spray fineness and DRE, and to examine the potential of "secondary atomization" to improve DRE through in-flame reduction in droplet size.

The approach was to characterize the droplet size distribution produced by a series of sub-scale nozzles. This was done under cold-flow conditions by laser diffraction. This droplet size data was directly compared with DRE results from a small-scale reactor (8) to evaluate the influence of droplet size on DRE.

In a second portion of the study, the potential of "secondary atomization" as a means of improving DRE was investigated. Secondary atomization is the term used to describe the in-flame fragmentation of droplets with broad boiler point distributions (9). The fuel is blended with a volatile compound; upon introduction into the flame the volatile constituent is evaporated from the surface of the droplet. The surface temperature approaches the boiling point of the less volatile component.

Heat from the surface conducts to the droplet interior, which can cause homogeneous vaporization of the volatile constituent. This internal vapor generation causes the droplet to expand into a bubble, which eventually ruptures. This fragments the droplet and effectively reduces the mean droplet diameter. Secondary atomization has been explored as a means of improving spray fineness for liquids with poor primary atomization qualities (e.g., highly viscous fluids and slurries).

The hypothesis investigated here is that the volatile wastes present in a multicomponent waste stream can, in high concentrations, induce secondary atomization and improve overall DRE. The approach was to screen a series of wastes for secondary atomization potential and compare the DRE in the small-scale reactor for conditions where secondary atomization

was present against conditions for which it did not occur. These tests were performed under a previously characterized atomization failure mode.

EXPERIMENTAL SYSTEMS

Three experimental rigs were used during this study. The slip-flow reactor was used to screen mixtures of No. 2 fuel oil and waste compounds for secondary atomization intensity. A cold flow spray chamber with laser diagnostics was used to characterize atomization quality from the test nozzles. A turbulent flame reactor (TFR) was used to obtain DRE measurements.

Slip-Flow Reactor

The reactor was originally designed to study the thermal decomposition characte-istics of synthetic fuel oils; it has proven useful for the examination of physical processes accompanying the thermal decomposition and combustion of all liquid fuels. The reactor consists of a 5 x 28 cm flat-flame burner downfired into a chimney of similar dimensions. The flat flame is supported on a water-cooled sintered stainless steel plate. The chimney is fitted with four 156 x 28 cm Vycor windows for optical access. As shown in Figure 1, the fuel droplets are injected ballistically normal to the hot gas flow. The key attributes of the rig for the present study are 1) the controlled generation of droplets of known diameter by a vibrating orifice technique, 2) the exposure of these droplets to a high temperature gas stream and 3) the ease of visual access for determination of secondary atomization intensity. The final point is the principal reason the reactor configuration is used. The intensity of the secondary atomization reaction can be visually gauged through the large windows by the disruption of the droplet stream. When no secondary atomization is present the droplets move smoothly through the laminar gas stream. Even a small amount of activity can be easily distinguished against this time steady background. The intensity of the secondary atomization is subjectively graded by a scale similar to that developed at Princeton (9).

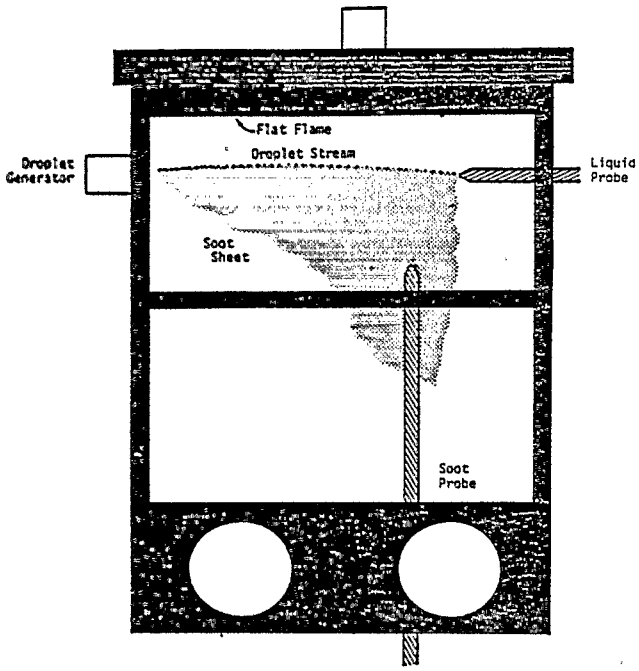

Figure 1. Slip-flow reactor.

Spray Characterization Rig

The spray characterization rig was developed to determine dropsize distributions of small scale atomizers under cold flow conditions. The rig, illustrated in Figure 2, consists of a plexiglass cylinder in which the nozzle is mounted on centerline downfired. Air is co-flowed axially around the nozzle to simulate the combustion air field and to prevent recirculation of droplets into the optical path.

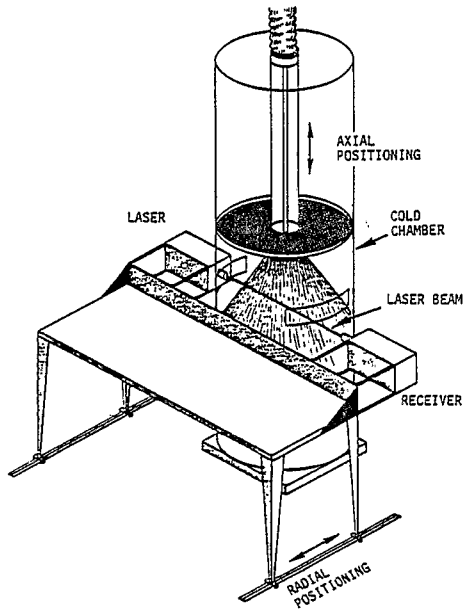

Figure 2. Spray characterization system.

Two ports at opposite sides of the chamber provide access for the Malvern 2600 HSD particle size analyzer. The Malver measures dropsize distribution by measuring the diffraction of a laser beam as it passes through the spray field. The diffraction pattern is collected by a Fourier transform lens and is focused onto a detector array. This can be either a two parameter size fit (e.g., log-normal or Rosin-Rammler) or a model independent fit capable of resolving multimodel distributions.

Turbulent Flame Reactor

The Turbulent Flame Reactor (TFR) was designed to simulate a number of aspects of the flame zone performance of liquid injection incinerators. These include swirl, recirculation, broad drop-size distribution, and high variation in droplet number density. It is particularly important that the reactor be capable of simulating the compound escape mechanisms that can occur for flame zones of liquid injection incinerators. Very high heat removal rates are utilized to quench post-flame reactions. Thus, the destruction which occurs in the turbulent diffusion flame is emphasized over non-flame decomposition which occurs in the post-flame region.

The design of the reactor is detailed elsewhere (7). The reactor is shown in Figure 3; it consists of a 30 cm diameter by 90 cm long stainless steel cylindrical enclosure with water-cooled walls. The burner consists of a pressure-atomized nozzle (Delavan WDA series) located level with the bottom plate of the reactor as shown in Figure 3. The nozzles have a 60° angle hollow coned spray pattern and are used in sizes corresponding to 1.9, 2.85, 3.8, 5.7 liters/hour (0.5, 0.75, 1.0, and 1.5 gallons/hr). The fuel, here No. 2 fuel oil, is doped with waste compounds and supplied from a pressurized tank.

The main burner air is introduced through the annular space around the nozzle. A research-type variable swirl block burner is used to introduce the burner air. The burner air is supplied from the compressed air supply and metered by a venturi meter prior to introduction into the swirl burner. Gas samples are obtained downstream of a series of mixing baffles at the reactor exit by an uncooled stainless steel probe.

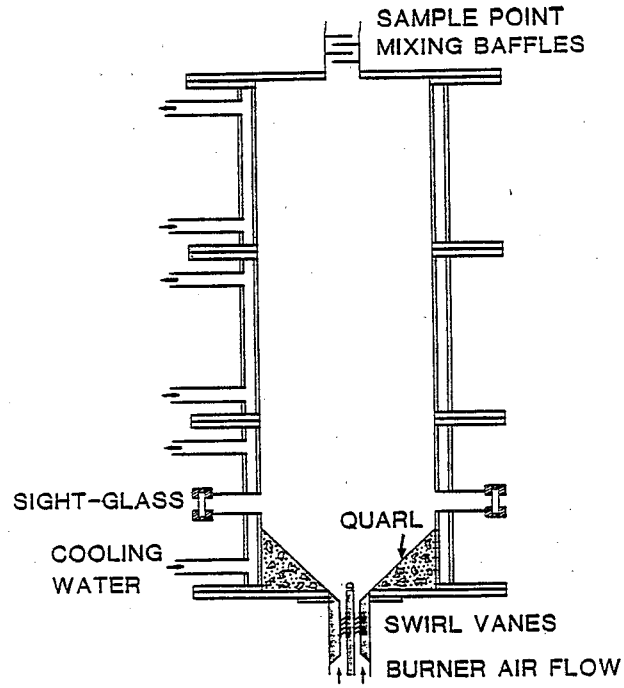

Figure 3. The turbulent flame reactor.

Volatile Organic Analysis

The DRE of the waste compounds was measured in the exhaust of the turbulent flame reactor by use of a Nutech Volatile Organic Sampling Train (VOST). This train is described in detail elsewhere (6). In brief, gas samples are drawn through chilled cartridges within which the volatile organic compounds are absorbed onto Tenax-GC. After sampling the compounds are released by thermal desorption and analyzed on a gas chromatograph equipped with a flame ionization detector (7).

RESULTS AND DISCUSSION

Atomizer Characterization and DRE Performance

The purpose of the tests reported in this section was to quantitatively characterize the droplet size distributions from the test nozzles and to compare these characterizations with DRE performance. The nozzles were operated at both the design points and under off-design conditions to obtain atomization qualities characteristic of failure modes. These results were compared with the DRE obtained using these nozzles in the TFR.

The Delavan WDA series nozzles used in this study generate a 60° hollow spray

pattern. Liquid is forced through small slots under pressure into a swirl chamber. The swirling liquid leaves the chamber through an endport and establishes the characteristic hollow-coned spray pattern. Thus, the energy needed to overcome surface tension and form droplets is supplied by the fuel pressure drop across the nozzle. The nozzles are supplied for fixed flow rates; these are set to yield the required pressure drop across the nozzle for design operation. Substitution of a larger capacity nozzle at the same flow rate will reduce fluid pressure and nozzle performance. This is illustration in Figure 4 where the area-mean diameter is plotted against fuel pressure for four nozzles. The design pressure is approximately 200 psi. As flow and pressure are reduced the mean diameter increases from 30 to over 70 microns. However, changes in mean size do not fully represent the situation. The change in the size distribution is key because evaporation time limited behavior will tend to be dominated by the largest droplets present.

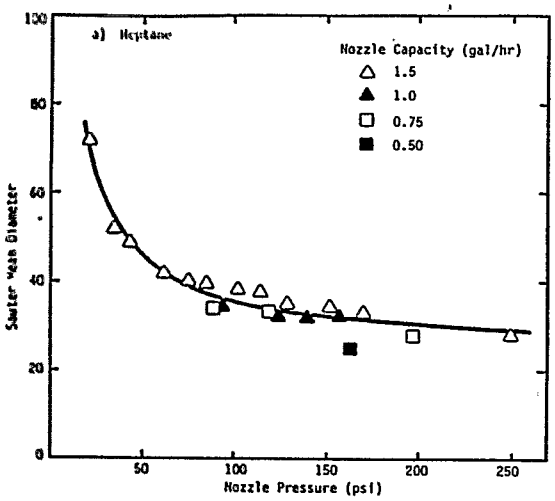

Figure 4. Droplet diameter as a function of nozzle pressure

Figure 5 illustrates the droplet size distributions obtained at 3.8 liters/hour (1.0 gallons/hour). The data set labeled "Design Operation" was for a 3.8 liter/hour capacity nozzle, and thus represents the size distribution resulting from correct operation. The "Off-Design" data set is for the identical flow rate, but an oversized (5.7 liters/hour) nozzle. As described above, use of oversized pressure atomized nozzles result in low fluid pressure, and low atomization energy. Thus, the off-design results show the dropsize

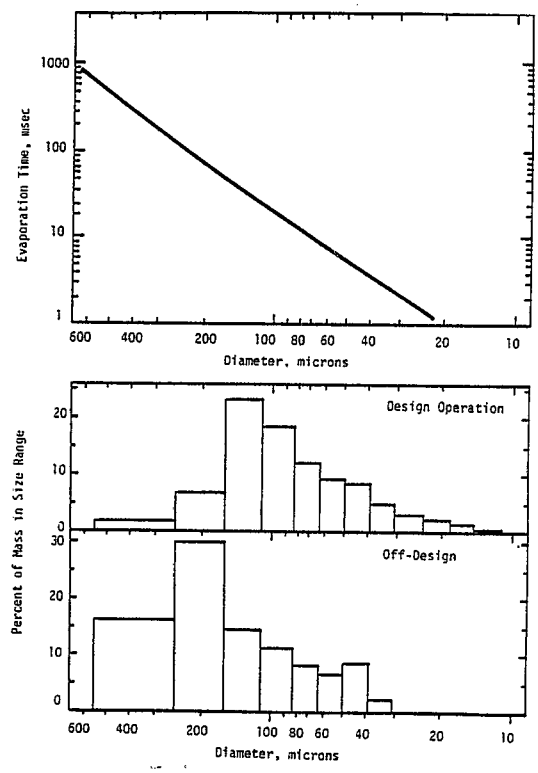

Figure 5. Droplet size distributions and estimated evaporation time as a function of diameter

is shifted toward larger values. The key to interpreting the effect of the shift in droplet size is found in the evaporation time plot of Figure 5. This plot shows evaporation time as a function of droplet diameter for No. 2 fuel oil, based on the "d^2 law" (5). The on-design data shows approximately 10 percent of the mass is above 170 microns. According to the evaporation rate plot, this 10 percent will require more than 50 msec to evaporate. The off design data indicate that fully 46 percent of the mass is greater than 170 microns. Also note that the largest size class (250-560 microns) has increased from 2 to 16 percent of the total mass. Since the evaporation times for this category range from 100-700 msec, it is evident that the effect of moving from on-to-off design operation is a substantial increase in the evaporation time of a significant fraction of the fuel.

The on-design and off-design atomizer conditions were used in the TFR to determine the influence of atomization quality on DRE. The No. 2 fuel oil was doped to 3.0 weight percent with an equimolar mixture of test compounds. These test

compounds were selected to represent the various classes of organic hazardous wastes; they were acrylonitrile, chloroform, chlorobenzene, and benzene. These compounds were used in our previous subscale testing, and a discussion of their incineration related properties is available elsewhere (7).

The TFR was operated under both the on-design and off-design conditions as defined above, and theoretical air was the independent variable. Figure 6 shows the fraction of each of the compounds that escaped destruction for each of the nozzle conditions.

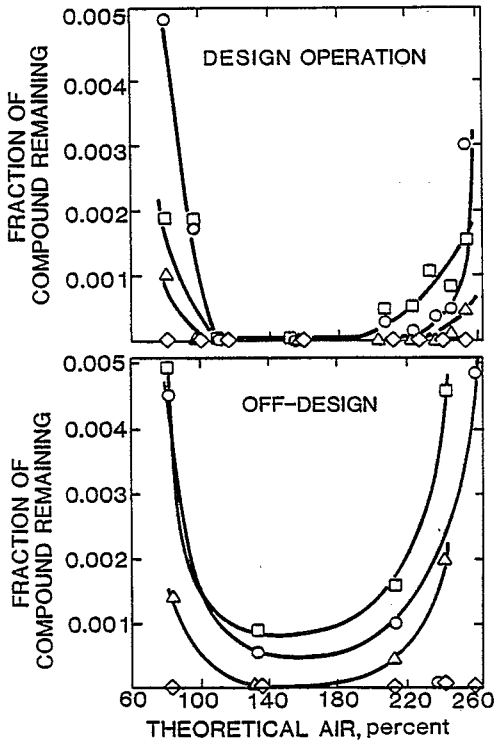

Figure 6. Waste destruction for the nozzle conditions identified in Figure 5.

The on-design nozzle results show behavior similar to those documented in our previous work (7,8):

- A range of high DRE between 100-200 percent theoretical air.
- At low theoretical air the increased waste emissions indicate a failure mode due to fuel-rich pockets breaking through the flame.
- At high theoretical air the increased waste emissions indicates a quenching failure mode in which the high air flow is quenching portions of the flame prior to complete reaction.

Comparison of the on-design and off-design plots shows that the emissions at the rich and lean failure modes are not significantly different. However, the DRE in the region between 100 and 200 percent theoretical air has degraded markedly from the previous high efficiency. Thus, the change in atomization quality that accompanied the use of the oversized nozzle induced an atomization failure mode; the DRE, which was much greater than 99.99 percent was reduced to the order of 99.9 percent.

Two general mechanisms can be identified by which poor atomization can influence DRE. In the first, droplets which are too large to evaporate in the available time penetrate to the reactor wall. The liquid evaporates and exits the reactor along the cold boundary layer at the wall. In the second mode, the droplets penetrate through the flame-zone without fully evaporating until well into the post-flame region. Here, mixing or temperature may not be sufficient to ensure complete destruction.

Estimation of the maximum droplet diameter for which the droplets avoid striking the wall involves 1) determination of fraction of the hydrodynamic energy released by the nozzle that is converted into droplet velocity, and 2) determination of the aerodynamic drag on the droplets as they simultaneously evaporate and burn. While such calculations cannot be performed to a great degree of accuracy, the estimation indicates that the threshold diameter for striking the wall is approximately 200-300 microns. This is consistent with the shift in DRE behavior associated with the spray degradation and it indicates the following methodology for evaluating the atomization adequacy of full-scale nozzles:

- Evaluate atomization quality in cold flow on either the actual waste stream or on a surrogate stream of identical properties. If possible, both dropsize and droplet velocity information should be obtained.

- Use the spray information to evaluate the adequacy of the match between the combustion chamber and the spray pattern.

The actual evaluation of a full scale setup by this methodology cannot presently be done to a great degree of accuracy. However, the approach does indicate future research directions.

Influence of Secondary Atomization on DRE

Large-scale atomizers generally fail to provide acceptable atomization quality for two reasons:

1. The liquid is unusually viscous or it contains solids (i.e., slurry).

2. Portions of the nozzle have degraded during use such that design operation cannot be obtained.

Since the liquid hazardous waste designation covers a wide variety of fluids and slurries, there is little doubt that a certain portion of these will be difficult to atomize. Also, many wastes have corrosive and abrasive properties that will accelerate nozzle wear during service. Thus, under certain conditions primary atomization quality can be expected to be a limiting factor in overall DRE.

As discussed in the first section of this paper, the secondary atomization phenomena has been investigated as a means of improving combustion efficiency through the in-flame reduction of droplet diameter via fragmentation. Reviews of the experimental data (9) and theory (12) are available in the literature. Most wastes are multicomponent mixtures of varying volatility. Since waste atomization can be a critical deficiency in the incineration process, secondary atomization can occur either naturally or be induced by addition of a volatile component as a means of improving performance.

The two questions addressed on secondary atomization in the present work were 1) whether secondary atomization can be induced by the presence of hazardous compounds in fuel oil, and 2) whether this secondary atomization has the capability of improving DRE. Five compounds were selected for doping into No. 2 fuel oil for secondary atomization screening. These were selected to represent a broad range of boiling points: dichloromethane, 39°C; acrylonitrile, 79°C; benzene, 80°C; isopropanol, 82°C; and benzal chloride, 205°C. These were also selected to represent a wide range of volatility differences with respect to No. 2 fuel oil (boiling point: 210-260°C).

Each of the compounds were screened in the slip reactor at 0.5, 2, 5, 10, 20, and 40 weight percent in the No. 2 fuel oil. The results are presented graphically in Figure 7 as a plot of secondary atomization intensity vs. concentration for each of the compounds. These results indicate that secondary atomization is active only for compound concentrations above two percent (except) for isopropanol, which was active above 0.5 percent). Also, for secondary atomization to occur there must be some difference

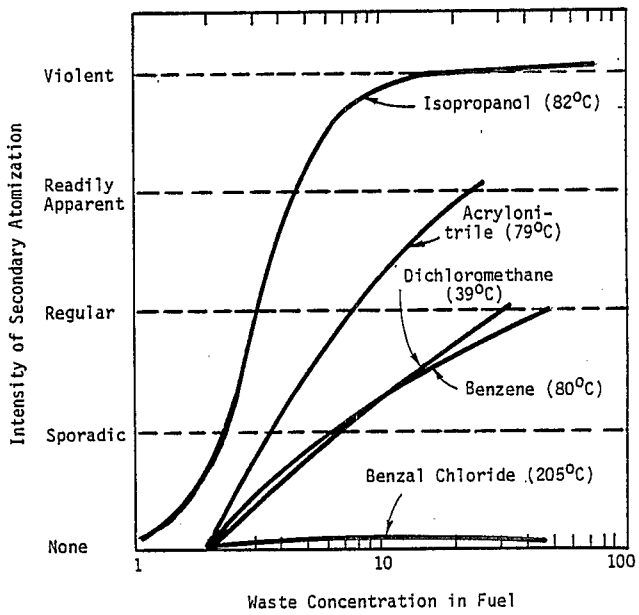

Figure 7. Effect of waste concentration on secondary atomization intensity.

between the boiling points of the base fuel and the additive. For example, benzal chloride, which has a boiling point comparable with that of No. 2 fuel oil, showed no activity at any concentration. The results indicate that intensity is not entirely a function of boiling point differential. For example, isopropanol has a boiler point of 82°C, but it induced a substantially more active reaction than dichlormethane (39°C). Thus, other factors than boiling point differential

(e.g., compound polarity) are related to intensity.

The screening tests indicated that isopropanol and benzal chloride represent the limits of secondary atomization intensity. These two compounds were selected for DRE testing in the TFR. The compounds were tested at 0.5, 2.0, and 10.0 weight percent in No. 2 fuel oil. The experiments were designed to determine the effect of compound concentration DRE for 1) a compound for which no secondary atomization occurs across the entire concentration range, and 2) a compound for which no secondary atomization occurs at low concentrations, but a strong response is obtained at high concentrations. Thus, benzal chloride yields the concentration dependence in the absence of secondary atomization. Any strong additional concentration dependence for isopropanol can be attributed to an increase in secondary atomization intensity with concentration.

The test condition corresponded to the off-design atomization condition illustrated in Figure 5. In all other respects, the TFR was set for high efficiency operation (120 percent theoretical air, 0.8 swirl number). Thus, the only variables were test compound type and concentration.

The results for DRE of the test compounds are shown in Figure 8. Waste penetration (fraction of original waste escaping the reactor) is plotted against the percent waste in the fuel for the two test compounds. Benzal chloride shows an approximately one order of magnitude decrease in penetration between 0.5 and 10 percent waste concentration. Since no secondary atomization takes place for this compound, the concentration effect on penetration must be due to other factors. For isopropanol, however, the effect of concentration is much more pronounced. Between 0.5 and 10 percent concentration DRE improves from less than 99.9 percent to greater than 99.9999 percent. Significantly, this increase in DRE occurs concurrently with an increase in secondary atomization intensity from none to violent. Thus, at least a substantial portion of the difference in behavior between benzal chloride and isopropanol can be attributed to the secondary atomization behavior of isopropanol.

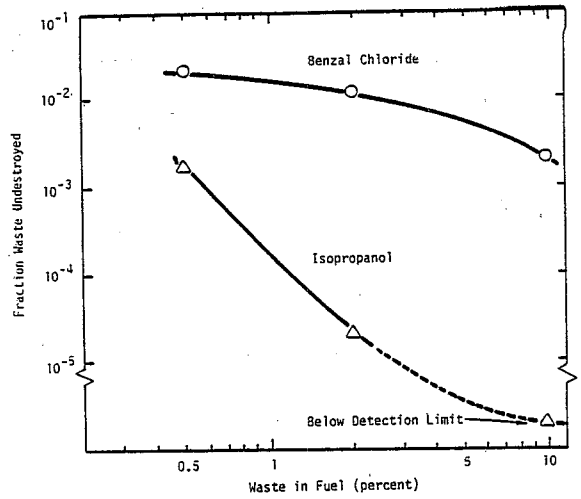

Figure 8. Comparison of compound penetration for benzal chloride and isopropanol as a function of compound concentration in the auxiliary fuel. Results are for the turbulent flame reactor operating under an atomization failure condition.

This work suggests that the DRE of liquid injection incinerators operating under atomizer limited conditions can be improved by the blending of small amounts of high volatility liquids into the waste stream. The blending agent may be a second waste stream of markedly different volatility rather than a pure organic liquid. These blending agents may be particularly appropriate for slurry atomization, whose primary atomization quality is usually limited.

CONCLUSIONS

The results of this study have shown that atomization quality and DRE are strongly correlated. The specific conclusions are:

- Degradation of atomization quality appears to influence DRE primarily through the penetration of droplets through the flame zone or to the walls.
- A potential methodology for evaluating nozzle performance in relation to a particular incinerator geometry was identified. This consisted of evaluation of the nozzle for spray angle, droplet size and droplet velocity. This information

is matched with the incinerator geometry to yield the approximate maximum tolerable droplet size to avoid wall or fireball penetration.

- Secondary atomization has been indicated to be a mechanism for improving DRE in situations in which atomizer performance limits DRE. A means of obtaining this effect and improving DRE could be the selective blending of waste streams of varying volatility.

ACKNOWLEDGEMENTS

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EVALUATION OF A PILOT SCALE CIRCULATING BED COMBUSTOR WITH A SURROGATE HAZARDOUS WASTE MIXTURE

Daniel P.Y. Chang and Nelson W. Sorbo
Department of Civil Engineering
University of California, Davis

ABSTRACT

Circulating bed combustors (CBC) appear to be an emerging technology for the destruction of hazardous wastes. A cooperative study among the CBC manufacturer, the California Air Resources Board, the California Department of Health Services and the Environmental Protection Agency was carried out on a pilot-scale CBC. A surrogate waste mixture having a heating value of about 19 MJ/kg (8000 Btu/lb) and comprised of water, xylene, ethylbenzene, toluene, hexachlorobenzene, 1,2,4 trichlorobenzene, Freon 113, and carbon tetrachloride was fed to a CBC at a heat release rate of about 530 MJ/hr (0.5 MMBtu/hr). The destruction and removal efficiency (DRE) and formation of products of incomplete combustion (PIC) were evaluated. Samples were drawn throughout an 18 hour test period for volatile and semi-volatile compounds. Combustion parameters such as oxygen, total hydrocarbons, carbon monoxide, carbon dioxide, oxides of nitrogen, CBC bed temperature and air flowrate were also measured continuously. In addition, a refractory tracer SF_6 was injected into the combustion zone and monitored on a continuous basis as well as by grab samples. Results of those tests indicate that the CBC was being operated in a near "failure mode" condition throughout much of the test. Nevertheless, high DRE was observed (>99.99%) for the majority of samples. Formation of volatile PIC chlorine compounds appeared to be correlated with carbon monoxide and total hydrocarbons.

INTRODUCTION

The California Air Resources Board (CARB) staff evaluated emissions from a circulating bed combustor (CBC) owned and operated by GA Technologies, Inc., (GA) San Diego, California. This test was the first in a series of three, funded by the Environmental Protection Agency (EPA) and the California Department of Health Services (DOHS), to evaluate the performance of different types of hazardous waste incinerators. The goals of this study were to evaluate specific combustion units, to increase the database on emissions of non-criteria pollutants, and to evaluate methods for permitting and monitoring such units in the future. The CBC was included in this study because of its potential application to on-site waste destruction by generators of small quantities of waste.

The overall objective of the GA test was to evaluate the operational characteristics of the CBC when fueled with a simulated liquid waste mixture. This included defining an envelope of operation of the CBC using typical parameters such as CO and THC in the effluent gases, and measuring the destruction and removal efficiencies (DRE) of a number of refractory compounds under various combustion conditions. A complete description of all aspects of this project is found in Reference 1.

DESCRIPTION OF CIRCULATING BED COMBUSTOR

The CBC is an outgrowth of coal combustion technology involving fluidized bed combustion. The bed solids in a CBC are continually carried out of the top of the main combustor, collected by a cyclone, and continuously returned to the bottom of the combustor, while the bed solids in a conventional fluidized-bed combustor maintain a relatively stationary position. Operation in a circulating mode offers the advantage of a greater range of turndown ratios and improved mixing and temperature uniformity over that of conventional combustors (2). The CBC is operated at substantially lower temperatures than conventional incinerators resulting in relatively low NO_x concentrations. The mean gas temperatures in a CBC are maintained below 870°C (1600°F) to prevent slagging of the bed material. Complete oxidation of the fuel is enhanced by mixing of bed solids with excess oxygen and by a substantial residence time afforded by recirculation of solids. The presence of reactive bed solids offers the potential for capture of halogen and sulfur reactants in the bed materials. GA has demonstrated SO_2 and HCl removal ranging from 88 to >99% (3).

The nominal thermal rating of the CBC tested was 2100 MJ/hr (2 MMBtu/hr). It had an inner diameter of 40 cm (15.5 in), and a height of 7.6 m (25 ft). Bed solids were stored externally and transported pneumatically to the bed as needed to maintain the quantity of material in the bed. The test was designed to determine the response of the CBC to an aqueous-organic fuel mixture. Therefore no solid fuel was used during the test except during the initial warm-up period. Natural gas was used to augment the heat release rate as needed during the test to maintain the combustion bed temperature. A forced draft fan supplied primary and secondary combustion air to the combustor. Solids carried out of the bed were collected in a cyclone and returned to the bed through a proprietary return seal. Gases exiting the combustor were cooled by a liquid water heat exchanger. Supplemental cooling and dilution air were permitted to enter between the gas cooler and the inlet to the baghouse. Gas flows were drawn into the baghouse by two induced draft fans, one of which failed during the test. The CBC was operated so that atmospheric pressure was maintained at the exit of the combustor.

GA gas sampling instruments (CO_2, CO, THC, O_2, NO_x, HCl, SO_2) were located downstream of the gas cooler and upstream of the dilution air inlet. In addition, GA continuously recorded pressure drop, average bed temperature, and total combustion air. The volumetric flowrate of the dilution air stream was estimated by chemical mass balances of N_2, CO_2, and O_2 concentrations. The dilution air flowrate was found to be about 10% of the combustion air flowrate and thus this value was assumed throughout the test period. Fuel and water flowrates were also recorded periodically. CARB instruments (CO_2, CO, THC, CH_4, O_2, NO_x, SO_2) were located downstream of the baghouse. Tracer Technologies injected sulfur hexafluoride (SF_6) into the CBC and monitored the SF_6 with a semi-continuous GC/ECD system located at the CARB sampling point. Integrated samples were obtained by CARB for volatile organic compounds (Tedlar bag samples) and semi-volatile organic compounds (XAD-2 resin) for the DRE and PIC determinations. Bag sample analyses were carried out by CARB's Haagen-Smit Laboratories in El Monte, California. Analysis of the XAD-2 resin samples were performed by the California Air Industrial Hygiene Laboratory in Berkeley, California.

The fuel mixture used for this test was selected to simulate a refractory hazardous waste stream and to provide comparability to other EPA tests. The composition and analysis (% total mass) of the fuel used for this test was: xylene (74.38%), ethylbenzene (20.97%), Freon 113 (1.00%), toluene (0.35%), hexachlorobenzene (0.26%). The heating value of this fuel was about 39 MJ/kg (17,000 Btu/lb). Because the test was designed to simulate the combustion of an aqueous mixture of organo-chlorine fuels, water was dynamically mixed with the surrogate fuel to achieve an effective heating value of about 19 MJ/kg (8000 Btu/lb).

RESULTS AND DISCUSSION

The operation of the CBC was characterized by combustion parameters and by analysis of bag samples, resin samples, and SF_6 DRE data.

Combustion Parameters

A graph of CO, THC, O_2, and bed temperature as a function of run time is presented in Figure 1.

The unsteady nature of the combustion gas composition is evident. A careful examination of this figure would suggest that there was a relationship between O_2, CO, and THC concentrations. To evaluate this relationship the data were stratified for O_2 concentration into 1% intervals and the averages of CO and THC of all points in each interval were calculated. The results of this analysis are shown in Figure 2.

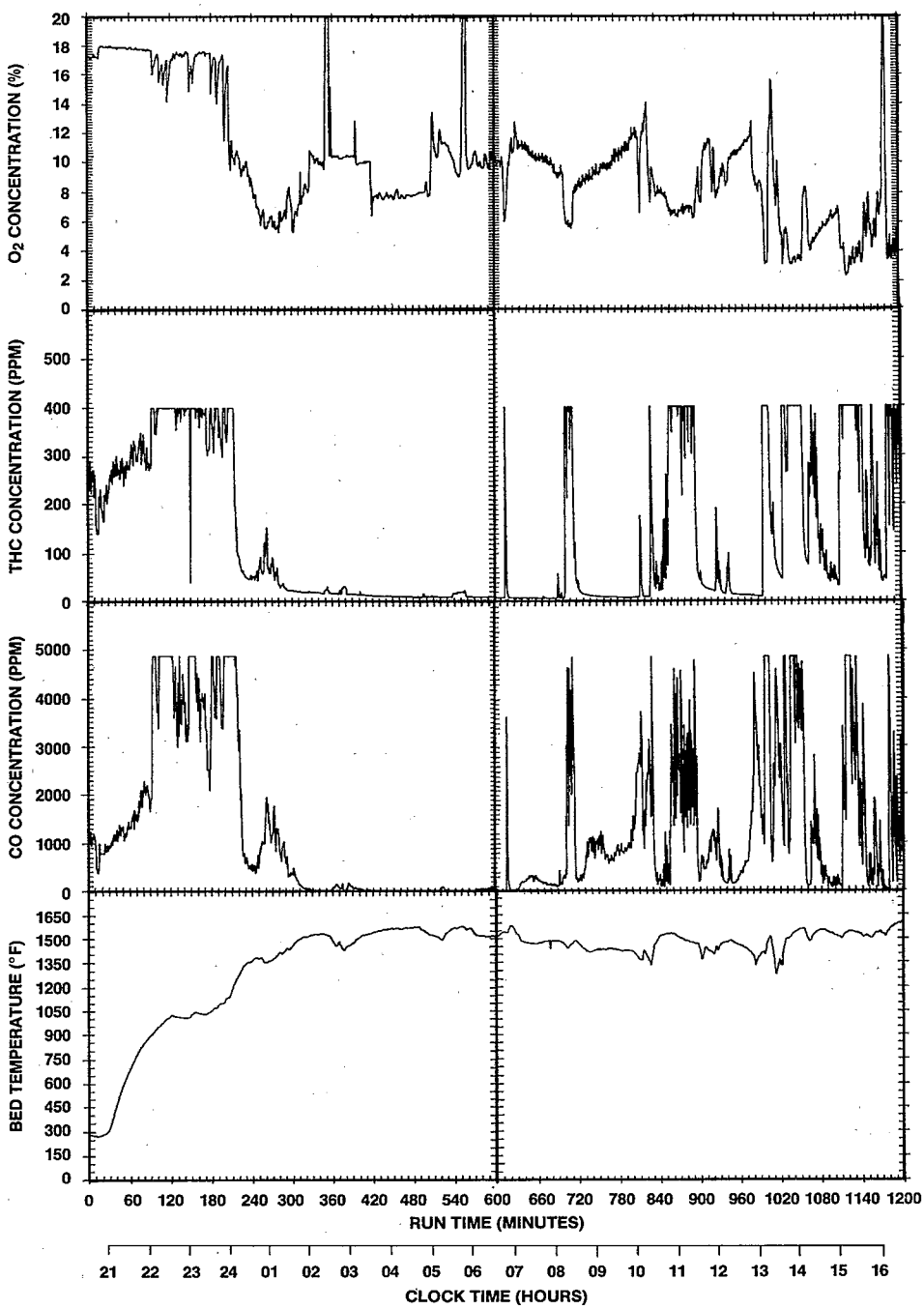

Figure 1. O_2 concentration, THC concentration, CO concentration, and bed temperature versus run time and clock time for the first 1200 minutes of the test.

High CO and THC emissions occurred at conditions of low or very high O_2 concentrations. An analysis of the temperatures that occurred during high CO and THC concentrations indicated that low O_2 was responsible for more of the CO and THC excursions than was low temperature. The frequency of CO and THC excursions increased with decreasing O_2 levels, particularly below about 5 to 6% O_2. The GA Technologies THC and CO analyzers went off scale at about 400 and 5000 ppm, respectively, thus the apparent leveling off of THC and CO readings did not occur in reality. This range of O_2 concentration was somewhat higher than anticipated in order to achieve high combustion efficiency. GA Technologies staff suggested that a possible reason for the deterioration of combustion efficiency was the size of the positive displacement pump used to deliver fuel to the CBC. It had a nominal rated capacity of about 110 liters per minute (ℓpm) (30 gallons per minute), where as fuel was being fed to the bed at about 0.44 - 0.50 ℓpm (7-8 gallons per hour). Thus there may have been "surges" of fuel that resulted in fuel rich pockets of gas passing through the bed in spite of the fact that the overall stoichiometry was slightly fuel-lean. In a sense, the CBC was being operated in a "failure mode" or "non-optimum combustion" condition throughout the test.

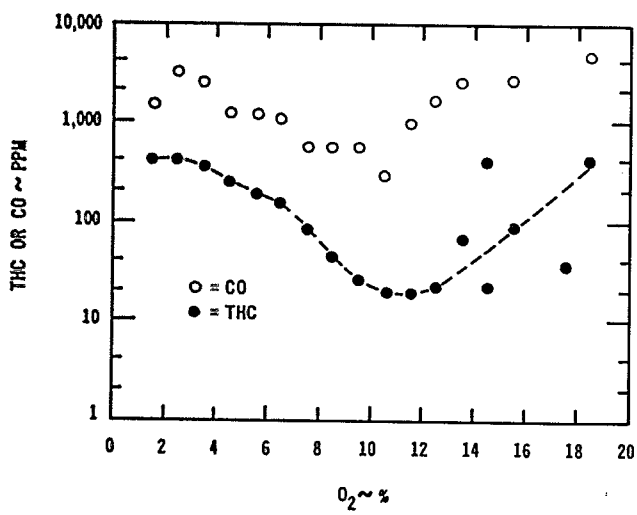

Figure 2. Comparison of average THC and CO concentrations as a function of O_2 concentration.

A minimum in THC can be discerned from Figure 2. The considerable scatter in the data at high O_2 concentrations can be explained simply as a result of the small number of data points in this range. It is reasonable to hypothesize "quenching reactions" at extreme O_2 concentrations. This form of "quenching" could result from pockets of fuel lean mixtures where reaction propagation may have been hindered.

Based on a careful analysis of Figure 1 it was found: a) increases in CO and THC concentrations were correlated with decreases in O_2 concentrations, b) rapid fluctations of CO and THC concentrations were virtually independent of the average O_2 concentration, and c) the response of the O_2 analyzer lagged the responses of the THC and CO analyzers by about 3 minutes (1).

Low combustion temperature appears to have resulted in excessive CO and THC emissions on three occasions. Two were momentary periods when the bed temperature fell below 700°C (1300°F) and were accompanied by CO and THC spikes at 825 and 1012 minutes (Figure 1). The other period was during the start-up of the CBC.

Bag Samples

Bag samples were drawn over nine sampling periods. These were analyzed for the POHCs Freon 113 and carbon tetrachloride, and for a variety of PICs including chloroethane, chloromethane, dichlorodifluoromethane, dichloromethane, trichlorofluoromethane, trichloromethane, 1,2-dichloroethane, 1,1,1-trichloroethane, 1,2-dichloropropane, trichloroethylene, tetrachloroethylene, and benzene. Concentrations were expressed as parts per billion (ppb) on a dry basis, and average values of fuel flowrate, air flowrate, total gas flowrate, and effluent gas concentrations are presented in Table 1. Concentrations of CO and THC normalized to the CO_2 concentration also appear in Table 1. To provide an indication of volatile organo-chlorine PIC formation, a parameter Volatile PIC-Cl/Cl-in is also presented in Table 1. This parameter is defined as the ratio of the mass of chlorine in chlorinated PICs to the total chlorine input with the fuel.

Based on an examination of the bag sample analyses shown in Table 1,

TABLE I

SUMMARY OF BAG SAMPLE RESULTS

Bag Sample Concentration / Compound Name	Time 0934-1035	1100-1124	1345-1418	1443-1623	1630-1705	1954-2054	2102-2140	2315-0020	0030-0100
POHCs - [ppb]									
Trichlorotrifluoroethane (Freon 113)	28	0.41	0.46	0.096	0.056	0.042	0.063	0.025	0.045
Average DRE (Penetration)	0.9994538 5.46E-04	0.9999950 4.98E-06	0.9999969 3.08E-06	0.9999987 1.33E-06	0.9999996 3.82E-07	0.9999994 5.81E-07	0.9999996 3.92E-07	0.9999997 3.17E-07	0.9999997 2.55E-07
Tetrachloromethane (Carbon tetrachloride)	0.31	0.33	0.24	0.47	0.21	0.22	0.27	0.92	1.4
Average DRE (Penetration)	0.9999952 4.75E-06	0.9999969 3.10E-06	0.9999987 1.26E-06	0.9999948 5.22E-06	0.9999989 1.13E-06	0.9999976 2.39E-06	0.9999987 1.32E-06	0.9999909 9.06E-06	0.9999938 6.23E-06
PICs - [ppb]									
Benzene	n.a.	7,400	n.a.	n.a.	n.a.	37,000	n.a.	n.a.	n.a.
Total Volatile PIC without Benzene - [ppb]	115.8	2034.1	4074.0	1528.4	611.9	2058.8	511.7	255.8	103.8
PIC-Cl - [ppb as Cl]	129.8	2039.9	4079.4	1536.8	616.3	2063.8	515.7	258.9	108.4
(Volatile PIC-Cl/Cl-in)	1.33E-04	1.30E-03	2.87E-03	1.15E-03	4.42E-04	1.50E-03	3.38E-04	1.73E-04	6.46E-05
Fuel flowrate - [LB/HR]	52.7	83.3	74.6	68.4	73	56.2	61.2	70.1	78.5
Air flowrate - [DSCFM]	316	311	307	300	306	239	234	273	273
Total gas flow - [DSCFM]	347.6	342.1	337.7	330	336.6	262.9	257.4	300.3	300.3
Average 02 - [%]	10.8	6.8	4.4	5.8	4.9	5.8	7.7	7.3	8.0
Average CO2 - [%]	7.7	11.1	12.7	11.8	12.5	11.9	10.4	10.3	9.3
Average CO - [ppm]	1493	2630	2792	1406	738	1851	523	260	23
Average CO/CO2	2.10E-02	2.36E-02	2.07E-02	1.05E-02	5.66E-03	1.47E-02	4.89E-03	3.23E-03	2.56E-04
Average THC - [ppm]	38	384	321	224	194	240	n.a.	49	30
Average THC/CO2	4.40E-04	3.45E-03	2.45E-03	2.09E-03	1.51E-03	1.96E-03	n.a.	4.42E-04	3.21E-04

generalizations can be drawn regarding the performance of the CBC during this series of tests. Although the average CO concentrations were high (greater than 500 ppm in seven of nine samples), the DREs of the volatile POHCs (Freon 113 and carbon tetrachloride) were also high in most cases. However, the penetration of organochlorine compounds (volatile PIC-Cl/Cl-in) was greater than 1×10^{-4}. The predominant halogenated PICs identified were chloromethane and chloroethane. The 0934 bag sample yielded low DRE for Freon 113, appreciable amounts of fluorinated PICs, and the lowest SF_6 DRE. An examination of the combustion parameters during this period (Figure 1) suggests that low bed temperature was the probable reason for reduced DRE of fluorinated compounds.

A plot of the normalized PIC chlorine content against both CO/CO_2 and THC/CO_2 is presented in Figure 3. A linear least-squares regression analysis was performed on the logarithms of the respective quantities yielding the dashed line correlations shown in Figure 3. The correlation of THC/CO_2 with PIC-chlorine formation is high with a regression coefficient of about 0.94. The correlation of CO/CO_2 with PIC-chlorine formation was

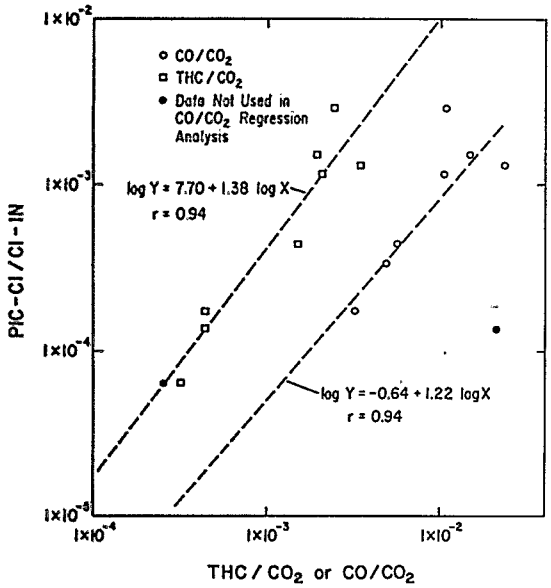

Figure 3. Correlation of volatile PIC chlorine normalized by total fuel chlorine input versus THC and CO concentration normalized by the CO_2 concentration.

not as high if all points were considered. The correlation of CO/CO_2 with PIC-chlorine formation was low as a result of two points (marked as • in Figure 3). One of the points which exhibits high CO but low PIC chlorine can readily be explained since it occurred during a period (0934 - 1035, Table 1) when natural gas was being injected into the bed to supplement the fuel heating value. Thus it was eliminated from subsequent regression analyses. The second questionable sample (low PIC and very low CO) was taken during a period (0030 - 0100, Table 1) when water was not being mixed with the fuel. All other bag samples were taken during periods when an approximately constant amount of water was mixed with the fuel. During the 0030 - 0100 period, both the fuel heating value and the bed temperature were higher than those occuring in other bag sample periods. Thus the point corresponding to 0030 - 0100 period was eliminated from the regressioon analysis. The resulting correlation coefficient of CO/CO_2 with PIC-chlorine formation was also 0.94. The results presented in Figure 3 are qualitatively similar to those presented by Waterland (4).

Resin Samples

XAD-2 resin samples were collected over five distinct time periods during this test. The POHCs analyzed were toluene, hexachlorobenzene, ethylbenzene, xylene, Freon 113, and trichlorobenzene. Concentrations, DRE, and penetration values were calculated for each POHC. The only PIC recovered by the resin analysis was benzene, although toluene was probably both a POHC and a PIC.

Based on the resin analyses it was determined that the DREs of each compound detected were fairly uniform throughout the series of samples. Toluene had the lowest DRE of all POHCs reported with DRE values exceeding 99.9% in all samples except one where the DRE exceeded 99.99%. All other POHCs showed excellent DREs. For example, trichlorobenzene had DREs exceeding 99.999% for all samples while hexachlorobenzene, ethylbenzene and xylene exhibited DREs greater than 99.9999% for all samples. PIC benzene concentrations ranged from about 5500 ppb to almost 20,000 ppb. Correlations between the benzene concentration, normalized to the fuel rate, with both CO/CO_2 and THC/CO_2 proved to be insignificant.

A comparison of the results from the bag and resin samples showed that the only compound in common was the PIC benzene. During the time period common between the resin and bag samples, the benzene concentrations were 20,000 and 37,000 ppb respectively. Although bag and resin samples exhibited reasonable agreement during similar time periods, CARB had only validated the bag sampling technique. There was evidence of benzene breakthrough in the resin samples.

SF_6 Test

Gaseous sulfur hexafluoride was injected into the CBC and monitored throughout the run. The average DRE of the SF_6 for the bag and resin sample periods is shown in Table 2. No correlation between SF_6 penetration and "volatile PIC-Cl/Cl-in" (Table 1) was found. The only other apparent feature in these data was a gradual increase of SF_6 DRE as the test progressed, corresponding to an increase in the average bed temperature. Assuming the CBC to be plug-flow reactor with temperature as the only significant variable throughout the duration of sampling, an elementary model assuming an Arrhenius temperature dependence of rate and equilibrium constants predicted that the SF_6 penetration would have the form:

$$\ln(-\ln(Pt)) = A + B/T \qquad (1)$$

where Pt represents SF_6 penetration and A and B are constants. Based on this model and data in Table 2 a regression equation was developed:

$$\ln(-\ln(Pt)) = 9.68 - (9.26E + 3)/T \qquad (2)$$

Table 2

Summary of Average SF_6 DRE Values for Bag Samples

TIME	DRE
0934-1035	.8342
1100-1124	.9140
1345-1418	.9789
1443-1623	.9786
1630-1705	.9799
1954-2054	.9786
2102-2140	.9826
2315-0020	.9917
0030-0100	.9916

This correlation is remarkable in that the total range of average bed temperatures for the data sets was only slightly greater than 100°C, yet about 60% of the variance appeared to be explained by temperature, in spite of the fact that fueling rates and combustion air flowrate were not held constant. Thus, considering both the bag sample data on the DRE of Freon 113 and the SF_6 data, it appears that temperature is the key parameter in the thermal decomposition of fluorocarbons in the CBC.

CONCLUSIONS

Based on an analysis of the data presented in this paper, the following conclusions can be drawn.

1. The DRE of volatile and semi-volatile POHCs under less than optimum combustion conditions met RCRA requirements (99.99% DRE).

2. Total volatile PIC formation was found to correlate well with CO and THC, normalized to fuel flowrate (CO_2). Penetration of volatile chlorinated PICs (based on total chlorine content of the fuel) exceeded 1×10^{-4}. PIC benzene appeared in substantial concentrations in several samples and was not correlated with any conventional combustion parameters.

3. The DRE dropped sharply when the bed temperature fell below 700°C. Temperature appeared to be a major factor in the destruction of the fluorinated compounds and a moderate correlation between SF_6 DRE and temperature was observed.

4. An analysis of rapid changes of CO and THC concentrations compared with changes in O_2 suggests that a minimum O_2 level would not be adequate to guarantee low PIC formation.

5. The CBC seemed to behave as a plug-flow reactor, susceptible to pockets of non-stoichiometric air/fuel mixtures passing through the bed causing increased PIC formation. This observation suggests the importance of the fuel feed system on CBC performance and should be evaluated carefully by permitting authorities.

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DISCLAIMER

The statements and conclusions in this article are those of the authors and not necessarily those of the California Air Resoures Board or the Environmental Protection Agency. The mention of commercial products, their source or their use in connection with material reported herein is not to be construed as either an actual or implied endorsement of such products.

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SUMMARY OF TESTING AT CEMENT KILNS COFIRING HAZARDOUS WASTE

Marvin Branscome, Wayne Westbrook
Research Triangle Institute
Research Triangle Park, NC 27709

Robert Mournighan
U.S. Environmental Protection Agency
Cincinnati, OH 45268

Jon Bolstad, John Chehaske
Engineering - Science
Fairfax, VA 22030

ABSTRACT

The incineration of chlorinated and other liquid organic wastes was investigated in 6- to 9-day test programs at dry- and wet-process cement kilns. Testing was conducted initially under baseline conditions with no burning of waste fuels. During the waste fuel burn, the waste fuel replaced a portion of the coal and coal/coke used as the primary fuel. Different replacement rates were used for each test day. The test program included monitoring for principal organic hazardous constituents (POHCs), products of incomplete combustion (PICs), particulate matter, SO_2, NO_x, HCl, CO, CO_2 O_2, and total hydrocarbons. The fate and distribution of chlorine and metals were also determined.

Test results for POHCs showed that these cement kilns generally could achieve a destruction and removal efficiency (DRE) of 99.99 percent or greater. Most of the additional chlorine introduced with the waste fuel is removed with the kiln's waste dust. An increase in HCl emissions was observed as the quantity of chlorine entering the kiln with the waste fuel increased. The data indicate that waste combustion changes the distribution of lead so a higher percentage of the lead is removed with the waste dust.

At the wet-process kiln, no significant difference in emission rates of particulate matter and PICs was found between the baseline and waste burn test conditions. Toluene and benzene were found in trace quantities and are attributable to coal combustion. Particulate matter results at the dry-process kiln are inconclusive because of a malfunctioning electrostatic precipitator (ESP).

The burning of waste fuel at the wet-process kiln decreased SO_2 emissions from an average of 636 ppm at the baseline to 265 ppm. SO_2 concentrations at the dry-process kiln remained relatively low with a baseline range of 2 to 12 ppm compared to 5 to 38 ppm during the waste burn.

INTRODUCTION

Preliminary feasibility studies and tests have indicated that the high-temperature combustion process of cement kilns may offer an effective alternative to other disposal methods for hazardous waste. The promising characteristics of cement kilns include:

- Existing high-temperature combustion process at 1,350° to 1,650 °C (2,500° to

3,000 °F) with a gas residence time on the order of seconds.

- Numerous plants scattered through out the country, which could handle large quantities of combustible hazardous waste liquids.

- Large-scale equipment in place, including process control and pollution control; relatively small capital investment required.

- Instantaneous temperature excursions unlikely because of the huge thermal inertia.

- The alkaline environment in a cement kiln absorbs HCl from chlorinated waste combustion.

- Kilns are operated under draft (slight vacuum); therefore, there would be little outward leakage of fumes, mostly inward leakage of air.

- Ash may be incorporated into the product.

- Energy savings from substitution of waste fuel for oil, coal, or gas.

PURPOSE

The purpose of this study was to develop additional data on the destruction of hazardous waste in cement kilns. These data will be used, along with data from other tests, to evaluate the environmental impacts of this method of waste disposal. To this end, the test program was designed to:

- Calculate DREs of principal organic hazardous constituents (POHCs).

- Compare baseline operation (no waste fuel burned) to the operation with waste fuel.

- Determine if products of incomplete combustion (PICs) are formed and, if so, identify them.

- Determine the fate and distribution of metals.

- Measure the effect of fuel burning on HCl emissions, and determine the fate and distribution of chlorine through a material balance.

- Examine the effects of waste fuel burning and process conditions on other pollutants (e.g., particulate matter, NO_x, SO_2, and total hydrocarbons).

APPROACH

The primary focus of the sampling efforts was the kiln's electrostatic precipitator exhaust gas. Volatile organics were collected in Tenax® and Tenax®/charcoal sorbent tubes with the volatile organic sampling train (VOST). The sorbent cartridges were thermally desorbed and analyzed by gas chromatography/mass spectroscopy (GC/MS). Less volatile organic compounds were collected by XAD resin in a Modified Method 5 (MM5) sampling train. Both sorbents were analyzed to determine POHCs identified in the waste fuel and were also examined for products of incomplete combustion. Particulate matter emissions were determined from the MM5 sampling train. Metals emissions were estimated from analysis of the MM5 particle catch.

HCl emissions were sampled through a separate sampling train. The impinger solution was analyzed for HCl by ion chromatography. The exhaust gas was analyzed by continuous emission monitors for O_2, CO, CO_2, NO_x, SO_2, and total hydrocarbons.

Process samples taken included the raw material feed, cement product (clinker), ESP dust, primary fuel, waste fuel, and process water. The major process streams were analyzed for metals and chlorine content to attempt a material balance. In addition, the waste fuel and water were analyzed for organic compounds by GC/MS. Process operating parameters were recorded at 15-minute intervals throughout each test period.

The testing sequence first established baseline operating conditions burning only the primary fuel and no hazardous waste. The hazardous waste was then burned at different fuel replacement rates. This sequence permitted comparisons between the baseline and waste fuel test conditions and also provided information on the impacts of waste combustion in the cement kiln.

PROBLEMS ENCOUNTERED

The major problem encountered was

methylene chloride contamination of blank samples at levels roughly equal to those found from stack gas samples. The result is a bias toward high methylene chloride emission rates and a bias toward low DREs. Blank values were relatively low or nil for the other POHCs and yielded meaningful results. For the dry-process kiln test, one set of samples was invalidated because of lengthy storage time, cracks in sorbent tubes, and contamination. The ESP malfunctioned during the test on the dry-process kiln, and no meaningful data on controlled particulate matter emission rates were obtained for this test.

RESULTS

DREs

The designated POHCs for the two tests were methylene chloride, methyl ethyl ketone (MEK), toluene, 1,1,1-trichloroethane (TCE), and 1,1,2-trichloro-1,2,2-trifluoroethane (Freon 113). The concentration of the POHCs in the waste fuel ranged from 0.3 to 4 percent. The waste fuel was spiked with Freon 113 to determine the DRE of a compound that is difficult to destroy by combustion and that was unique to the waste fuel. The DRE results are summarized in Tables 1 and 2. Results for methylene chloride are environmentally conservative and biased low because sample levels and blank levels were about the same. According to the VOST protocol, blank corrections were not applied because blank levels could not be distinguished from sample levels. No significant blank problems were experienced with the other POHCs. DRE calculations for Freon 113, MEK, and 1,1,1-TCE show 4 to over 5 nines. Toluene was shown to originate from coal combustion. Toluene emission rates were unchanged by the cofiring of waste fuel. Therefore, the DRE for toluene entering only with the waste fuel is likely to be much higher than was measured. Even without subtracting the baseline level of toluene, DREs of 99.99 percent or greater were achieved at the dry-process kiln and one day at the wet-process kiln. The highest DREs for both tests were observed for compounds that had the lowest baseline and blank levels (Freon 113 and 1,1,1-TCE) with DREs on the order of 99.999 percent or greater.

The MM5 results from the dry-process kiln test were also examined to determine the DREs of compounds that were not predesignated as POHCs. Styrene, ethylbenzene, o-xylene, and benzaldehyde were present in the waste fuel at concentrations of 10 to 20 g/L. Benzaldehyde was detected in the stack gas for both the baseline and waste burn tests and yielded a DRE of 99.998 percent without correction (subtraction) of the baseline level. None of the other three compounds were found in the stack gas, which resulted in DREs greater than 99.999 percent for each based on detection limit values.

A review of kiln tests indicate that the highest DREs and lowest emission rates were observed when baseline or blank levels of the POHC were clearly not a problem. The two tests with apparently the least interference in measurements were at Rockwell Lime (5) and Stora Vika (1,2), where wastes similar to those previously discussed were burned. At Stora Vika, DREs consistently exceeded 4 nines and included 6-7 nines for several compounds. Similarly, at Rockwell Lime the DREs consistently exceeded 4 nines and were as high as 6 nines for several chlorinated compounds. Background and blank interferences were noted at St. Lawrence Cement (9); however, DREs exceeding 4 nines were obtained on a worst-case basis by not subtracting background levels. The results for the test at Los Robles were limited by method detection limits rather than by interferences, but DREs exceeding 4 nines were generally observed (8). A test with PCBs at Peerless Cement (12) found more PCBs entering with slurry feed (river water) in the cooler end of the kiln than was emitted during the PCB burn. However, DREs of 4 to 5 nines were reported without correction for the contribution from the water.

PICs

Organic compounds that were potential PICs from waste combustion were emitted at similar rates during the waste fuel and baseline tests. At the wet-process kiln, compounds such as toluene, benzene, xylene, biphenyl, naphthalene, and methylnaphthalenes were observed in the stack emissions with coal as the only fuel. During both the baseline and waste burn tests, benzene emission rates ranged from 15 to 50 mg/s. Emission rates of the other compounds were on the order of 1 to 10 mg/s. The highest emission rates were observed on a test day with a kiln upset (ring formation) with coal as the only

TABLE 1. DREs[a] AT THE WET-PROCESS KILN

Compound	Percent DRE at Given Replacement Rate					
	59%	43%	61%	39%	58%	Average
Methylene chloride[b]	99.998	99.995	99.956	99.975	99.993	99.983
Freon 113	------	------	------	>99.999	>99.999	>99.999
Methyl ethyl ketone	99.991	99.978	99.990	99.983	99.997	99.988
1,1,1-Trichloroethane	99.991	99.991	99.996	99.996	99.999	99.995
Toluene[c]	99.952	99.940	99.974	99.951	99.988	99.961

TABLE 2. DREs[a] AT THE DRY-PROCESS KILN

Compound	Percent DRE at Given Replacement Rate		
	25%	37%	Average
Methylene chloride[b]	99.94	99.99	99.96
Freon 113	99.999	99.999	99.999
Methyl ethyl ketone	99.997	99.999	99.998
1,1,1-Trichloroethane	>99.999	>99.999	>99.999
Toluene[c]	99.992	99.998	99.995

[a] Uncorrected for blanks.
[b] Blank values were comparable to sample values for methylene chloride.
[c] Trace quantities of toluene are produced from coal combustion.

TABLE 3. CHLORINE RESULTS FOR THE WET-PROCESS KILN

Condition	Cl in fuel (kg/hr)	HCl emissions (kg/hr)	Cl in dust (%)	Cl in clinker (ppm)
Baseline	6	0.57	0.2	<200
Day 5	32	0.27	0.7	705
Day 6	21	1.0	0.7	<200
Day 7	41	1.5	0.7	<200
Day 8	72	2.3	1.0	<200
Day 9	128	5.4	1.7	<200

TABLE 4. CHLORINE RESULTS FOR THE DRY-PROCESS KILN

Condition	Cl in fuel (kg/hr)	HCl emissions (kg/hr)	Cl in recycle dust (%)	Cl in waste dust (%)
Baseline	10	1.3	0.73	3.5
Day 3	60	2.2	1.3	5.7
Day 4	71	5.5	1.4	6.1
Day 5	72	27.	1.9	8.1

[a] Clinker results were <125 ppm chlorine.

fuel. No statistically significant increase in emission rates was observed when the waste fuel was burned. No polychlorinated dibenzodioxins or dibenzofurans were found in any samples at a detection limit of less than 1 ppb by weight in the stack gas. Similar results were obtained at the dry-process kiln except that the quantity of these compounds was lower (roughly 10 times the detection limit). The emission rates at this kiln were on the order of 0.3 mg/s.

Particulate Matter Emissions

No statistically significant difference was noted in particulate matter emissions between the baseline and waste fuel burn at the wet-process kiln. The control device was an ESP, and emissions averaged about 0.65 lb/ton. The maximum chlorine loading reached 4.7 kg/Mg of clinker.

A review of particulate matter results from kiln tests conducted to date shows similar results for pairs of tests:

- The testing of two kilns equipped with baghouses (San Juan and Rockwell Lime) showed no increase in particulate matter emissions when chlorinated wastes were burned (5,11). Emissions were 0.65 and 0.25 lb/t for the cement and lime kilns, with chlorine inputs of approximately 5.5 and 2.7 kg Cl/Mg product.

- The testing of two kilns equipped with ESPs (St. Lawrence Cement's dry-process kiln and Alpha Cement) showed a decrease in emissions when wastes were burned that were low in chlorine content (3,10). Baseline emissions of 1.1 lb/t decreased to 0.7 and 0.8 lb/t.

- The testing of two kilns equipped with ESPs (the wet-process kiln we tested and Marquette Cement) showed no change in particulate matter emissions when chlorinated wastes were burned at rates of 1.1-4.7 kg Cl/Mg clinker (7). Emissions were 0.65 and <1 lb/t for these two kilns.

- The testing of two kilns equipped with EPSs (St. Lawrence's wet-process kiln and Stora Vika) yielded results for different wastes and different chlorine loadings. Emissions were positively correlated with chlorine loading; however, the extent of the increase in emissions varied for different compounds and different kilns. Chloride accumulation, as evidenced by ring formation and subsequent release or pluggage, begins to occur in the range of 6-9 kg Cl/Mg clinker (1,2,9).

Although increased chlorine loading at the St. Lawrence and Stora Vika kilns increased particulate matter emissions, there was no known attempt to compensate for changes in the dust's resistivity. However, emissions were still comparable to those observed at other tests. Baseline test results at these two kilns ranged from 0.2 to 0.5 lb/t compared to 0.5 to 1.1 lb/t during the cofiring of waste fuels. The results do not include a kiln upset from a chloride ring formation at St. Lawrence Cement when emissions averaged about 3 lb/t. The tendency for chloride rings to form during high chlorine loading provides an incentive to the kiln's operator to limit the chlorine entering the kiln. Limiting the chlorine input may avoid plugging and process disruptions as well as limit chlorine concentrations in the dust going to the ESP. The test data suggest that particulate matter emissions from chlorinated waste combustion are controllable by a properly operating control device and a reasonable limit on chlorine loading to avoid ring formation and excessive dust loading. Adjustments may be required on a site-by-site basis to optimize ESP performance and thus account for changes in dust resistivity.

Fate of Chlorine

Results for chlorine are summarized in Tables 3 and 4 and show that 90 to 99 percent of the chlorine is retained in the process solids. At the dry-process kiln, the waste fuel contained an average of 2 percent chlorine and was fired at an average rate of about 1.2 kg Cl/Mg clinker. The waste fuel at the wet-process kiln contained 1 to 4 percent chlorine and was fired at an average rate of 2.2 kg Cl/Mg clinker (maximum of 4.7). HCl emissions, percent chlorine in the dust, and percent chlorine in the recycled dust increase as the total chlorine input

increases. On the first waste fuel test day (second day of waste fuel burning) at the wet-process kiln, HCl emissions were lower than during the baseline period. Chlorine was detected in the clinker. It is possible that an equilibrium chlorine cycle had not been obtained at this point. On the last day of testing at the dry-process kiln, the chlorine cycle evidently shifted to the cooler end of the kiln. More chlorine exited with the stack gas and waste dust than in previous tests, and the chlorine concentration of the recycled dust appeared to increase although the total chlorine input remained unchanged.

A review of other tests showed that during the combustion of highly chlorinated wastes at St. Lawrence Cement, over 99 percent of the chlorine was retained in the process solids and HCl emissions were <1 lb/hr during both the baseline and waste fuel burns (9). The total chlorine input was up to 6.8 kg Cl/Mg clinker. An increase in HCl emissions from 0.6 to 1.0 lb/hr was observed at Los Robles (8), and an increase from 2.4 to 5.8 lb/hr was observed at Alpha Cement (10). An increase from <0.2 to 0.8 lb/hr was observed at San Juan Cement (11), and at Rockwell Lime the increase was from 0.2 to 0.4 lb/hr (5). During the tests at San Juan Cement, the waste fuel was highly chlorinated (up to 35 percent Cl) and was fired at an average rate of 5.5 kg Cl/Mg clinker. Over 99 percent of the chlorine was retained in the process solids, primarily the clinker. For other tests, most of the chlorine was removed with the waste dust. These tests indicate that HCl emissions can increase from chlorinated waste combustion; however, 90 to over 99 percent of the chlorine is retained in the process solids.

Fate of Lead

The lead content of the waste fuel ranged from roughly 100 to 1,000 ppm for both kiln tests. Lead emissions at the wet-process kiln increased from about 1.5 mg/s at the baseline to about 6.9 mg/s during the waste burn. The malfunctioning ESP prevented useful results at the dry-process kiln test, but a previous test at the same kiln with a similar waste fuel showed an increase in lead emissions from 5 to 9 mg/s. A material balance showed that over 99 percent of the lead was retained in the process solids. The lead concentration in the waste dust increased at both kilns. At the wet-process kiln, the increase was from 395 to 1,530 ppm compared to an increase from 116 to 2,650 ppm for the dry-process kiln.

A review of lead emissions during other kiln tests shows varying results. At St. Lawrence Cement, burning lead-contaminated waste oil with a low chlorine content did not affect lead emissions (3). Similarly, burning chlorinated aliphatics did not increase lead emissions, but burning PCBs resulted in an increase from ~1.5 mg/s at the baseline to ~4.6 mg/s (9). Lead emissions appeared to increase also at Alpha Cement (from ~4 to ~17 mg/s) (10) and Rockwell Lime (from <0.4 to 0.47 mg/s) (5). The lead content in the waste dust also increased in most cases.

For perspective, consider that total lead emissions are relatively small and on the order of emissions from several automobiles burning leaded gas. Also consider that over 99 percent of the lead is retained in the process solids. By comparison, a boiler burning used oil emits 50 to 60 percent of the lead, and may emit a higher percentage because of losses during soot blowing (3,6).

SO_2, NO_x, Total Hydrocarbons, and CO Emissions

At the wet-process kiln, SO_2 concentrations decreased from an average of 636 ppm to 265 ppm when the waste fuel replaced the sulfur-containing coal (4.3 percent sulfur). Approximately 60 percent of the total sulfur was retained in the process solids for both test conditions. At the dry-process kiln, SO_2 concentrations were low, with baseline concentrations of 1.5 to 12 ppm. During the waste burn, SO_2 concentrations ranged from 5 to 38 ppm and were shown to be strongly affected by O_2 input. The kiln exit oxygen increased to 6.7, 7.3, and 7.5 percent on successive test days with corresponding SO_2 concentrations of 38, 13, and 5 ppm. Approximately 99 percent of the sulfur entering with the fuel was retained by the process solids at the dry kiln.

Similar results have been observed at other tests, i.e., a reduction in SO_2 from waste combustion. At Alpha Cement (10), SO_2 concentrations decreased from 78 to 33 ppm, from 93 to 18 ppm at Marquette

Cement (7), and were constant at 27 ppm at Los Robles (8).

NO_x concentrations ranged from 370 to 480 ppm at the wet-process kiln and from 600 to 800 ppm at the dry-process kiln. The NO_x concentrations at the dry-process kiln were strongly affected by kiln oxygen input: an increase in kiln exit O_2 from an increased air rate yielded corresponding increases in NO_x. NO_x emissions are not obviously affected by burning waste fuels. Other investigators have found that NO_x concentrations are primarily affected by oxygen input, primary/secondary air ratio, and temperatures (4).

Concentrations of total hydrocarbon ranged from 6 to 7 ppm during three baseline tests at the wet-process kiln and increased to 21 ppm during a kiln blockage for one baseline test. The overall average was 10 ppm compared to an average of 21 ppm (16 to 28 ppm) during the waste fuel burn. The baseline test at the dry-process kiln revealed concentrations of 2 to 4 ppm compared to daily averages of 1, 5, and 9 ppm for the three waste burn tests. Tests at San Juan Cement, Rockwell Lime, and Stora Vika showed that total hydrocarbon concentrations on the order of 10 ppm or less were attained during both the baseline and waste burn test conditions.

Carbon monoxide concentrations at the wet-process kiln averaged 212 ppm (100 to 400 ppm) during the baseline compared to 190 ppm (130 to 340 ppm) during the waste burn. The baseline tests at the dry-process kiln revealed CO concentrations of 35 to 40 ppm compared to an average of 39 ppm during the waste fuel burn. The difference between CO concentrations during the baseline and waste fuel test conditions is not significant.

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EVALUATION OF HAZARDOUS WASTE DESTRUCTION IN A BLAST FURNACE

Radford C. Adams, Thomas A. Buedel,
Carol A. McCarthy, and Michael A. Palazzolo

Radian Corporation
Research Triangle Park, North Carolina 27709

ABSTRACT

At least one steel company utilizes organic waste liquids as a heat and carbon content source to partially replace the coke that is used to charge the blast furnace. The waste liquids fed to the blast furnace are likely to contain hazardous constituents. Temperature and residence time in the blast furnace favor total destruction of the principal organic hazardous constituents (POHCs) of the waste fuel but verification of destruction efficiencies has not been attempted up to now. Also, reduction reactions that occur in a blast furnace may promote the formation of products of incomplete combustion (PICs).

Tests were conducted while feeding waste fuel to a blast furnace located at a major steel mill. The primary objective of the test program was to determine the fate of the POHCs of the waste fuel and to look for formation of PICs, notably dioxins and dibenzofurans.

INTRODUCTION

At least one steel company is burning liquid hazardous wastes in blast furnaces to supplement fuel and coke requirements. Tests were conducted during the burning of a waste fuel containing hazardous constituents (POHCs) in a blast furnace at a major steel plant. The blast furnace tested under this program is typical of blast furnaces used for iron production throughout the steelmaking industry. The blast furnace had been retrofitted with a liquid feed system for injecting waste fuel, replacing natural gas, into the combustion zone.

Blast furnaces are prime candidates for thermally destroying POHCs due to the extremely high temperatures that are generated in the combustion zone. On the other hand, unburned POHCs are subjected to reducing conditions when leaving the combustion zone and entering the iron oxide reduction area. As a consequence, hazardous waste destruction may be limited or products of incomplete combustion (PICs) may form.

A blast furnace produces molten iron from iron ore and other iron bearing feed materials. A moving bed of iron ore, carbon (as coke), and limestone descends through the blast furnace tower. In the combustion zone, located between the moving bed and the hearth of the furnace, oxygen of hot blast air and steam react with the carbon monoxide and hydrogen. Temperatures in the combustion zone exceed 3000°F. CO and H_2 travel upward through the moving bed and react with the iron oxide (as iron ore) to produce elemental iron. The molten iron and slag are collec-

ted in discrete layers on the hearth of the furnace and are removed through tap holes at regular intervals.

Figure 1 depicts the overall blast furnace system. Excess CO and H_2 are produced to drive the iron oxide reduction reaction to completion. Therefore, blast furnace off gases have a heating value of about 90 Btu/scf. This energy is used to produce steam for air compression and other process steam requirements. Only about 1/4 of the blast furnace gas is needed to heat the blast air. A set of three stoves are used to heat the blast air to approximately 1800°F (only one stove is shown in Figure 1). The stoves, which are filled with a refractory brick checkerwork, cycle between combusting blast furnace gas, and heating blast air so that one stove provides hot blast air while the other two stoves are being heated up. Products of combuston from the stoves are emitted through a stack. Dust is removed from the blast furnace before entering either of the combustion devices.

PURPOSE

The objective of this test program was to evaluate typical waste disposal performance of a blast furnace when burning a liquid organic waste. A major goal was to determine the fate of the major components of the waste and their products of incomplete combustion (PICs), if any, that are emitted from the blast furnace and a downstream combustion process. For this program, the blast furnace stove set was selected as the downstream combustion process. The alternative would have been the plant power house where blast furnace gas is burned in boilers that produce process steam. Specifically, the following objectives were to be met.

1. Determine the fate and destruction removal efficiency (DRE) of waste fuel POHCs (principal

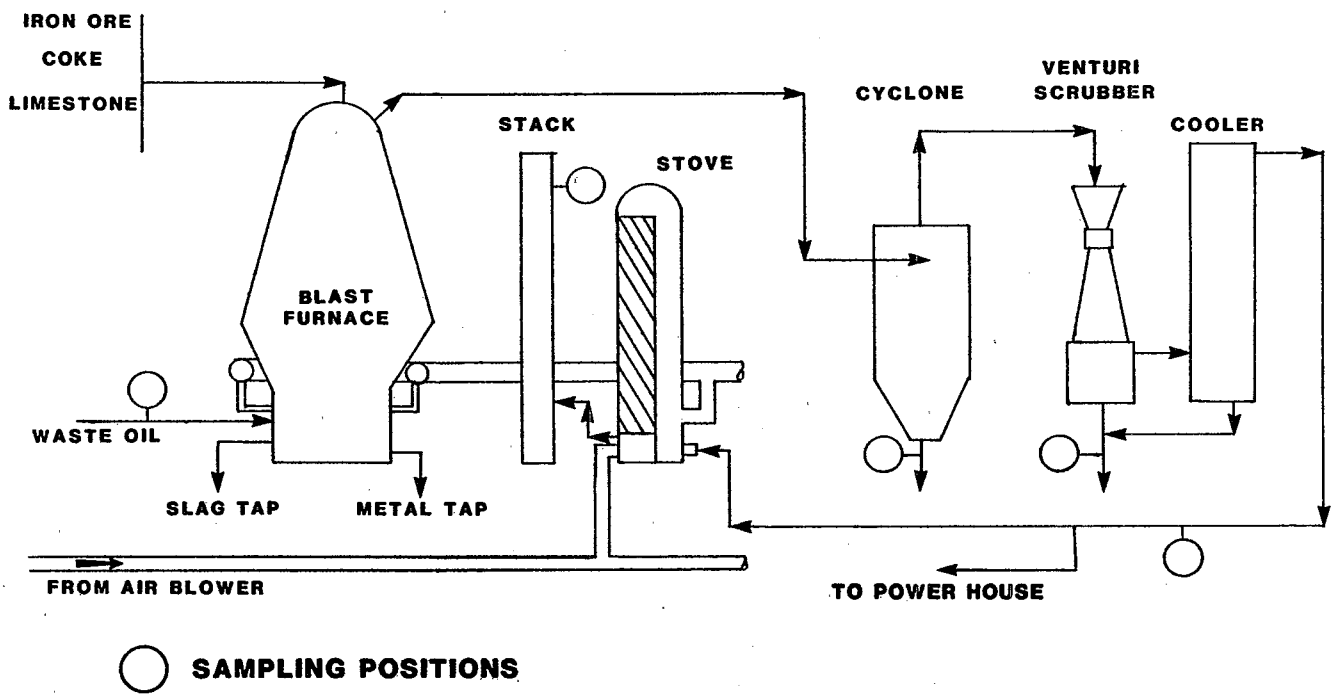

Figure 1. Blast Furnace Process Flow

organic hazardous constituents) by monitoring blast furnace gas, scrubber water, and combustor flue gas for identified POHCs.

2. Determine PIC formation and, if detected, their fate.

3. Determine relative emissions of volatile organic components of waste fuel from the waste fuel storage tank compared with emissions of these components from the combustor.

It was also an objective to determine if any dioxin/dibenzofurans were present at levels greater than one part per trillion in the emission/effluent streams.

APPROACH

Blast furnace process streams were sampled simultaneously to meet the data requirements. These are:

- waste fuel to identify and quantitate POHCs and chlorine content,
- blast furnace gas to determine fate and DRE of POHCs and to identify and quantitate PICs (sampling position is downstream of dust collector and wet scrubber),
- stove stack gas to determine fate and DRE of POHCs and fate of identified PICs,
- dust collector sample to archive for expansion of performance evaluation if needed, and
- waste fuel storage tank emissions to compare magnitude of tank emissions with stove emissions.

Identify and Quantitate POHCs in Feed

The waste fuel was fed to the blast furnace continuously at about 60 gpm. The pumping rate was 100 gpm; thus, excess liquid was recirculated back to the feed tank. The liquid was sampled just before the blast furnace burner at intervals of one hour and composited for and quantitation was accomplished by gas chromatography/mass spectroscopy (GC/MS).

The feed tank also served as storage tank. Additions to the feed tank during sampling and resultant variations in composition could not be avoided. Tank trucks were off loaded to the feed tank during each sampling run. The waste liquid was blended with No.6 fuel oil to maintain a preset level in the feed tank. The combination of these two events created cyclic waste to fuel ratios of the waste fuel fed to the blast furnace. During sampling, this ratio averaged 0.8 to 1.0, 0.6 to 1.0 and 0.6 to 1.0, respectively for each run.

Fate and DRE of POHCs

Destruction and removal efficiencies (DRE) were determined for two cases; across the blast furnace and across the blast furnace and combustion process. For both cases, any removal by the particulate control devices (a cyclone dust collector and a wet scrubber in series) was accounted for. Since the POHCs were unknown at time of sampling, both volatile (VOST) and semi-volatile (modified method 5) sampling methods were employed. Stove products of combustion were sampled at near atmospheric pressure from the stack. Blast furnace gas after cleaning was sampled at inlet to the stoves at a positive pressure of 50 inches w.c. Table 1 shows the fixed gas compositions for each location. Hydrogen should account for a substantial portion of the four percent not identified in the stove inlet gas. Analysis of POHC data of the scrubber waters was not completed in time to include in this paper.

Identify and Determine Fate of PICs

The following outlet streams were sampled for compounds not found in the waste fuel:

- scrubber makeup water
- scrubber discharge water
- blast furnace gas inlet to stoves
- blast furnace gas outlet of stoves

Classification of these compounds as PICs is avoided because they may have originated in the blast air or the iron ore/coke mixture.

Waste Fuel Storage Tank Emissions

The storage tank gas phase was sampled by integrated bag sampling and analyzed by GC/flame ionization detection. A portion of the sample was passed through a Tenax resin trap for later analysis by GC/MS. Liquid temperature in the tank averaged 117°F.

PROBLEMS ENCOUNTERED

Two major types of problems were encountered:

1. The potential for CO leaks introduced the need for specific safety precautions during sampling.

2. Site specific sampling installations and operating inflexibility required some sacrifice of best test protocol.

The duct that was sampled for blast furnace gas was at a positive pressure of 50 inches w.c. Also, high concentrations of CO and H_2 if released created both a CO poisoning and fire hazard to sampling personnel. Special sampling equipment was devised to protect personnel and equipment and to maximize sample collection efficiency. The steel company safety rules required that their safety personnel be present at all times. They continually monitored for dangerous CO levels and they had the authority to evacuate the area when CO levels were exceeded. Air masks required to be worn during periods of maximum risk, e.g., when probe changes were made. The special probe for modified method 5 sampling was inserted through a packing gland that allowed movement of the probe to the next traverse point with a minimum of gas release. Pressure connections were used throughout the sampling train and both positive pressure and negative pressure leak tests were made. The heated filter box was fitted with a fan to purge any possible release into the box of explosive gases.

The site specific limitations were as follows:

- Lack of consistent feed composition was described earlier.

TABLE 1. FIXED GAS ANALYSIS RESULTS

Location	Parameter	Concentration (Volume percent)
Stove inlet	O_2	4.3
	CO	22.0
	CO_2	15.6
	N_2	54.1
Stove outlet	O_2	5.9
	CO_2	21.8
	N_2	69.5

- The waste liquid feed could not be shut off without upsetting the blast furnace carbon and heat balances. The baseline data could not be collected.

- Access problems prevented traversing for sampling and for velocity measurements two diameters of the round ducts at the stove inlet and stove outlet sampling positions. Federal Register methods stipulate traversing on two diameters at right angles.

The latter limitation introduced significant error in the velocity and flow measurements at the inlet location. Therefore, process flow measurements were used. The outlet velocity measurements appeared to be valid when compared with a mass balance calculated from the inlet process flow measurements and gas composition.

RESULTS

Analysis of all data had not been completed in time to include in this report. This includes primarily the fate of PICs and the tank emissions results. Complete results will be reported to the EPA's Hazardous Waste Engineering Research Laboratory in a final report. Program accomplishments that can be reported now are are as follows:

- Characterization of liquid waste fed to the blast furnace,

- DRE's across the blast furnace with and without downstream combustion,

- Determination of dioxin/dibenzofuran emissions, and

- Blast furnace operating data.

Three sampling runs were conducted on successive days.

Liquid Waste Characterization

A waste broker supplies the organic liquid waste to the steel company. The waste is blended with No. 6 fuel oil to create a waste fuel for blast furnace use. Table 2 shows POHC average concentration and feed rates for the three sampling runs. Toluene is the predominant POHC in the fuel, although chlorinated POHCs account for over 6400 ppm of the liquid.

The potential for considerable variation in waste fuel composition was discussed earlier. Table 3 summarizes the variabil-

Table 2. Concentration of POHCs in the Waste Fuel

Compound	Waste Fuel (ppm by wt.)	Feed Rate (Kg/hr)
1,1-Dichloroethene	1,210	15.7
Chloroform	254	3.3
1,1,-Trichloroethane	999	13.0
Trichloroethene	1,185	15.4
Benzene	553	7.2
Tetrachloroethene	2,800	36.3
Toluene	56,200	731.0
m/p-Xylene	940	12.2
o-Xylene	5,280	68.8
Naphthalene	880	11.4
Total Chlorine	835	10.8

Table 3. Variation of POHCs in Feed

	Range, ppm by Weight	CV, %
Chloroform	33-469	70
1,1,1-Trichloroethane	817-1215	16
Benzene	543-569	2
Toluene	49901-65417	12
o-Xylene	3050-9500	56

ity of POHCs in the feed as expressed by the coefficient of variation (CV) of the standard deviation of 3 samples. Table 3 shows standard deviations varying from 2% from the mean to 70% from the mean. All other POHCs fall between the values shown. Surprisingly, benzene exhibits a CV of only 2%. Precision this good is highly unusual. Close examination of the analytical records has so far not revealed any anomalies or errors.

DRE

Destruction/removal efficiency (DRE) is defined as the disappearance of a feed constituent due to thermal destruction followed by removal by an air pollution control device, expressed as a percentage. In this paper, (1-DRE) will be reported expressed as one part per 100,000 parts by weight. If the breakpoint between an acceptable and unacceptable DRE is 99.99%, a (1-DRE) less than 10 exceeds 99.99% and is acceptable. Table 4 summarizes (1-DRE) results for the blast furnace before combustion inlet to stoves). Best DRE's were accomplished with the combustion device. This should be typical of all blast furnaces.

Dioxin/Dibenzofuran Emissions

Blast furnace gases before and after combustion and scrubber waters were analyzed by high resolution GC/MS. Neither class of compound was detected at the 1 ppt detection limit for the gas sample and the 1 ppb detection limit for the water samples.

Table 4. (1-DRE) - Blast Furnace

	Before Combustion	After Combustion
	(Parts per 100,000 parts)	
1,1 Dichloroethene	ND-24	ND-<1
Chloroform	ND-15	2-6
1,1,-Trichloroethane	ND-32	10-16
Trichloroethene	ND-3	ND-1
Benzene	842-1437	2-470
Tetrachloroethene	<1	<1
Toluene	9-16	<1
m/p-Xylene	8	<1-40
o-Xylene	12	2-7
Naphthalene	105	7-38

ND: not detected

Blast Furnace Operation

Table 5 summarizes the operating data, for the most part collected from plant instruments. At steady state, the blast furnace produces 4000 ton/day of metal. Total oxygen in the blast exceeds that of air because the air is oxygen enriched. Maintaining the blast air temperature above about 1725°F and constant is critical for maintaining combustion zone reactions. Therefore, the blast cycle for each stove is kept fairly short to avoid excessive temperature cycling.

Table 5. Summary of Blast Furnace Operating Data

Parameter	Average Value		
	Run 01	Run 02	Run 03
Blast Air Temperature, °F	1743	1770	1756
Blast Air Flowrate, dscfm x 10^3	116.5	116.6	116.2
Blast Air Pressure, psig	31.5	30.4	30.2
Total Oxygen in Blast, %	23.4	23.4	23.4
Flame Temperature, °F (calculated)	3389	3487	3402
Furnace Top Temperature, °F	337	379	325
Top Gas HV, Btu/scf (calculated)	90.7	89.3	91.5
Total Blast Gas Volume, scfm x 10^3	128.3	127.1	127.9
Waste Fuel Injection, gpm	60.6	59.5	60.4
Waste Fuel HV, Btu/lb	14,776	14,708	14,851

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FIELD EVALUATION OF SULFURIC ACID REGENERATION UNIT BURNING HAZARDOUS WASTE AS FUEL

R. C. Adrian, P. K. Ouchida
California Air Resources Board
Sacramento, California 95814

ABSTRACT

Rarely does an existing chemical processing facility provide the qualities needed for a hazardous waste destruction process without significant modifications to the facility. The system which is the subject of this study is a waste sulfuric acid regeneration unit. It is designed for combustion of many organic wastes from petroleum processing that contain high sulfur levels and have a high heating value. The furnace operates above 1600°F, has a large flame volume and long residence time. The combustion products are passed through a scrubber and a wet electrostatic precipitator for production of sulfuric acid. Thus, the organic feed is subjected to thermal, chemical and catalytic oxidation and combustion products are subject to absorptive and electrostatic separation.

The testing program for the system includes varying the operating conditions to evaluate emission effects of combustion air, furnace temperature, firing rate and fuel heat content. Baseline conditions are evaluated, with no added hazardous materials, burning spent acid and auxiliary natural gas fuels. Waste burn effects incorporate the addition of surrogates including carbon tetrachloride, Freon 113, 1,2,4 trichlorobenzene and penta chlorophenol. Analysis of emissions provide for DRE determination of the surrogates, POHCs dioxins and furans, and normal gaseous emissions.

INTRODUCTION

In a continuing investigation of alternative methods of hazardous waste disposal, the California Air Resources Board (CARB) has evaluated several existing commercial scale incineration systems. The selection of processes to be tested was guided not only by the severe Environmental Protection Agency (EPA) requirements of high temperature and long residence time but also by adjunct oxidative chemical reactions and possibilities of removal or neutralization of products of incomplete combustion (PICs).

Emission testing and chemical analysis of effluents for hazardous waste processing tend to be very labor intensive as well as requiring very specialized apparatus. It is thus neccessary to thoroughly prepare a test plan well in advance of testing. Analytical limitations may be a major factor in the sequence and duration of the tests.

Stauffer Chemical Company (SCC) has for years operated a spent sulfuric acid recovery plant in an industrial section of Los Angeles. The spent acid is primarily refinery alkylation acid, containing a variable percentage of organic compounds, some of which would be considered hazardous materials.

PURPOSE

The goals of this project were multifaceted. The primary objective was to measure emissions to determine if the California Department of Health Services (DHS) and the South Coast Air Quality

Management District (SCAQMD) would be justified in issuing operating permits for burning hazardous wastes in conjunction with the normal plant feedstocks. Additional objectives included evaluation of the destruction and removal efficiency (DRE) of the principal organic hazardous constituents (POHCs) across the burner, characteristics of PICs formed in combustion, and evaluation of operating conditions (failure modes) to define permit limitations in terms of temperature, feed composition, and firing conditions.

PROCESS DESCRIPTION

The SCC unit evaluated in this project was essentially a double contact-double absorption sulfuric acid plant. The facility incorporates a proprietary combustion chamber into which molten sulfur, alkylation acid, and waste materials can be injected either singly or in combination. The combustion chamber is ell-shaped, permitting either in-line firing (face firing) or impinging firing by injecting one or more of the fuels into the branch of the chamber (dutch-oven firing). Thus turbulence and residence time can be modified to optimize combustion efficiency. Additional heat to provide an approximately 1800°F temperature at the combustion chamber exhaust was supplied by augmenting natural gas.

Contiguous with the combustion chamber is an ash settling chamber which can also act as a secondary combustion chamber when a large flame volume is present. Normal feed to the system may contain as much as 10% ash; however, little of the ash drops out at this point or in the immediately following waste heat boiler. The waste heat boiler reduces the combustion gas temperature to about 700°F, while also producing process steam and electrical power.

Following the waste heat boiler, the cooled gas enters a direct spray, brick-lined scrubber (quench tower) which further cools the gas by flashing water from recirculating weak acid. The scrubber also removes most of the ash that may have carried through the boiler along with other minor impurities.

After this first scrubber, the gas is further cooled, condensed water is removed and the gas is compressed before passing through the first of two wet electrostatic precipitators (ESPs).

In various stages the gas is passed through a strong acid drying column and then through the first stage of a catlytic converter. SO_3 is then removed in a first stage absorber. Dilution air is added to promote SO_3 conversion and the gas passes through the converter second stage. The balance of SO_3 is removed in a second absorber. The gas then passes through a second ESP before being vented through the stack.

APPROACH

Emission standards for combustion of hazardous waste materials have not yet been developed except for the EPA acceptance of 99.99% or in some cases 99.9999% combustion efficiency for POHCs.

Prior to drafting the test plan, a panel of experts in the fields of combustion, chemistry, kinetics, and testing met to discuss the best test program for the Stauffer system. The test plan incorporated the panel recommendations. To evaluate the destruction efficiency of this process, it was concluded that the fuel normally encountered, spent alkylation acid, represented conditions equivalent to the most extreme chemical decomposition likely to be encountered if POHCs could be identified and remain constant. However, the evaluation of decomposition of certain added organics would provide a basis for comparison with other processes and hazardous material conversion efficiency.

It was concluded that the addition of a synthetic waste mixture consisting of carbon tetrachloride, 1,1,1 trichloroethane, 1,2,4 trichlorobenzene and hexachlorobenzene would provide a surrogate equivalent of the most difficult to destroy organic compounds and produce the least desirable PICS. Subsequently, it was found that hexachlorobenzene was not available and pentachlorophenol was substituted. Heating value, viscosity and laboratory detection limits were considered when determining the composition of this waste.

STAUFFER CHEMICAL COMPANY TEST OBJECTIVES

The test objectives for the Stauffer Chemical Company test were to allow determination of the baseline emissions while the plant is burning spent acid and natural gas. Specifically the following were to be determined:

1) Emissions while the plant was burning spent acid and typical waste fuels.

2) Destruction and removal efficiency of the process under at least three different operating conditions by using a special mixture of organic compounds as surrogates for the waste fuel.

3) HCl emissions from the stack.

4) Flow rate through the process using SF_6.

5) O_2, CO_2, CO, CH_4, TUHC, NO_x and SO_2 concentrations at the exit of the boiler and the stack.

6) Dioxin and dibenzofuran concentrations in the exhaust gases under different operating conditions at the exit of the boiler and at the stack.

7) Effects on emissions of modified modes of operation.

Also, as part of the test program, the capability to perform onsite chromatographic (GC) analysis was to be continued to be developed.

To accomplish the objectives set forth above, the following operating conditions were to be evaluated.

a) Baseline conditions: Spent acid was to be fed into the furnace at a rate of 20 to 30 gallons per minute. Natural gas was to be used to provide the balance of the heat requirements. Furnace conditions were to be varied in order to determine the operating range (envelope) for this process.

b) Normal waste fuel conditions: The furnace was to be operated under normal steady-state conditions except when the effects of operating parameters were being evaluated. The synthetic waste was to include carbon tetrachloride, hexachlorobenzene, trichlorobenzene, chlorophenols and sulfur hexafluoride.

c) Modified Furnace Operating Mode: The waste used in Section b was also be to be used for these tests, except perlite was to be added to represent typical solids content for expected waste fuels.

   i) Waste injected through burner in front face (when furnace at 1600°F and again when 1% excess O_2 in furnace).

   ii) Waste injected through burner in dutch oven at furnace conditions of 1600°F and 1% excess O_2 in furnace.

The total test time was to be approximately 7 days.

Parameters such as temperature, CO, TUHC, O_2 and NO_x were to be used in determining the acceptable ranges. Operating curves were to be obtained for excess O_2 ranging from 1% to 4% and temperature from 1600°F to 2000°F.

SCC was to monitor and record all operating conditions necessary to determine if the desired conditions have been reached and was be responsible for determining the length of time that these conditions can be expected to be maintained.

TEST PROGRAM

Testing actually took place over a three-week span. The first week was used in getting equipment set up, calibration, getting the process stabilized and running the baseline tests. The second

week was taken up with runs using the spent acid/synthetic waste mixture under normal firing conditions but with some variation in operating conditions. During the third week the failure modes of low temperature and burner reconfiguration were examined. Extremely low or high temperatures could not be met.

Samples were taken at two locations; in a horizontal duct between the waste heat boiler and the quench cooler, and in the stack about 90 feet above ground level. At each point, four Tedlar bag samples for volatile organics were taken per day. At the stack, two modified M-5 trains were run per day using XAD-2, one HCl train per day except the four days on which dioxin trains were run (also with XAD-2), and one M-5 train per day. At the boiler, one modified M-5 train per day for semi-volatiles, and intermittent bag samples for SO_2 and CO were taken.

Additionally, SCC personnel obtained process samples during the test periods for spent acid fuel, synthetic waste, stack precipitator rundown, quench cooler rundown and product acid.

The synthetic waste nominally contained 22.39% carbon tetrachloride, 21.22% 1,1,1 trichloroethane, 3.00% pentachlorophenol, 10.61% 1,2,4 trichlorobenzene, 30.62% diesel oil, 1.16% methanol and 11.00% perlite. This augmenting mixture was fired at about ten pounds per minute. This mixture was used throughout the program.

PROBLEMS ENCOUNTERED

Testing was originally planned to begin in September 1984; however, delays in receiving necessary experimental permits and variances resulted in an actual start time of February 26, 1985. Once testing had begun, there were surprisingly few delays caused by mechanical problems. Perlite in the synthetic waste mixture created a high erosive rate in the pumps and some clogging of the fuel system, but these were usually repaired at night or on weekends with little effect on the test schedule.

The fittings of the Teflon-lined stainless steel flexible sampling line at the waste heat boiler were found to deteriorate in the 13% SO_2, high temperature and high moisture atmosphere, and the line was replaced with Teflon. Also, at this sampling point a 50:1 dilution system was used to avoid damage to the continuous monitoring instruments.

The on-site chromatograph could not be used for quantitation during the test because of a shortage of standards in the proper concentration range. These data were reduced after the test.

It was not found possible to measure the combustion chamber exhaust flow rate by SF_6 injection. These rates were instead calculated by mass and heat balance around the waste heat boiler.

The low temperature failure mode test (1600°F) was found to be impractical. Unburned carbon and ash were not carried through the combustion chamber and caused an early shutdown. The test was later carried out at 1700°F successfully.

RESULTS

Field tests for the project were not completed until March 15, 1985, and laboratory analyses are not yet complete. Therefore, a discussion of the test data cannot be made at this time.

NONSTEADY INDUSTRIAL BOILER WASTE COFIRING TESTS

Robert J. DeRosier, Howard B. Mason, Ursula Spannagel, C. Dean Wolbach
Acurex Corporation
Mountain View, CA 94039

ABSTRACT

Hazardous waste thermal destruction field tests were conducted on a 13.9 kg/s (110,000 lb/hr) single burner package watertube boiler to evaluate the effect of nonsteady and off-design operation on destruction and removal efficiency (DRE) of principal organic hazardous constituents (POHC's). These tests were done to extend the earlier results for 11 boilers tested at nominally steady conditions which showed a mass weighted average DRE of 99.998 percent. The test series comprised triplicate baseline runs at steady conditions; 24 nonsteady runs with gas/waste cofiring; and 21 runs with oil/waste cofiring. For the baseline and selected nonsteady runs, POHC's were sampled with the volatile organic sampling train (VOST). for the majority of the nonsteady runs, POHC's were quantified with a "mini-VOST" protocol adapted for shorter sampling times and onsite analysis with the GC-Hall detector. The raw waste, containing methyl methacrylate, was spiked with carbon tetrachloride and monochlorobenzene. DRE results showed minimal effect of nonsteady operation on thermal destruction. The average DRE for 112 combinations of POHC and test runs was 99.998 percent. Only six values of DRE were less than 99.99 percent. The DRE showed no discernable correlation with carbon monoxide emissions. Two additional tests are planned to assess the general applicability of these results.

INTRODUCTION

Cofiring of combustible hazardous wastes with conventional fuels in industrial boilers is widely practiced in industry for energy recovery and as an economical means of disposal. Regulation of boiler cofiring was temporarily exempted from the 1981 Resource Conservation and Recovery Act (RCRA) which limited incineration DRE to 99.99 percent or higher. In the interim, EPA's office of Solid Waste and Emergency Response has conducted a regulatory impact assessment of cofiring thermal destruction pursuant to a boiler regulation. To support this assessment, the Hazardous Waste Engineering Research Laboratory has performed a boiler cofiring field test program (1).

An initial series of 11 boiler field tests were conducted to obtain a representative sampling of waste thermal destruction over the spectrum of design/waste combinations in use in industry, (2) through (5). The 11 test sites were selected to cover the range of industry practice with emphasis on gas- or oil-fired watertubes which is the predominant cofiring application. The test boilers were operated at nominally steady load, excess air and waste-to-fuel ratio to obtain a reference data base under steady operation. Within this context, the boiler settings corresponded to normal plant practice. A boiler test at each site generally consisted of triplicate POHC measurements at the nominal steady set point.

Composite results for the 11 test boilers showed generally high levels of thermal destruction. The composite DRE for a specific POHC averaged over all sites was 99.99 percent or higher for each of the volatile POHC's quantified. For semivolatile POHC's, average DRE's of 99.96 to 99.98 were experienced for four POHC's in a wood-waste-fired stoker operated at very high levels of excess air which partially quenched the combustion. The site specific DRE (averaged over all volatile POHC's) exceeded 99.99 percent for all sites except one boiler where unstable

burner operation was experienced. No definitive trend of DRE with carbon monoxide emissions was observed. However, the range of CO variation was small.

The test discussed in this paper was conducted to extend the earlier data base in two ways. First, nonsteady and off-design operating conditions were tested to evaluate how DRE is affected by upsets or transients. Second, a wide range of steady levels of load, excess air and waste-to-fuel ratios were tested to quantify DRE variations over the boiler operating envelope. As a secondary objective, a simplified version of the volatile organic sampling and analysis protocol was implemented to facilitate this type of transient and parametric testing.

APPROACH

The test boiler was a forced draft Combustion Engineering type 30-A-12 package watertube with a maximum capacity of 13.9 kg/s (110,000 lb/hr) of superheated steam. Natural gas or No. 6 oil is fired through a dual air register Coen dual-fuel burner. The burner has been retrofit with two steam atomized waste guns to fire a distillation byproduct containing methyl methacrylate. The waste was spiked with varying concentrations (0.5 to 4.5 percent) of carbon tetrachloride (CCl_4) and monochlorobenzene (C_6H_5Cl) to broaden the range of POHC's quantified and to introduce chlorinated compounds so that onsite GC-Hall analyses could be performed. Waste firing typically supplied 15 to 40 percent of total heat input to the boiler. The boiler normally operates in the range of 45,000 to 75,000 lb/hr with daily load variations of 20,000 lb/hr and occasional spot steam demands of 15,000 lb/hr. The boiler is normally operated automatically with a microprocessor controlled oxygen trim system. Waste flow is regulated manually.

Six test series, summarized in Table 1, were performed from April 24 to May 11, 1984. The initial boiler performance tests were performed to determine operational characteristics needed to plan the subsequent transient and off-design tests. Boiler characteristics monitored included: CO/O_2 relationships for gas and gas/waste cofiring; temperatures and emissions over the operating range; thermal response to transients; and O_2/fuel/waste response to transients. Baseline tests were run for comparison to earlier steady-state tests and as a reference for subsequent nonsteady tests. The baseline tests used the full sampling and analysis protocol as in the previous 11 boiler tests:

- Continuous flue gas monitoring for O_2, CO, CO_2, NO_x and unburned hydrocarbons
- Particulate and semivolatile organic sampling by the modified Method 5 train; post-test semivolatile analyses by GC/MS
- Volatile organic sampling by VOST; post-test analyses by direct desorbtion on GC/MS
- HCl sampling by a modified Method 6 train; analyses by titration
- Grab sample of waste and fuel oil; GC/MS POHC analyses

For the nonsteady tests, alternate volatile sampling protocols were needed with shorter sampling times and onsite analysis capability for refinement of the test matrix. Three approaches were tested: a semi-continuous VOST; a mini VOST; and a total organic chloride (TOCL) monitor.

The semi-continuous VOST used a single tenax trap directly plumbed to the stack via a heated sample line and gas conditioning system. A sample was drawn through the trap for approximately five minutes after which the trap was directly desorbed to a GC-Hall and the cycle repeated. Tests of this protocol during April 30 to May 4 showed good system response and sample recovery. Results were suspect, however, due to possible POHC deposition on the sample delivery system.

The TOCL protocol used a Hall detector to quantify total organic chlorides. Flue gas samples scrubbed, for HCl by a water or NaOH impinger, were drawn through a heated line directly to the Hall detector. The detector response was read on a recorder. Trial runs with this protocol showed qualitative correspondence with POHC throughput. Although the protocol needs further development, particularly for calibration procedures, it does show promise for indicating relative levels of POHC emissions.

The bulk of volatile organic sampling for the nonsteady tests was done with a simplified mini-VOST protocol. A single tenax trap was used with the VOST train for sample extraction at the stack. A 10 liter sample was drawn at 0.5 l/min. Following sampling, the traps were taken to an onsite GC-Hall and thermally desorbed. Trap preparation prior to testing was also done onsite. The nonsteady test protocol from May 7 to May 11 generally used the mini-VOST together with continuous monitors for flue gas criteria species, and waste grab samples. Occasional full VOST runs with post-test GC/MS were made for reference. No modified Method 5 sampling was done for nonsteady runs.

The variables tested in the nonsteady and off-design test series included:

- Upper and lower ranges of load, excess air and waste flowrate
- Increasing and decreasing excess air, load and waste flowrate
- Waste startup
- Poor waste atomization
- Waste atomizer spatial orientation relative to oil guns
- Sootblowing

Table 2 summarizes the baseline and nonsteady test runs. Runs with semi-continuous VOST are excluded because of suspected hysteresis in the POHC concentrations entering the tenax trap. The values for load, excess O_2, and waste flow are nominal values from plant board data. During transient runs, frequent or continuous recording of these parameters was made. The boiler operational settings were selected to deliberately induce smoking or CO excursions in the range of 200 to 1,000 ppm.

RESULTS

For the cofiring of the spiked waste, volatile POHC quantitation was made for three steady baseline tests, using full VOST, 24 gas/waste nonsteady tests (3 with full VOST), and 21 oil/waste nonsteady tests (3 with full VOST). On an overall basis, these test series produced 112 DRE data points for the composite of baseline and nonsteady quantitation of carbon tetrachloride, monochlorobenzene and methyl methacrylate thermal destruction.

DRE results show notably high levels of thermal destruction even during substantial upset conditions (Table 3). Of the 112 DRE values, only 6 were less than 99.99 percent. One of these low values, a DRE of 99.7 for CCl_4, is suspect due to apparent coelutriation of other compounds in the gas chromatograph during tenax desorption. For conservatism, the entire GC response was assumed CCl_4. Excluding this DRE value, the overall average DRE for the entire test program was 99.998 percent, which is the same average as for the earlier 11 steady-state tests.

Although there were significant variations in DRE from one run to another, the average DRE values were in a fairly narrow range. Table 4 compares the average DRE values for the three POHC's and for gas and oil firing. The DRE for methyl-methacrylate, averaged for both the VOST and modified method 5 measurements, was higher than the organic chlorides. Excluding the one outlier point, there was not a significant difference between the average DRE values for CCl_4 and monochlorobenzene, or between gas and oil firing. There was also a lack of marked difference in DRE due to boiler operating condition (Table 5). Although several of these conditions, particularly atomizer upsets and low O_2 firing, produced significantly degraded combustion efficiency, the average DRE's were mostly in the range 99.992 to 99.999 with no consistent trend in DRE variation. In this regard, there was a general lack of correlation with combustion efficiency indicators such as CO emissions, as shown in Figure 1. There was, however, a general agreement in magnitude between a pseudo-DRE for natural gas computed for the gas-fired runs (99.997) and the average POHC DRE (99.998).

The lack of DRE correlation or of consistant variation with operating conditions may mean that the near burner flame region is very efficient in destroying or at least pyrolyzing POHC's thereby suppressing effects of any physical or chemical variation. The resultant low levels of POHC in the stack appear to be in the range of background emissions. It is also suspected that gummy organic deposits on the boiler surfaces upstream of the sampling station were modulating the POHC

concentration somewhat by serving as a reservoir for adsorbtion and desorbtion.

Significant quantities of products of incomplete combustion (PIC) were quantified for nine compounds not present in the waste in detectable concentrations. The highest PIC concentrations were evident for tetrachloroethene and dichloromethane. The program average PIC/POHC mass ratio was 15 but individual run ratios varied from 0.3 to 190.

Two additional field tests are planned in 1985 to assess the generality of these results. Additional development and application of the mini-VOST protocol will also be performed.

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TABLE 1. SUMMARY OF TEST MATRIX

Date	Test Series	Fuel	Waste	Waste Percent of Thermal Input	Load lb/hr	O_2 Percent	Additional Variables	Sampling Protocol
April 24,26	Boiler Performance	Gas	NA	0	45,000-55,000	0.5-3.0		Continuous monitors
April 25	TSB Baseline	Gas	TSB	27-30	57,000-64,000	6.3-7.5		Full Protocol
April 27	Chlorinated Waste Baseline	Gas	TSB Spike	26-30	57,000-62,000	3.4-6.1		Full Protocol
April 30 May 04	Semi Continuous VOST Evaluation	Gas	TSB Spike	21-36	54,000-72,000	2.4-7.5	Load and O_2 Transients	Semi-continuous VOST, TOCL
May 07 May 09	Nonsteady and Off Design	Gas	TSB Spike	8.8-56	25,000-76,000	1.2-7.5	Load and O_2 Transients; Waste flow transients; Atomization; soot blow	Continuous monitors, mini-VOST, TOCL, periodic full VOST
May 10 May 11	Nonsteady and Off Design	Oil	TSB Spike	7.3-34	27,000-62,000	2.5-7.9	Load and O_2 Transients; Waste flow transients; Atomization; soot blow	Continuous monitors, mini-VOST, TOCL, periodic full VOST

TABLE 2. SUMMARY OF VOST RUNS

DATE	TIME	PRIMARY FUEL	STEAM LOAD (lb/hr)	O2 (%)	WASTE FLOW (gpm)	TEST CONDITIONS
25-Apr	1445	GAS	64000	6.40	3.7	TSB BASELINE UNSPIKED WASTE, VOST
25-Apr	1606	GAS	58000	6.70	3.7	TSB BASELINE UNSPIKED WASTE, VOST
25-Apr	1732	GAS	57500	7.00	3.8	TSB BASELINE UNSPIKED WASTE, VOST
27-Apr	1446	GAS	62000	5.38	4.0	TSB BASELINE, VOST
27-Apr	1626	GAS	57000	5.48	3.2	TSB BASELINE, VOST
27-Apr	1755	GAS	60000	4.70	3.7	TSB BASELINE, VOST
08-May	1154	GAS	60000	5.15	3.9	HIGH GPM BASELINE
08-May	1430	GAS	58000	4.92	3.9	HIGH GPM BASELINE
08-May	1447	GAS	60000	5.25	1.4	LOW GPM
08-May	1600	GAS	57000	4.70	2.4	NO WASTE ATOMIZATION
08-May	1642	GAS	59000	2.58	0.8	LOW WASTE GPM/O2
08-May	1710	GAS	55000	2.20	1.9	LOW O2 WASTE INCREASE
08-May	1740	GAS	54000	2.62	3.0	LOW O2 BASELINE
08-May	2108	GAS	60000	2.37	3.0	WASTE OIL STARTUP, VOST
08-May	2224	GAS	61000	2.90	4.2	LOW WASTE ATOM STEAM (VARY), VOST
08-May	2332	GAS	62000	4.30	2.8	SOOT BLOW
08-May	2357	GAS	76000	3.38	2.9	EA TRANSIENTS
09-May	20	GAS	73000	3.25	2.9	EA TRANSIENTS
09-May	643	GAS	62000	2.98	0.0	GAS BASELINE
09-May	921	GAS	63000	3.90	1.9	START UP DUAL VOST
09-May	1038	GAS	57000	3.98	3.5	LOW O2
09-May	1142	GAS	53000	2.87	1.0	LOW O2 & WASTE GPM
09-May	1311	GAS	51000	3.07	1.4	LOW O2 & WASTE GPM
09-May	1410	GAS	52000	3.70	3.5	GAS BASELINE
09-May	1508	GAS	25000	4.00	2.9	LOAD REDUCTION
09-May	1702	GAS	25000	4.08	3.3	LOW LOAD, MODERATE O2, VOST
09-May	1801	GAS	28000	4.00	3.1	LOW LOAD, LOW O2
09-May	1946	GAS	27000	3.50	0.9	LOW LOAD/O2/ WASTE GPM
09-May	2018	GAS	25000	4.17	2.6	WASTE & GPM TRANSIENTS
09-May	2153	GAS	55000	3.40	2.1	LOAD INCREASE
09-May	2301	GAS	35000	4.30	1.5	LOAD DECREASE
09-May	2346	GAS	32000	4.92	1.5	SOOTBLOW LOW LOAD
10-May	716	OIL	32000	4.80	0.0	BASELINE OIL
10-May	945	OIL	28000	4.72	0.0	BASELINE OIL
10-May	1030	OIL	28000	6.33	1.1	WASTE STARTUP
10-May	1132	OIL	27000	5.22	0.5	LOW LOAD/O2/GPM
10-May	1408	OIL	27000	5.22	0.4	LOW LOAD BASELINE
10-May	1452	OIL	40000	5.10	0.9	LOAD INCREASE
10-May	1647	OIL	44000	5.00	2.7	BASELINE OIL, MODERATE LOAD
10-May	1750	OIL	46000	4.36	3.0	HIGH WASTE GPM/MODERATE LOAD
10-May	1831	OIL	50000	4.64	2.6	MODERATE O2/HIGH GPM
10-May	1917	OIL	47000	4.69	1.5	WASTE GPM TRANSIENTS
10-May	2012	OIL	47000	4.62	2.7	START INVERTED SPRAY
10-May	2055	OIL	50000	4.63	3.4	INVERTED SPRAY
10-May	2134	OIL	47000	4.87	0.9	INVERTED SPRAY
10-May	2222	OIL	46000	4.87	2.9	SOOTBLOW
10-May	2313	OIL	50000	3.64	3.1	MIN. USABLE WASTE ATOMIZATION
11-May	7	OIL	50000	3.85	2.9	MIN. USABLE WASTE ATOMIZATION
11-May	1330	OIL	50000	5.32	0.0	LOAD INCREASE, NO WASTE
11-May	1430	OIL	62000	3.88	2.9	WASTE STARTUP
11-May	1528	OIL	60000	5.29	2.9	HIGH BASELINE
11-May	1723	OIL	60000	5.40	2.5	HIGH BASELINE
11-May	2033	OIL	60000	4.48	3.0	REDUCED WASTE ATOMIZATION
11-May	2118	OIL	60000	4.30	2.9	SOOTBLOW
11-May	2225	OIL	60000	4.30	3.0	POOR WASTE ATOMIZATION, VOST
11-May	2319	OIL	61000	4.86	3.5	HIGH O2, VOST
12-May	9	OIL	60000	5.00	3.3	HIGH O2, VOST

TABLE 3. DRE GROUPED BY TEST CONDITIONS

DATE	TIME	GC #	FUEL	LOAD	CONDITIONS	CCL4	CHLORO-BENZENE	MMA
25-Apr		MM5	GAS	59000	TSB BASELINE	NA	NA	99.9997
27-Apr		MM5	GAS	59000	TSB BASELINE	NA	NA	99.999987
10-May	1408	96	OIL	27000	LOW LOAD BASELINE	99.996	99.9996	
10-May	945	90	OIL	28000	LOW LOAD BASELINE	NA	NA	
10-May	716	87	OIL	32000	LOW LOAD BASELINE	NA	NA	
10-May	1647	101	OIL	44000	BASELINE OIL, MODERATE	99.9988	99.9997	
10-May	1750	103	OIL	46000	HIGH GPM/MODERATE LOAD	99.9996	99.9998	
10-May	1831	104	OIL	50000	MODERATE O2/HIGH GPM	99.99997	99.99993	
09-May	1410	67	GAS	52000	GAS BASELINE	99.998	99.9986	
08-May	1740	48	GAS	54000	LOW O2 BASELINE	99.9997	100	
27-Apr	1626	FULL VOST	GAS	57000	BASELINE	99.997	99.99991	99.99992
25-Apr	1732	FULL VOST	GAS	57500	TSB BASELINE	NA	NA	99.99989
08-May	1430	36	GAS	58000	TSB HIGH GPM BASE	99.9995	99.997	
25-Apr	1606	FULL VOST	GAS	58000	TSB BASELINE	NA	NA	99.99987
27-Apr	1755	FULL VOST	GAS	60000	BASELINE	100	99.99988	99.999897
08-May	1154	35	GAS	60000	TSB HIGH GPM BASE	99.99990	99.99991	
12-May	9	FULL VOST	OIL	60000	HIGH O2	99.99994	99.99988	99.9997
11-May	1528	144	OIL	60000	HIGH BASELINE	99.98	99.998	
11-May	2319	FULL VOST	OIL	61000	HIGH O2	99.9997	99.9998	99.9996
27-Apr	1446	FULL VOST	GAS	62000	BASELINE	99.996	99.99989	99.9998
25-Apr	1445	FULL VOST	GAS	64000	TSB BASELINE	NA	NA	99.9997
11-May	7	122	OIL	50000	MIN. USABLE ATOM	99.9997	99.99989	
10-May	2313	118	OIL	50000	MIN. USABLE ATOM	99.9998	99.998	
08-May	1600	40	GAS	57000	NO WASTE ATOMIZER	99.998	99.98	
11-May	2225	FULL VOST	OIL	60000	POOR ATOM	99.9998	99.9998	99.9997
11-May	2033	1 TRAP VO	OIL	60000	REDUCED ATOM.	99.99989	99.9997	99.9988
08-May	2224	FULL VOST	GAS	61000	LOW ATOM STEAM (VARY)	100	100	99.996
09-May	20	53	GAS	73000	EA TRANSIENTS	100	99.994	
09-May	2108	77	GAS	25000	GPM TRANSIENTS	99.9990	99.9994	
10-May	1030	92	OIL	28000	WASTE STARTUP	99.989	99.993	
10-May	1917	105	OIL	47000	GPM TRANSIENTS	99.9997	99.99989	
08-May	2108	FULL VOST	GAS	60000	WASTE OIL STARTUP	99.9997	99.997	99.9996
11-May	1430	143	OIL	62000	WASTE STARTUP	99.998	100	
10-May	2134	109	OIL	47000	INVERTED SPRAY	99.9990	99.99992	
10-May	2012	107	OIL	47000	START INVERTED SPRAY	99.9989	99.9998	
10-May	2055	108	OIL	50000	INVERTED SPRAY	99.9994	99.99994	
09-May	1508	69	GAS	25000	LOAD REDUCTION	99.997	99.9990	
09-May	2301	83	GAS	35000	LOAD DECREASE	99.9995	99.9997	
10-May	1452	97	OIL	40000	LOAD INCREASE	99.998	99.9996	
09-May	2153	81	GAS	55000	LOAD INCREASE	99.9997	99.99993	
09-May	921	57	GAS	63000	START UP DUAL VOST	99.99994	99.9994	
09-May	1702	FULL VOST	GAS	25000	LOW LOAD, MODERATE O2	99.9997	99.9997	99.9997
09-May	1946	76	GAS	27000	LOW LOAD/O2/GPM	99.998	99.998	
10-May	1132	94	OIL	27000	LOW LOAD/O2/GPM	99.994	99.995	
09-May	1801	74	GAS	28000	LOW LOAD, LOW O2	99.998	99.9989	
09-May	1311	66	GAS	51000	LOW O2 & GPM	99.987	99.995	
09-May	1142	62	GAS	53000	LOW O2 & GPM	99.999904	100	
08-May	1710	46	GAS	55000	LOW O2 WASTE INCREASE	100	99.9998	
09-May	1038	60	GAS	57000	LOW O2	99.9998	99.9989	
08-May	1642	42	GAS	59000	LOW GPM/O2	99.998	99.998	
08-May	1447	38	GAS	60000	LOW GPM	99.7	100	
11-May	2118	1 TRAP VO	OIL	60000	SOOTBLOW	100	99.9998	99.9995
10-May	2222	111	OIL	46000	SOOTBLOW	99.9993	99.9998	
08-May	2332	50	GAS	62000	SOOT BLOW	99.998	99.97	
09-May	2346	86	GAS	32000	SOOTBLOW LOW LOAD	99.9996	99.9998	

TABLE 4. DRE SUMMARIES

POHC	No. tests	Series	Average DRE
MMA	16	All runs	99.9995
CCl_4 + Clϕ[b]	96	All runs	99.9949 (99.9980)[a]
CCl_4	48	All runs	99.9919 (99.9981)[a]
Clϕ	48	All runs	99.9980
CCl_4	21	Oil firing	99.9975
CCl_4	27	Gas firing	99.9874 (99.9985)[a]
Clϕ	21	Oil firing	99.9991
Clϕ	27	Gas firing	99.9971

[a]Excluding one low (99.7 percent) value for CCl_4.
[b]Monochlorobenzene

TABLE 5. DRE SUMMARIES

Test series	Points	DRE percent	
		CCl_4	$Cl\phi$
Baseline	14	99.9974	99.9994
O_2 transients	1	100	99.994
GPM transients	5	99.9971	99.9979
Load transients	5	99.9988	99.9995
Low O_2, load, waste	10	99.9674 (99.9972)[a]	99.9983
Atomization upsets	6	99.9995	99.9962
Inverted atomizer	3	99.9991	99.9999
Sootblowing	4	99.9992	99.9924
Total	48	99.9919 (99.9981)[a]	99.998

[a]Excluding one low value for CCl_4.

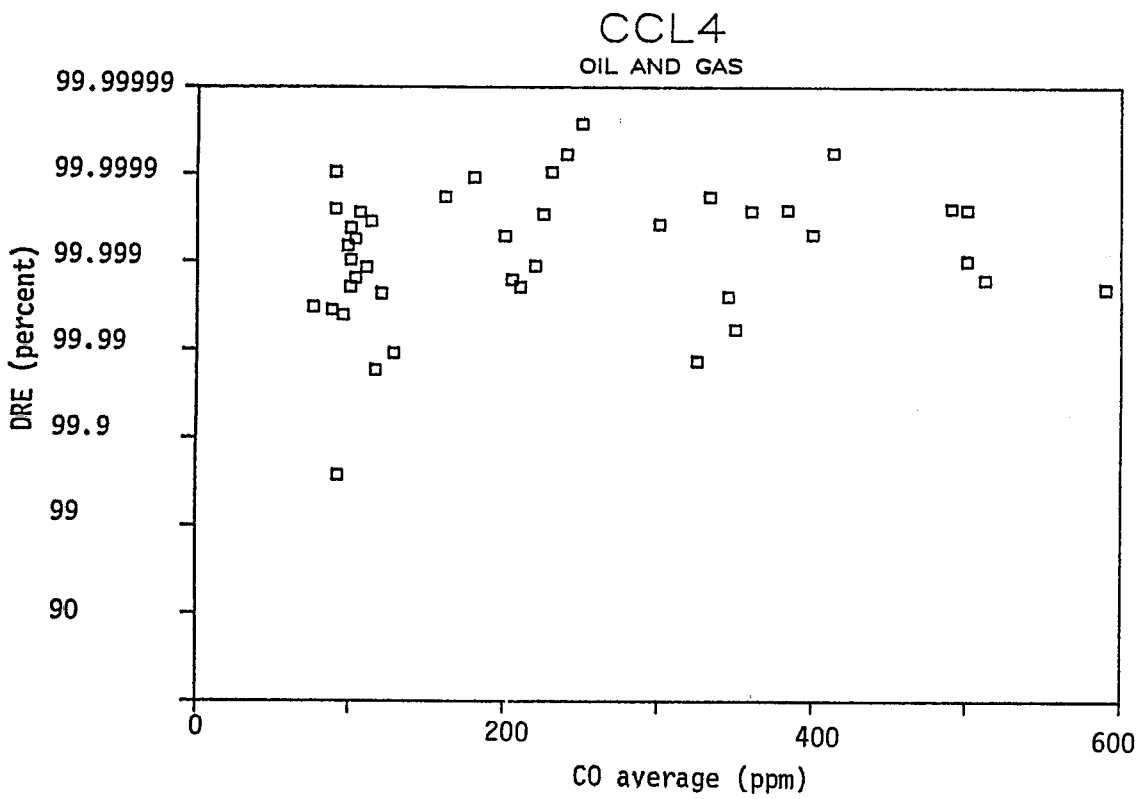


Figure 1. CCl_4 DRE versus CO average.

MOUSE - A COMPUTERIZED UNCERTAINTY SYSTEM FOR ENVIRONMENTAL ENGINEERING ANALYSES

Albert J. Klee
Hazardous Waste Engineering Research Laboratory
U. S. Environmental Protection Agency
Cincinnati, Ohio 45268

ABSTRACT

Environmental engineering calculations involving uncertainties expressed as probability distributions are far beyond the capabilities of hand analysis for any but the simplest of models. There exist a number of computer simulation languages involving Monte Carlo methods that certainly can do the job, but learning such languages and implementing them on all computers is not the quickest nor the easiest of tasks.

MOUSE (an acronym for Modular Oriented Uncertainty System Emulator) deals with the problem of uncertainties in models that consist of one or more algebraic equations. It was designed to be used by those with little or no knowledge of computer languages or programming. It is compact (and thus can run on almost any digital computer), easy and fast to learn, and has most of the features needed for substantive uncertainty analysis (built-in probability distributions, plotting and graphing capabilities, sensitivity analysis, interest functions for cost analyses, etc.).

MOUSE has been used within USEPA for studying the migration of pollution plumes in streams, for analyzing the uncertainties in establishing regulations for hazardous wastes in landfills, and for investigating the variabilities inherent in pollution control cost estimation.

INTRODUCTION

If we define a model as a physical or symbolic representation of reality, we find among the set of all models one called the mathematical model of which one particular type consists of a series of one or more algebraic equations. Mathematical models of this type are extremely important for they are found almost everywhere, including economics, engineering, and science. The use of an equation is understood by almost everyone; in a somewhat "inelegant" sense, numbers "go into" the equation and an answer is obtained. For example, consider the following very simple equation,

$$Y = AB \qquad [1]$$

where Y might stand for the cross-sectional area of a heating duct, given that A is its height and B is its width. To "solve" equation 1 one has to know the values of A and B. If A is equal to 2, for example, and B is equal to 15, then Y = 2(15) = 30. Often, however, we are not sure of the values of A or of B. A might be 3 and B might be 20; in such case, Y would be equal to 60, not 30. The greater our uncertainty about the input variables A and B, clearly the greater our uncertainty about the output variable, Y.

TRADITIONAL APPROACHES TO UNCERTAINTY

The most often encountered approaches to uncertainty in mathematical models are (1) the best value approach, (2) the conservative approach, and (3) sensitivity analysis. The first two are single-value approaches. The "best" in "best value" is not precisely defined; generally it refers

to some measure of central tendency such as an average or a mode. In our duct problem, we might suppose that the value of A of 2 and of B of 15 are average values. Hopefully, the answer of 30 is also some sort of average value. As we shall see, however, this is not always the case. Admittedly a simple technique, in reality the best value approach is more a matter of ignoring uncertainty than it is of any conscious effort to come to grips with it.

The conservative approach does make an attempt to consider the consequences of uncertainty. As the name implies, the input values selected are not the average or most likely ones but rather those that produce conservative results with regard to the consequences of over- or underestimating. For example, in the conservative approach for the duct example, the values of A and B selected to go into equation 1 would be greater than their average values of 2 and 15 since overestimation is probably better than underestimation in this case. If "best" values were used, there is a good chance that the duct area would be underestimated.

The popular, traditional approach to the problem of uncertainty is sensitivity analysis. Sensitivity analysis is a combination of both the best value and conservative approaches since it usually starts with a best value estimate, followed by a change or perturbation in one of the input variables (holding all other input variables at their previous values). The perturbation can be either an increase or a decrease in the value of the variable and hence can be either of a "conservative" nature or a "liberal" one. For example, to examine the effects of a modest change in A in equation 1, we might increase the value of A by 10% over its "best" estimate value of 2. A 10% increase in A (to 2.2) results in an estimated Y-value of 33. If a value of A of 2.2 is "reasonably likely" to occur, then the sensitivity analysis suggests that a value of Y of 33 is also "reasonably likely" to occur.

PROBLEMS WITH TRADITIONAL APPROACHES

As has been mentioned, the best value approach really does not address the problem of uncertainty at all. For one thing, best input values do not necessarily have high probabilities of occurring. There is another difficulty with the best value approach which is not generally recognized. The difficulty arises when the algebraic model contains non-linear elements such as multiplications or divisions and the variables are correlated. If variables A and B of equation 1 were correlated, for example, the average of Y would not be equal to the average of A times the average of B. In point of fact, if A and B were positively correlated, then the average of Y would be greater than the product of the averages; conversely, if A and B were negatively correlated, the average of Y would be less than the product of the averages.

The conservative approach also has its deficiencies. For one thing, in a complex calculation involving many equations and many input variables (some of which may be correlated) it may not be obvious what values of the input variables constitute "conservative" ones with respect to the output. Secondly, because conservative input values generally are those with a low probability of occurring, the estimates obtained by using such values perforce will not have a high probability of occurring. It should be recognized that the point estimates involved in using either the best value or the conservative approach do not utilize all of the information that is usually available. One usually has at least <u>some</u> idea of the uncertainties in the input figures.

Sensitivity analysis, being largely an amalgamation of elements of both the best value and conservative approaches, suffers the defects of both methods. An arbitrary change in the value of an input variable, even though the change falls within the expected range of the variable, tells us little about the likelihood of occurrence of the new estimate obtained. In other words, if we know little about the likelihood of such a change occurring, it follows that we know little about the likelihood of the calculated output occurring. Furthermore, in sensitivity analysis all other variables are held at their previous values, the so-called "all other things being equal" view of the world. The problem is that "all other things" are seldom equal. In actuality, the change we introduce in a variable under sensitivity analysis may well be either mitigated or intensified by what is happening to the other variables. In short, sensitivity analysis does not show the combined net

effect of changes in all variables or the likelihood of various changes occurring together. Viewed in this manner, the traditional sensitivity analysis can be misleading.

ALTERNATIVE SOLUTIONS TO THE UNCERTAINTY PROBLEM

Let us examine three alternative solutions to the problem of uncertainty. The first method, illustrated in Figure 1, is Direct or Complete Enumeration. The model of equation 1 is employed, and we assume the uncertainties of A and B as given in the two probability distributions for these variables shown in the upper left-hand corner of the figure. In other words, we suppose that there is a 25% chance that A is equal to 1, 50% that it is equal to 2, and 25% that it is equal to 3. For B, there is a 50-50 chance that it is equal to either 10 or 20. (For this simple example, we assume no correlation between the two input variables.) In complete enumeration we list all of the possible combinations of the input variables and then calculate the probabilities of these combinations occurring. In this example there are 3 choices for A and 2 for B, resulting in 6 possible outcomes for Y. The probabilities of these combinations are shown in the middle top of the figure. Since some of the combinations are duplications, the table of combinations of A and B may be simplified to the 5 entries shown at the upper right of the figure for method 1. The average value of Y is shown to be 30. At the bottom of the figure for method 1 is a graph of the frequency or probability distribution of Y. Note that the most likely value is not the average but rather values to either side of it. Furthermore, one of the extreme values (Y = 60) has a higher probability of occurrence than has the average value. As can be seen, the complete enumeration method tells us everything about the distribution of Y, including its mean, standard deviation, minimum, maximum, and the probability of occurrence of any value of Y.

The second method is the Probability Calculus method. The method, as the name implies, requires some knowledge of the calculus of probabilities (sometimes known in engineering as the "propagation of error"). Using the model of equation 1 as before, the method is also illustrated in Figure 1. The error formula is given in the figure, and involves three terms and knowledge of the variances of A and B. The latter are calculated, as is shown in the figure, from the probability distributions of A and B given previously in the Direct Enumeration method. The error formula shows the variance of Y to be 225, i.e., its standard deviation = 15. The probability calculus method produces no more than the mean and the standard deviation of the output (i.e., Y) distribution. The standard deviation alone, however, is not sufficient to determine the nature of the uncertainty in a mathematical model.

The third method is a form of Monte Carlo simulation known as Model Sampling. The idea of Model Sampling is relatively simple:

a. A value for each of the input variables is drawn at random from its respective probability distribution, and the model is computed using this particular set of values.

b. The above process is repeated many times. Since the results vary with each iteration, the outputs themselves (i.e., the Y's) are gathered in the form of a probability distribution. Thus the uncertainties of the model's in- puts are transferred to the output which can then be studied and subsequently utilized in decision processes.

The procedure is shown schematically in Figure 1. The output of the Monte Carlo simulation method becomes almost identical to that of complete enumeration as the number of iterations becomes large. Unlike Direct Enumeration, however, large and/or complex problems are tractable and continuous uncertainty distributions are easily handled. The Monte Carlo simulation method forms the basis for MOUSE, the computerized uncertainty analysis system which is the subject of this paper.

MOUSE, A COMPUTERIZED UNCERTAINTY ANALYSIS SYSTEM

Monte Carlo simulation requires the use of a digital computer for any substantive problem. It is important, therefore, to consider the desirable characteristics

METHOD 1: DIRECT (COMPLETE ENUMERATION)

MODEL: Y =AB

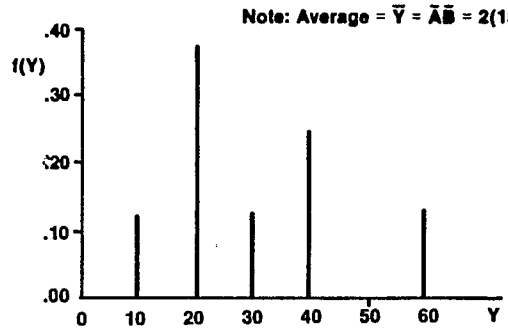
A	p(A)
1	.25
2	.50
3	.25

B	p(B)
10	.50
20	.50

A	B	AB	p(AB)
1	10	10	.125
2	10	20	.250
3	10	30	.125
1	20	20	.125
2	20	40	.250
3	20	60	.125

AB	p(AB)
10	.125
20	.375
30	.125
40	.250
60	.125

Note: Average = $\bar{Y} = \bar{A}\bar{B} = 2(15) = 30$



PROBABILITY DISTRIBUTION OF Y (= AB)

METHOD 2: PROBABILITY CALCULUS

MODEL: Y = AB

ERROR FORMULA IS var (AB) = var (Y) = $\bar{A}^2$ var (B) + $\bar{B}^2$ var (A) + var (A) var (B)

$\bar{A} = 2$ and $\bar{B} = 15$

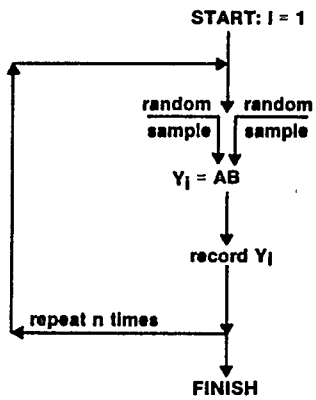
p(A)	A	$(A - \bar{A})^2$	$p(A)(A - \bar{A})^2$
.25	1	1	.25
.50	2	0	.00
.25	3	1	.25
		var(A) =	.50

p (B)	B	$(B - \bar{B})^2$	$p(B)(B - \bar{B})^2$
.50	10	25	12.5
.50	20	25	12.5
		var (B) =	25.0

therefore, var (Y) = 2^2 (25.0) + 15^2 (0.50) + (0.50)(25.0) = 225

and std (Y) = 15

METHOD 3: MONTE CARLO SIMULATION



FROM COLLECTION OF Y's OBTAIN:

1. MEAN
2. STANDARD DEVIATION
3. COEFFICIENT OF VARIATION
4. MINIMUM
5. MAXIMUM
6. GRAPH OF FREQUENCY DISTRIBUTION
7. GRAPH OF CUMULATIVE FREQUENCY DISTRIBUTION

Figure 1. Alternative Solutions to the Uncertainty Problem

of any computerized uncertainty analysis system.

Table 1 presents a comparison among general purpose computer languages, general purpose simulation languages, and MOUSE (the system introduced in this paper) for uncertainty problems that deal in sets of algebraic equations. Table 1 is not designed to devalue the capabilities of either general purpose computer languages or general purpose simulation languages. MOUSE is a restricted special purpose simulation language and the table makes its comparison assuming that the problem at hand is of this restricted form, i.e., that the model consists of one or more algebraic equations. For such restricted models, MOUSE is clearly superior to the other two groups of languages. It is concise, powerful, and convenient to use. MOUSE can solve uncertainty problems faster and easier than can other languages. With MOUSE, the user's attention is on problem-solving, rather than on the details of coding a program to compute a solution. Further, MOUSE programs are easier to understand, easier to explain to others, and easier to modify than are general purpose languages.

APPLICATIONS OF MOUSE

It is not possible to go into the details of MOUSE in this paper (a detailed example of a MOUSE application within USEPA will be presented in the following paper titled "Uncertainties and Incineration Costs: Estimating the Margin of Error," by Gordon Evans) but a typical output is shown in Figure 2. Other applications of MOUSE in EPA have included: a facilities design tool cost model to construct and close a surface impoundment or landfill facility, a waste pile costing model required to construct and close a waste pile facility, the use of engineering fault tree analysis in failure analysis of RCRA land disposal facilities, cost models for systems for the incineration of hazardous wastes, and an investigation of a model to determine an appropriate level for regulating organic toxicants in hazardous wastes.

TABLE 1. A COMPARISON OF COMPUTER LANGUAGES FOR UNCERTAINTY ANALYSIS

Element \ Language	General Purpose Languages (e.g., FORTRAN, PASCAL, BASIC)	General Purpose Simulation Language			MOUSE
		GPSS	SIMSCRIPT	SLAM	
Simplicity	complex	simple	complex	complex	simple
Built-in Probability functions	no	a few	yes	yes	yes
Built-in Interest functions	no	no	no	no	yes
Automatic Output	no	yes	yes	yes	yes
Decimal Numbers	yes	no	yes	yes	yes
Automatic Sensitivity Analysis	no	no	no	no	yes
Correlation Among Variables	must be programmed	no	must be programmed	must be programmed	yes
De-bugging Simple	no	no	no	no	yes
Transportability	any computer	mini and mainframes	mini and mainframes	mini and mainframes	any computer
Aid To Deriving Probability Distributions	no	no	no	no	yes
Ability to Expand by Modules	yes	no	no	yes	yes

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****************************************
*    DISTRIBUTION FOR QUANTITY FACTOR    *
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NUMBER OF ITERATIONS = 1000

MEAN = 19814.26758

MINIMUM = 5150.11523

MAXIMUM = 73638.00000

STANDARD DEVIATION = 12020.29688

COEFFICIENT OF VARIATION, % = 60.66485

LOWER LIMIT	NUMBER OF ENTRIES	PERCENT ENTRIES	CUMULATIVE % ENTRIES	CUMULATIVE COMPLEMENT	DISTRIBUTIONS * = FREQUENCY DISTRIBUTION O = CUMULATIVE DISTRIBUTION
1900.0000	21.	2.10	2.10	97.90	*O****
6600.0000	221.	22.10	24.20	75.80	**********O**********
11300.0000	253.	25.30	49.50	50.50	**********O**********
16000.0000	185.	18.50	68.00	32.00	**********O****
20700.0000	95.	9.50	77.50	22.50	********** O
25400.0000	55.	5.50	83.00	17.00	********** O
30100.0000	37.	3.70	86.70	13.30	********** O
34800.0000	46.	4.60	91.30	8.70	********** O
39500.0000	32.	3.20	94.50	5.50	********* O
44200.0000	22.	2.20	96.70	3.30	****** O
48900.0000	10.	1.00	97.70	2.30	*** O
53600.0000	5.	0.50	98.20	1.80	** O
58300.0000	12.	1.20	99.40	0.60	**** O
63000.0000	3.	0.30	99.70	0.30	** O
67700.0000	2.	0.20	99.90	0.10	* O
72400.0000	1.	0.10	100.00	0.00	* O

Figure 2. Statistics, Histogram and Graphs Produced by MOUSE for a Typical Problem

UNCERTAINTIES AND INCINERATION COSTS: ESTIMATING THE MARGIN OF ERROR

Gordon M. Evans
United States Environmental Protection Agency
Hazardous Waste Engineering Research Laboratory
Cincinnati, Ohio 45268

ABSTRACT

It is standard practice in cost estimation to place percentage confidence bands around final estimates in order to indicate the expected margin of error. This envelope of variability offers no useful information of the expected occurance of any point estimate within that band. An estimation procedure that utilizes an in-house computer program overcomes this limitation by producing estimates in the form of frequency distributions which represent the the probabilities associated with points along the entire range of expected outcomes. This paper presents the results of an application of this technique to the problem of estimating the costs involved in the incineration of hazardous wastes. The end result is the production of information that allows a decisionmaker to explicitly relate the consequences of a wrong decision (in terms of dollars lost) to the margin of error he chooses to accept.

INTRODUCTION

The goal of this paper is to provide the reader with a description of an economic uncertainty analysis conducted on hazardous waste incineration costs at the U.S. Environmental Protection Agency's (USEPA) Hazardous Waste Engineering Research Laboratory (HWERL). This project utilized MOUSE (Modular Oriented Uncertainty Systems Emulator) (1), a computer utility program developed by Dr. Albert J. Klee of that Laboratory. This computer program allows an analyst to define a model's crucial variables in probabilistic terms. These probabilities provide information on the uncertain nature of the crucial variables and are specified through sampling the opinions of revelant experts. The primary objective in applying this stochastic process to a cost engineering model (in this case, one constructed to provide estimates on the costs associated with the incineration of hazardous wastes) is simply to provide added information to the decision process.

With uncertainty analysis, the decisionmaker is offered cost estimates which allow him to explicitly incorporate his own risk preferences into the decision process. These estimates are generated with the help of the MOUSE program and come in the form of frequency distributions. In essence, these frequency distributions reflect expert opinion on the various sources of uncertainty inherent in the system under question. In the case at hand, the final MOUSE estimates show the range of values that selected direct and indirect cost items may take, the frequency with which each particular value within that range is predicted to occur, and the associated statistical information regarding each distribution. Thus, with the MOUSE output, the decision maker is not limited to a single point estimate for each system component; instead, he recieves both graphical and statistical information

that will allow him to ascertain with great confidence the margin of error associated with any estimate falling within that range.

The utility of this added information is highlighted through reference to the typical cost estimating situation. Normally, such a procedure produces an estimate in the form of a single point. The problem lies in the fact that this traditional estimating method offers no useful information on the possible range of outcomes or the probability of their occurance. Therefore, the traditional point estimate is subject to some overall margin of error.

It is important to understand that this term "margin of error" is often used without fully understanding it's meaning. As used within this paper, the phrase "margin of error" encompasses two separate and distinct notions; measurement error and the error that results from the effect of the system's underlying uncertainty (2). It should be clear that the decisionmaker, when offered a point estimate, is seldom given complete information regarding the meaning of the margin of error. It has been standard practice to attempt its representation through the construction of an envelope of variability around the point in question (e.g., "the probable accuracy is $\pm$ 40 percent") (3). While this technique provides an indication as to the possible range of outcomes (taking into account the potential for measurement error), it says nothing significant about the probability associated with any particular point within that range. For all intents and purposes, the occurence of each outcome within that confidence band is equally likely. Thus, while the technique of constructing an envelope of variability tries to deal explicitly with the margin of error concept by offering a solution to the problem of measurement error, it fails to provide the decisionmaker with any useful information on the underlying uncertainty. Nonetheless, it is possible to obtain a realistic appraisal of the margin of error. By utilizing a cost model which incorporates the uncertainty approach afforded via the MOUSE technique, a decisionmaker is given all the information he needs to fully comprehend the real margin of error associated with a given estimate.

Complete information on the margin of error has added significance when one considers the constraints placed on decisions that are often made within institutional settings. It is not at all unrealistic to assume that the average decisionmaker (or the institution he represents) will attempt to avoid risky situations; he will tend to be risk adverse. Economists recognize that people are primarly motivated to pursue their own self-interest. Thus it is assumed that the negative consequences to a decisionmaker are likely to be greater for underestimating the cost of a given project (here the cost to incinerate a hazardous waste) than for overestimating that same cost (4).

To help emphasize this point consider for a moment the plight of a risk adverse corporate executive (or government bureaucrat) who is asked to choose between two competing investment projects, "A" or "B". Both of these projects will accomplish the same goals and both will involve considerable capital expenditures. Suppose our executive is offered cost estimates for both projects; each with 40 percent envelopes of variability attached to them. Suppose as well that Project A has the lower point estimate value. With all other factors being equal, and recognizing the risk adverse nature of our decisionmaker, we may assume that he will likely choose Project A. After all, he possesses no real information on either project's underlying uncertainty. As far as he is concerned, all values falling within the two 40 percent confidence bands have an equal likelihood of occurring. As such, the expected value of Project A remains less than that of Project B.

Despite the addition of the envelopes of variability, this decisionmaker was offered no real understanding of the true margin of error associated with either Project's estimate. Now, if in retrospect, he finds that the expenditures on Project A were in fact lower than estimated, he can be certain that his credibility within that institutional setting will be enhanced. More importantly from his perspective, he will have successfully avoided placing himself (and the institution he represents) into the risky situation he had

hoped to avoid. Conversely, if the actual expenditures end up being significantly greater than estimated, our risk adverse executive will find himself in a most uncomfortable position.

Regardless of the final outcome, the point that needs to be emphasized is that this decisionmaker did not have access to any information that would have allowed him to ascertain the true margin of error associated with either estimate, thereby giving him final control over the level of risk he chooses to accept. By offering a decisionmaker a cost estimate in the form of a MOUSE generated frequency distribution, he will be able to explicitly relate the negative consequences of a wrong decision (in terms of dollars lost) to an acceptable margin of error. In other words, he will now be able to quantify his attitudes toward risk and act accordingly.

In terms of this example, suppose that a MOUSE output had indicated that the mean estimate for Project A was less than that for Project B. This is similar to the previous situation where the value of the point estimate offered for Project A was smaller. But suppose that after viewing the frequency distributions for both estimates it was obvious to this decision maker that the range of estimates generated for Project A exhibited a much greater variance. This risk adverse decisionmaker, now able to explicitly consider the system's uncertainity, might well find that selecting Project B actually minimizes the margin of error thereby reducing the level of risk he accepts. With the simple assumptions offered here, it is quite plausible that at a 95% confidence level the estimated cost of Project B would be lower. Once our decisionmaker determines the level of risk that is acceptable to him (5 percent) he is able to select from among the project estimates that which has the lowest cost and which, at the same time, satisfies his preferences toward risk.

By using an example of estimating the cost of hazardous waste incineration, this paper will show how the application of uncertainty analysis (via MOUSE) can improve the nature of the information provided in the decisionmaking process. Specifically, this paper will use the incineration issue to provide an answer to one major question: "How much more information regarding the margin of error does uncertainty analysis provide a decision maker over the traditional practices?"

APPROACH

Before an uncertainty analysis could be conducted, it was necessary to develop a mathematical model which would represent the engineering and cost relationships for each of the 3 major incinerator configurations (i.e., rotary kiln, liquid injection, and multiple hearth). The specification of these relationships had to be flexible enough to allow for a representation of incinerators operating under a variety of design parameters and utilizing various hazardous waste streams. Once specified, these engineering relationships could then be used to determine the type and size of the incinerators' structural components and to specify the resources (e.g. utilities, labor) necessary for its' operation. Experts could then be used to specify the cost of these items in probabilistic terms, and once formatted, these judgments could be incorporated into the MOUSE program.

Upon reviewing the incinerator cost literature, it became clear that none of the existing cost models readily lent themselves to the MOUSE programing requirements (5,6,7). For example, the cost model developed by Industrial Economics (6) for the USEPA's Office of Solid Waste was constructed using a linear programming approach (i.e., finding the least cost configuration on a production frontier). Unfortunately however, a linear programming approach was incompatible with the MOUSE technique. One model, however, was nearing completion and was being constructed in a format ideally suited to the MOUSE programming requirements.

Under contract to the EPA, Acurex, Co. was in the draft stage of a report entitled "Capital and O&M Cost Relationships for Hazardous Waste Incineration" (8). Their model asked its user to specify the incinerator's parameters from a menu of design and operating configurations. These design

parameters included items such as the type of air pollution control device (APCD), energy recovery system, and geographical location of the facility (which would effect input cost variables such as fuel and labor). Users were also asked to specify the chemical composition of the waste stream they wished to simulate in order to establish the systems stoichiometric combustion requirements.

By using the parametric information from the selected design options the user worked through a series of engineering calculations, which in turn completed the specification of the cost equations. Ultimatly these equations produced point estimates for numerous items including total capital cost and unit disposal cost, among others.

With the Acurex report serving as the basis for the underlying mathematical model, there now existed an expert on the incinerator's component costs; the author of the Acurex report. His judgment of the uncertainties that surround each of the input cost variables would provide the basis for the specification of appropriate probability distributions.

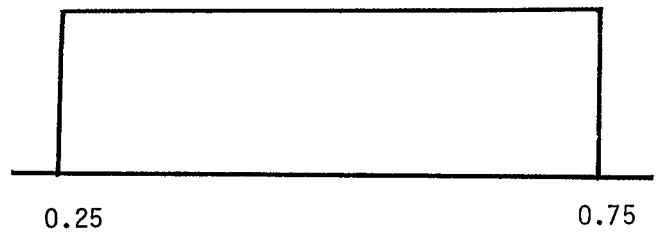
The construction of the computer program consisted of two activities. First the mathematical relationships expressed within the Acurex report had to be encoded into the MOUSE language and second, the expert's uncertainty judgments had to be fitted to probability distributions for their eventual encoding into MOUSE.

Given the clear presentation and organization of the Acurex report, the processing of encoding of the cost equations provided few technical problems. In the end, the cost relationships were reduced to a computer program of about 600 lines. With that portion of the program written, the next step was to solicit and encode our expert's uncertainty judgments.

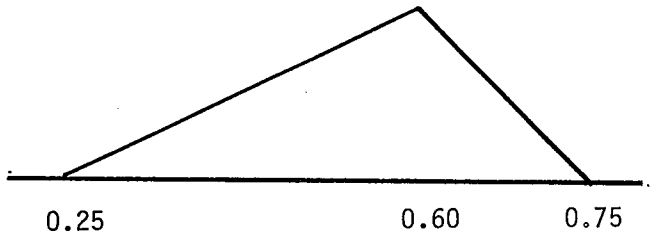
Under ideal conditions an analyst should seek to spend a considerable amount of time with the revelant expert to insure that an accurate assignment of probabilities takes place. A variety of interview techniques exist to help the analyst elicit these judgments (9). Research in this area has shown that an expert's judgment on a system's uncertainty is often clouded by a variety of biases. These biases are categorized as being either motivational or cognitive in nature. Motivational biases are defined as the conscious or unconscious influences on one's judgment that are caused by personal interests or previous commitments. Cognitive biases, on the other hand, operate on a persons judgment in a more subtle fashion. They can be viewed as problems created by ones intuitive perception of probabilities. Experience has shown that a structured elicitation process, such as an interview, helps the expert being surveyed to detect and reduce the influence that these biases have on the determination of uncertainties.

However, for the project at hand, access to our cost expert was limited, and as such it was decided to expedite the process by providing him with a list of the cost variables in question and allowing him to make the uncertainty determinations on his own. Recognizing the negative influence that bias may have on judgement, our expert was also given a short paper detailing the various types of bias and their effect. Lastly, to insure that he had a complete understanding of the project's methodology, he was provided with supporting materials that included an explanation of the aims of our uncertainty analysis and a listing of the probability distributions processed by MOUSE.

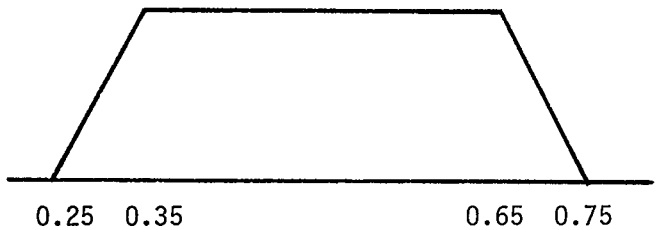
The final product of his probability estimates was limited to the specification of envelopes of variability for each of the individual input variables question. For example, the actual cost of a compressor, in his estimation, could be off the given point estimate by as much as $\pm$ 25 %, with the original point estimate being offered as the most likely. Because of the limited scope of this information on the cost uncertainties, it was decided to utilize only the three most basic probability distributions provided by the MOUSE program: continuous uniform, triangular, and trapezoidal (Figure 1). In the final version of the model, the continuous uniform distribution accounted for 48 percent of the 151 distributions



Continous Uniform Distribution



Triangular Distribution



Trapezoidal Distribution

(Figure 1)

specified, while the trapezoidal and triangular accounted for 46 and 6 percent, respectively.

Although the procedures followed in assigning these probabilities were less than ideal, they nonetheless produced acceptable estimates of the uncertainties involved and allowed the model to be excercised with some degree of confidence. The failure to employ a more structured interview process with our cost expert has been recognized as a major shortcoming of this analysis and will be given a higher priority in future applications of uncertainty analysis.

RESULTS

As stated earlier, this paper tries to answer one major question: "How much more information does the uncertainty analysis provide?"

In order to answer this question, it was first necessary to construct a scenario which would reflect a typical hazardous waste incineration facility (10). The one selected for this purpose was a commercial-scale rotary kiln hazardous waste incinerator operating at 80 million Btu/hr. It was assumed that this facility was burning a combination of a low Btu liquid waste, a medium Btu sludge, and a high Btu containerized waste. In addition, the facility was assumed to be efficiently operating at 80 percent of its peak capacity (where peak capacity is defined as a 24-hour, 7-day, 52-week operating schedule). Lastly, it was determined that this facility would employ a waste heat boiler, allowing for an energy recovery credit to be deducted from the annual operating costs.

After calculating the point estimates generated by the Acurex model, the MOUSE version of the model was exercised. While this paper will focus on the estimates of a few of the key individual cost components, the MOUSE model is capable of producing frequency distributions for any cost items found within the model. It should be noted that the costs estimates generated by the uncertainty model compare quite favorably to those costs reported in the hazardous waste literature for similar operations (11,12).

Figure 2 shows the MOUSE output for the unit disposal cost for incinerating the hazardous waste mix specified in the base facility on a per pound basis. The frequency distribution shows a range of estimates falling between $0.02658/lb and $0.050378/lb ($68.92/ton to $100.76/ton) with a mean value of $0.03646/lb ($72.92/ton). The point estimate, generated by the Acurex Model without the benefit of the uncertainty analysis, is $0.0353/lb ($70.60/ton). Keep in mind that the unit disposal cost reported here simply refers to costs faced by the waste disposer (averaged over the yearly throughput) and is not meant to reflect fees charged to waste generators.

From the information supplied by the MOUSE model in Figure 1, one can see that there is a 47 percent probability that the actual value of the unit disposal costs will be less than or equal to the value of the point estimate. More importantly to the risk adverse decision maker, this means that there is a 53 percent chance that the actual unit disposal cost will exceed the value of the point estimate. This 53 percent margin of error is likely to be too great. Suppose that this decisionmaker feels comfortable accepting no more than a 5 percent probability that he will underestimate the unit disposal cost. Given this risk preference, he would choose a value that corresponds to the 5 percent level in the cumulative complement column, or conversely the 95 percent level of the cumulative entries column. This value is 0.0418/lb ($83.60/ton).

At first glance the difference between the value of the point estimate and that at the 95 percent probability level appears small ($0.0065/lb or $13.00/ton). However, when one considers that the total yearly throughput of waste at the facility under question is 42,048 tons, the difference between the two estimates (on an annual basis) is $546,623. Making an error of this magnitude could be of significant consequence to any decision maker. Thus, the information gained on the margin of error by using the uncertainty approach, as measured by this dollar differnce, is appreciable.

Assume that this risk adverse decision-

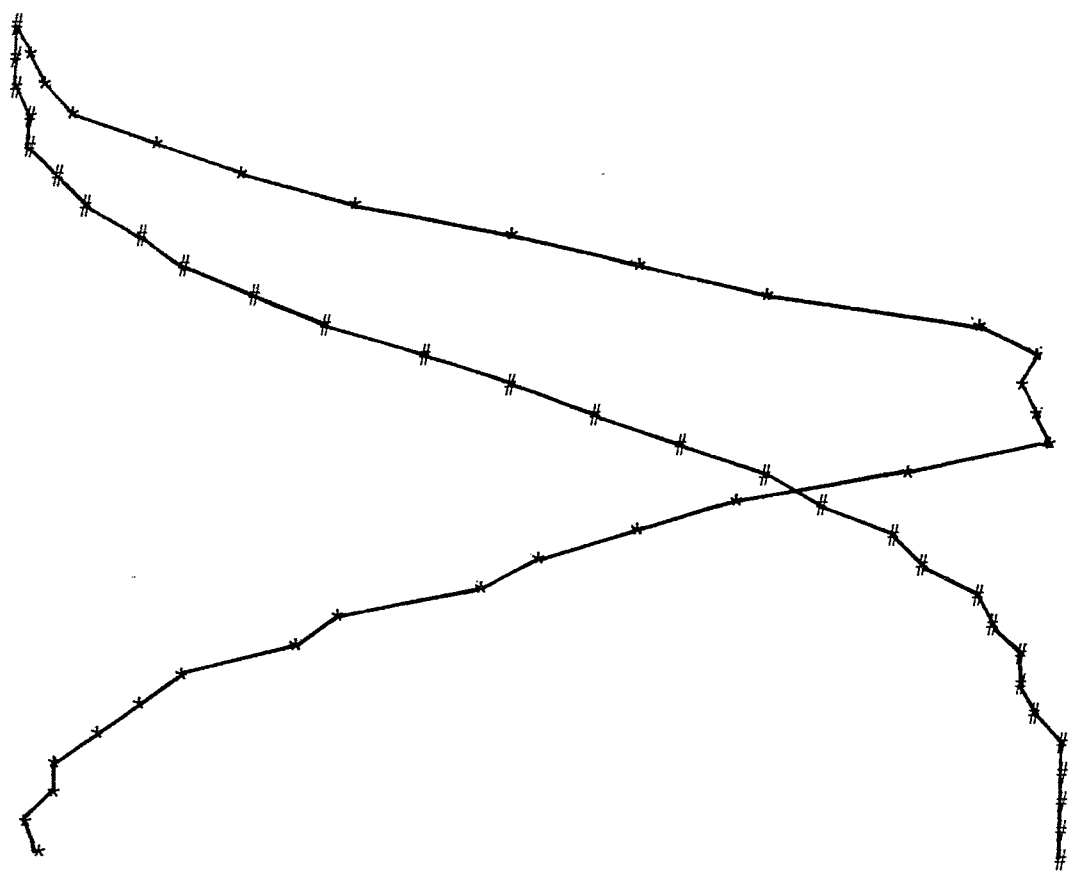
(FIGURE 2)

DISTRIBUTION FOR UNIT DISPOSAL COST - BASE MODEL

MINIMUM = $ 0.02658
MAXIMUM = 0.05038
MEAN = 0.03646

COEFFICIENT OF VARIATION, % = 9.65138
STANDARD DEVIATION = 0.00352

LOWER LIMIT	CUMULATIVE % ENTRIES	CUMULATIVE COMPLEMENT
0.0260	0.02	99.98
0.0268	0.10	99.90
0.0275	0.36	99.64
0.0283	0.98	99.02
0.0291	2.10	97.90
0.0299	4.00	96.00
0.0306	6.86	93.14
0.0314	10.98	89.02
0.0322	16.10	83.90
0.0329	22.38	77.62
0.0337	30.28	69.72
0.0345	38.78	61.22
0.0353	47.12	52.88
0.0360	55.70	44.30
0.0368	64.36	35.64
0.0376	71.78	28.22
0.0384	77.80	22.20
0.0391	82.94	17.06
0.0399	87.26	12.74
0.0407	91.06	8.94
0.0414	93.82	6.18
0.0422	96.06	3.94
0.0430	97.52	2.48
0.0438	98.52	1.48
0.0445	99.22	0.78
0.0453	99.48	0.52
0.0461	99.80	0.20
0.0468	99.92	0.08
OVERFLOW	100.00	0.00



maker had simply decided to construct a 40 percent envelope of variablilty around the original Acurex estimate. Now suppose that in order to obtain the most conservative estimate he had taken the upper limit of that range as his estimate. (The Acurex model predicts an accuracy of ± 40 percent.) The maximum value of an estimate within that confidence band is $0.0494/lb. or $98.80/Ton. By accepting this conservative estimate over the MOUSE value (taken at the 5 percent margin of error level) this decisionmaker would have needlessly over-estimated the yearly unit disposal cost by $639,130. Assuming that a 5 percent margin of error is an acceptable level of risk, this upper limit confidence band estimate represents a needless degree of caution.

Another example of the gain in usable information obtained from uncertainty analysis occurs when the point estimate for the total capital investment of this same base facility is compared to one generated by the MOUSE model. Figure 3 shows the MOUSE out put for that cost component. Compare that to the point estimate generated by the Acurex model, $8,614,669. By examining the MOUSE output, one finds that this point estimate corresponds to an approximate level of cumulative entries of 12 percent, indicating that there is an 88 percent probability the actual value will exceed this point estimate.

If the decisionmaker wishes to reduce his margin of error (and thus his level of risk) from the 88 percent level to a more acceptable 5 percent level (as in the preceding example), he will choose $11,164,258 as the value of his estimate for the total capital cost. The difference between these two estimates is $2,549,589. This is an increase of close to 30 percent over the point estimate generated by the original model. Once again this is a significant difference which reflects the dollar value associated with the margin of error. One should note that the MOUSE estimate taken at this 5 percent risk level falls well within a 40 percent envelope of variability constructed around the the point estimate, and as before, it provides the added information on probability which prevents an over-estimation of the total capital cost by $896,278 (given the risk preference of the decisionmaker).

CONCLUSION

After viewing the significant difference between the values of the final cos estimates generated with and without the MOUSE program, it is reasonable to conclude that this particular decision process was enhanced through the provision of additiona information on uncertainty. The advantage gained by offering cost estimates in the form of frequency distributions is that the decisionmaker has the ability to incorporat his risk preferences at the onset of the decision process.

In coming to this conclusion, one important issue has been purposely overlooked. The success of this analysis ultimately rests with the decision maker. He needs to bring to the decision process an appreciation of his personal preferences toward risk. There is no reason to believe that the typical decision maker will have taken the time and effort to objectivly review his attitudes toward risk, especially when considering that the opportunities for such reflection are rare. The chances are such that he will never have been placed in a situation which has required him to do so.

It is hoped that through the adoption and regular use of an uncertainty approach to cost estimation, the decision maker will be forced to deal with the concept of risk. Then, and only then, will he be motivated to recognize and act upon his own risk preferences.

This paper has concerned itself with the problems faced by the risk adverse decision maker, yet it should be made clear that the information obtained from these frequency distributions can benefit anyone, regardless of their preferences toward risk. All that is required is for one to judge what margin of error is acceptable and select that corresponding value from the distribution. As this paper has shown, when properly conducted, uncertainty analysis can vastly improve both the quality and quanity of information regarding an estimate's margin of error. The end result will be a more reliable decision process.

(FIGURE 3)

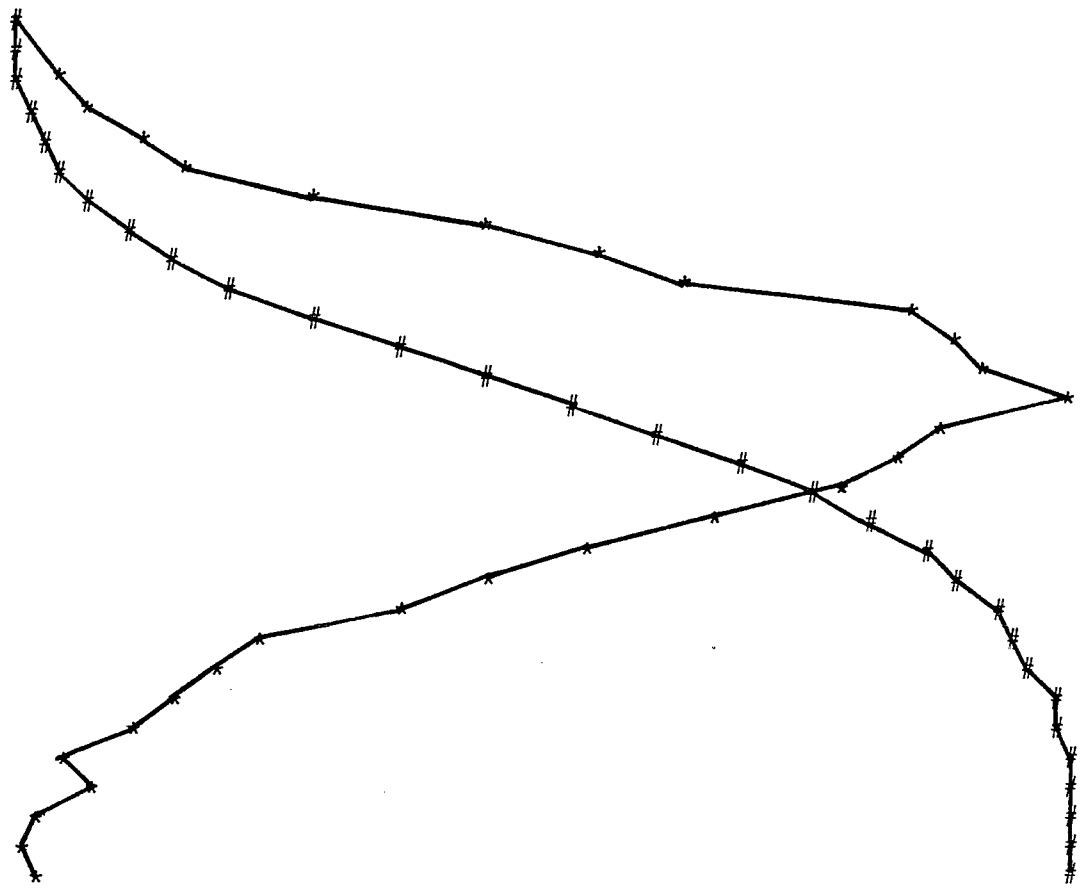
DISTRIBUTION FOR TOTAL CAPITAL INVESTMENT - BASE MODEL

MINIMUM = $ 7,306,316.00
MAXIMUM = 13,029,855.00
MEAN = 9,845,947.00

COEFFICIENT OF VARIATION, % = 8.85749
STANDARD VARATION = 872103.81250

LOWER LIMIT	CUMULATIVE % ENTRIES	CUMULATIVE COMPLEMENT
UNDERFLOW	0.04	99.96
7400000.	0.06	99.94
7590000.	0.34	99.66
7780000.	0.88	99.12
7970000.	1.94	98.06
8160000.	3.42	96.58
8350000.	5.84	94.16
8540000.	9.84	90.16
8730000.	14.76	85.24
8920000.	20.44	79.56
9110000.	28.00	72.00
9300000.	35.86	64.14
9490000.	44.10	55.90
9680000.	53.02	46.98
9870000.	60.94	39.06
10060000.	68.36	31.64
10250000.	75.40	24.60
10440000.	81.36	18.64
10630000.	86.24	13.76
10820000.	90.12	9.88
11010000.	93.36	6.64
11200000.	95.38	4.62
11390000.	97.00	3.00
11580000.	98.30	1.70
11770000.	99.12	0.88
11960000.	99.36	0.64
12150000.	99.76	0.24
12340000.	99.88	0.12
12530000.	99.94	0.06
OVERFLOW	100.00	0.00

* = FREQUENCY DISTRIBUTION # = CUMULATIVE DISTRIBUTION



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UPDATE ON CALIFORNIA PROGRAM TO RESTRICT HAZARDOUS WASTE LAND DISPOSAL

Jan Radimsky, P.E.
Division of Toxic Substances Control
California Department of Health Services
Sacramento, California 95814

ABSTRACT

In 1983, California adopted regulations restricting land disposal of certain hazardous wastes in order to reverse its hazardous waste management's reliance on land disposal and to stimulate development of technological alternatives to land disposal.

Realizing the real high "long-term" costs of land disposal, demonstrated by the multi-million cleanup costs estimates for the State's Superfund sites, California government sought a way to stimulate development of the needed alternative technology facilities by developing regulations with a definite schedule of phasing out of land disposal of specific hazardous wastes of concern. Such a schedule guarantees those who develop treatment facilities for the restricted wastes that they will not be competing with low-cost land disposal because the land disposal alternative will not be available to generators of such wastes.

Implementation of these regulations during the last two years has had positive effects on hazardous waste management in California. Several issues have arisen affecting monitoring of compliance with current and implementation of future land disposal restrictions in California.

INTRODUCTION

In 1983, California adopted regulations restricting land disposal of certain hazardous wastes in order to reduce its reliance on land disposal and to stimulate development of technological alternatives to land disposal. During explorations of status of alternative technologies, it became apparent that a great number of effective treatment, destruction, or recycling technologies were available. However, they were not utilized in California because of availability of "cheap" land disposal. Commercial disposal facilities' operators could not afford to make the investment necessary to develop and operate alternative technology facilities and be competitive with low costs of land disposal.

PURPOSE

Realizing the high "long-term" costs of land disposal, demonstrated by the multimillion dollar cleanup cost estimates for the State's Superfund sites, California government sought a way to stimulate development of needed alternative technology facilities by developing regulations with a definite schedule of phasing out of land disposal of specific hazardous wastes. Such a schedule guarantees those who develop treatment facilities for the restricted wastes that they will not be competing with low-cost land disposal, because the land disposal alternative will not be available to generators of such wastes. This "phased" schedule reflects need to allow time for designing, siting, and permitting of alternative technology facilities.

APPROACH

Major features of the California land disposal restrictions are:

1. Land disposal restrictions apply to all forms of land disposal, including, but not limited to, landfill, surface impoundment, waste piles, deep well injection, land spreading, and coburial with municipal garbage.

2. Restrictions apply to five categories of wastes (so-called "restricted wastes"), four of which include only the liquid phase, and for each component, there is a threshold concentration (see Table I).

3. Categorically exempted are the following wastes:

   a. Injected drilling fluids and produced wastes from production of natural gas or crude oil.

   b. Mining overburden.

   c. Contaminated soil from site cleanup pursuant to the Department's approval.

4. Variances from land disposal restrictions can only be made for a specific waste stream or site-limited land disposal method. Emergency variances can be granted if treatment or recycling facilities have unplanned shutdown.

5. Restrictions are being implemented according to a schedule of tentative dates included in the regulations (see Table II). Dates for restrictions are subject to confirmation by the Department and become effective only when this agency determines that available treatment and recycling capacity is available in the State of California.

California's approach relies on the initiative and cooperation of the hazardous waste processing industry to develop the treatment and recycling facilities needed for implementation of this land disposal restriction program.

TABLE I: CALIFORNIA RESTRICTED HAZARDOUS WASTES

a. Liquid hazardous wastes containing free cyanides at concentrations greater than or equal to 1,000 mg/1.

b. Liquid hazardous wastes containing the following dissolved metals (or elements) or compounds of these metals (or elements) at concentrations greater than or equal to those specified below:

Arsenic and/or compounds (as As)	500 mg/1
Cadmium and/or compounds (as Cd)	100 mg/1
Chromium (VI) and/or compounds (as Cr^{+}VI)	500 mg/1
Lead and/or compounds (as Pb)	500 mg/1
Mercury and/or compounds (as Hg)	20 mg/1
Nickel and/or compounds (as Ni)	134 mg/1
Selenium and/or compounds (as Se)	100 mg/1
Thallium and/or compounds (as Th)	130 mg/1

c. Liquid hazardous wastes having a pH less than or equal to two (2.0).

d. Liquid hazardous wastes containing polychlorinated biphenyls at concentrations greater than or equal to 50 mg/1.

e. Hazardous wastes containing halogenated organic compounds in total concentrations greater than or equal to 1,000 mg/kg.

TABLE II: CALIFORNIA LAND DISPOSAL RESTRICTIONS SCHEDULE

June 1, 1983	Cyanide Wastes
January 1, 1984	Toxic Metals Acid Wastes PCB Wastes
January 1, 1985	Halogenated Organic Waste Liquids
July 1, 1985	Halogenated Organic Waste Sludges and Solids

EXPERIENCE WITH IMPLEMENTATION OF INDIVIDUAL RESTRICTIONS

Cyanide Waste Restriction

The assessment of "restricted" cyanide waste generation and availability of treatment and recycling capacity conducted in 1983 produced the following information:

- Less than 7,000 tons of restricted cyanide wastes were generated in California.
- About 2,000 tons of these wastes were already treated, mostly at on-site facilities.
- There was no commercial recycling capacity for the "restricted" cyanide wastes.
- Less than 5,000 tons of "restricted" cyanide wastes were disposed of at off-site land disposal facilities.
- Restriction of cyanide wastes led to construction of three new facilities capable of treating their wastes and to increased utilization of the only off-site cyanide waste treatment facility in existence prior to the restriction implementation.

Restriction for cyanide wastes was implemented as originally scheduled in the regulations.

A year later, in June 1984, a review of hazardous waste manifests and on-site disposal reports was conducted to determine the effectiveness of the land disposal restrictions. The following were the findings:

- Almost 100 percent reduction of land disposal of restricted cyanide wastes was achieved.
- A lesser amount of restricted cyanide waste was being generated (approximately 3,000 tons per year prior to the restrictions and 2,600 tons per year after the restriction) in spite of improvement in the State's economy. Also generation of nonrestricted cyanide wastes increased by 42.8 percent.
- There was a 79 percent increase in wastes going to treatment facilities.
- Only 5 companies were responsible for over 50 percent of the prerestriction volumes of restricted wastes and 60 percent of the post-restriction volumes.

Because of the large number of variables, it is difficult to make any precise conclusion as to what the impact and effectiveness of the land disposal restrictions were without detailed evaluation of the generators and treatment at facilities involved. Among the variables which affect such evaluations are: unprecise reporting on hazardous waste manifests,

changes in generated volume due to the status of the economy, individual company production changes, on-site treatment and waste reduction efforts of generators.

Heavy Metal and Acid Waste Restriction

The land disposal restriction for heavy metal wastes was also implemented as scheduled in the regulations. This was made possible primarily due to California's definition of land disposal, which excludes surface impoundments used for treatment, as long as the residue is rendered nonhazardous within a year or, if it remains "hazardous", it is removed from the surface impoundment within a year.

This practice accounts for more than 50 percent of the restricted acid and heavy metal waste treatment, with the remainder being neutralized and/or precipitated in the tanks.

Solid residue is not subject to the land disposal restrictions, and it is being landfilled. Any variation in the generation of these wastes can easily be accommodated by the large capacity of existing in surface impoundments.

Liquid PCB-Containing Waste Restriction

Implementation of this portion of land disposal restriction program did not have any impact on management of liquid PCB-containing wastes. This is because of the Toxic Substances Control Act, which already bans land disposal of liquid PCB-containing wastes with concentrations over 500 ppm, and allows liquids with 50 to 500 ppm of PCB concentrations only with specially EPA-approved "secure landfills" which do not exist in California. Implementation of this restriction in California precludes the possibility of establishment of such a landfill in the future.

No variance requests were submitted in connection with the first two land disposal restrictions because of the excess capacity available and simplicity of treatment.

Liquid Halogenated Organic Waste Restrictions (See Tables III and IV)

In implementation of this restriction, the Department has run into the inherent weakness of the California restrictions program, its dependence on industry's cooperation in development of needed treatment and recycling facilities. As the treatment most generally applicable to this category -- incineration is very expensive and has high up-front capital costs -- industry has been reluctant to build new facilities. There is a risk that generators may not send their wastes to be incinerated in California, but will opt to send these wastes to land disposal facilities in other states which do not have to abide by California land disposal restrictions.

This fact, combined with difficulties in siting and permiting of incinerators in California, resulted in insufficient increase of thermal treatment (wet air oxidation and incineration) capacity due to the land disposal restrictions. It is anticipated that several projects currently in planning will move ahead with the prospect of a national land disposal restriction program as well as the demand for disposal without future liability potential increases.

A preland disposal restriction evaluation determined that although there is capacity for thermal treatment and recycling of 36,200 tons, only 22,200 tons are thermally treated or recycled. This is because the existing thermal treatment facilities have stringent limits on wastes to be treated such as minimum heat value, maximum chlorine concentration, maximum or minimum organic content, etc. Without building new thermal treatment facilities which could accept a broad range of wastes, about 23,000 tons cannot be recycled or thermally treated. Over 18,500 tons of these wastes are being generated by a single company, which requested and received a variance from land disposal restrictions for a period of 5 years as long as the low-concentration, nonvolatile halogenated organic-containing wastes are disposed of to a double-lined, leachate collection-equipped pond and the company pursues process and waste

disposal modification to eliminate generation of restricted liquid waste altogether. Remaining nonrecyclable or incinerable wastes will be allowed to be solidified.

Solid Halogenated Waste and Lab Packs Land Disposal Restriction (See Tables III and IV)

The restriction of solid halogenated organic wastes was tentatively scheduled for July 1, 1985. In the absence of

Table III. Management and Quantities of Hazardous Wastes Containing Halogenated Organic Compounds in California (1983)

Type of Waste	Recycled or Incinerated (TPY)	Land Disposal (TPY)	Total Quantity (TPY)
Solvents	21,800	2,400	24,200
Still Bottoms, Organic Liquids, and Sludges	500	2,800	3,300
Dry-Cleaning Wastes	-	3,800	3,800
Waste Waters	-	28,400 (18,500)2/	28,400
Solids and Lab Packs	300	4,100	4,400
Total	22,600	41,500	64,100

Table IV. Availability of Treatment for Recycling Capacity for Hazardous Wastes Containing Halogenated Organic Compounds in California (1985)

Waste Description	Total Quantity (TPY)	Not Recyclable or Incinerable (TPY)	Recycling Incineration Capacity Available (TPY)
Solvents	24,200	800	23,400
Still Bottoms, Organic Liquids, and Sludges	3,300	1,800	1,500
Dry-Cleaning Wastes	3,800	-	3,800
Waste Waters	28,400	20,900 (18,500)2/	7,500
Total Liquids	59,700	23,500	36,200
Solids, Lab Packs	4,400	4,100	0(300)1/
Total Volume	64,100	27,600	36,200

1/ Incinerated out of state.

2/ 18,500 TPY were generated by one company.

an off-site commercial rotary kiln in California, this restriction will not be implemented this year. The Department is considering postponing this deadline to coincide with the date indicated in the Resource Conservation and Recovery Act Amendments of 1984. Even that deadline appears difficult to meet as the siting and permitting of needed incinerators may require more time.

PROBLEMS ENCOUNTERED AND ISSUES TO BE RESOLVED

Major problems which were encountered during the implementation of the above land disposal restrictions include:

1. Obtaining of good detailed data on volume and composition of wastes is difficult as reporting on hazardous waste manifests is not always detailed enough and often plagued by errors.

   Restricted wastes can be listed under several waste categories (California's waste categories are not identical to EPA's) and, therefore, manual review of all manifests was necessary to obtain needed information. Much more detailed reporting is necessary in the future to enable us to evaluate treatability and recyclability of specific wastes.

   Continuous technical review of data reported on manifests and in annual (biennial) reports by generators' disposal, treatment, and recycling facilities' operators is needed. As we strive to maximize waste reduction, recycling and treatment of hazardous wastes annual reports will become an increasingly important source of information. The format of annual reports needs to be expanded to sufficiently provide detailed description of waste generation, composition, and information on the management practices which will enable us to determine recyclability, treatability, and waste reduction potential of each waste stream. At this time, the available information on existing waste streams obtained from manifests is not adequate for that purpose. Manifests have their place in that they help to track wastes from "cradle to grave", but should not and cannot be the sole source of information on hazardous waste management.

2. California's ban depends on the waste disposal industry's cooperation and initiative to develop new needed treatment and recycling facilities. Because of the industry's reluctance to build a rotary kiln incinerator, the last ban is not implementable for either solid halogenated wastes or lab packs.

3. Lack of a nationwide land disposal restrictions program was probably the primary reason for industry's hesitance to develop incineration facilities in California because of the anticipated exodus of wastes to neighboring states if the incineration facilities were built and restriction implemented in California. Recent RCRA changes and their implementation should assist California in implementation of future land disposal restrictions as long as the national restrictions will apply to underground injection of hazardous wastes. If underground injection is considered acceptable for hazardous wastes, there may be little incentive for building treatment and recycling facilities for hazardous wastes.

4. Future land disposal restrictions in California as well as in the United States will probably be developed in the legislative arena. Examples of such legislation are the recent RCRA amendments, as well as the recent California legislative bill, AB 3566 (Katz), which bans use of surface impoundment for storage and treatment of "restricted" wastes after July 1, 1985. This date may be postponed due to the "shortness" of notice to the dischargers (on October 1, 1984) who will not be able to comply so quickly and will need additional time to build tank storage and treatment facilities.

FUTURE OF THE PROGRAM

At the present time, the California hazardous waste management program is being expanded to include any strategy, which would ultimately result in reduction of volume of hazardous waste going to land disposal. These strategies include economic and regulatory incentives for waste reduction, waste reduction technical assistance, waste recycling and reuse support, as well as restrictions on land disposal of specific wastes.

The emphasis of the California hazardous waste management program will be on reduction of hazardous waste generation which is the ultimate waste management solution, as it decreases the need for transportation, treatment, recycling, and disposal facilities, all of which have some negative environmental and public health impact potential, as well as high costs and potential for long-term liability for industry.

THE THERMAL DECOMPOSITION CHARACTERISTICS OF A SIMPLE ORGANIC MIXTURE

John L. Graham, Douglas L. Hall, and Barry Dellinger
University of Dayton Research Institute
Dayton, Ohio 45469

ABSTRACT

Through previous efforts, the University of Dayton's Environmental Sciences Laboratory has gathered extensive data on the gas phase thermal decomposition of pure organic compounds. In this report, the thermal decomposition of a simple mixture is examined. Specifically, the effect of oxygen concentration on the thermal stability of the components and the formation of thermal reaction products are examined. Also, the thermal stability of the components in the mixture are compared with their stability as pure compounds.

The hazardous waste mixture consisted of carbontetrachloride, monochlorobenzene, 1,1,2-trichloro-1,2,2-triflouroethane (Freon 113), trichloroethylene, and toluene. Thermal decomposition studies were conducted in atmospheres in which oxygen was in excess, stoichiometric, and absent (absolute pyrolysis) with respect to complete combustion. For comparison, the components were run as pure compounds in an atmosphere with stoichiometric oxygen available.

Results indicate that the order of stability of the five components was strongly effected by oxygen concentration. Oxygen concentration had a pronounced influence on the thermal stability of monochlorobenzene, toluene, and trichloroethylene in the mixture, but no influence on the stability of the Freon 113 or carbontetrachloride. Furthermore, with the exception of Freon 113, the thermal stability of each component in the mixture was less than its stability as a pure compound. The stability of Freon 113 was identical as a pure compound and in the mixture.

It was also found that oxygen concentration had a significant effect on the production of thermal reaction products. In general, the number and complexity of thermal reaction products increased with decreasing oxygen concentration. In all cases, products ranged from simple chlorinated aliphatics to complex polynuclear aromatics, with the majority being chlorinated aromatics.

VOST APPLICATIONS AT THE USEPA COMBUSTION RESEARCH FACILITY

by

Robert W. Ross, II, F. C. Whitmore, R. H. Vocque,
T. H. Backhouse and B. M. Cottingham
Versar, Inc.
P. O. Box 1838
Pine Bluff, Arkansas 71613

and

Richard A. Carnes
Environmental Scientist
USEPA Combustion Research Facility
Jefferson, Arkansas 72079

ABSTRACT

The volatile organic sampling train (VOST) has been used to collect stack samples at the EPA's Combustion Research Facility (CRF) in Jefferson, Arkansas for the past year. During this time strengths and weaknesses of this sampling and analysis technique have become apparent. Among the advantages are ease of operation of commercially available equipment, short time required to take a sample, and rapid analytical turn around time - results are typically available from the on-site laboratories 1 1/2 hours after the sample is collected. The disadvantages of this technique include the time consuming nature of sample tube preparation and blanking, blockages in the flow path of the analytical thermal desorption unit, and high breakage rate of glass sample tubes of the I/I design. Solutions to these problems are presented along with extensive spike and recovery data collected during validation of innovative modifications to the basic VOST methodology.

INTRODUCTION

The research program at the Combustion Research Facility (CRF) has, to date, been largely concerned with the study of the incineration of several Environmental Protection Agency (EPA) soups in a pilot scale, rotary kiln, fired afterburner incinerator. Among other non-conventional attributes, this system is provided with sampling ports in the kiln transfer duct which conducts the kiln exhaust gases to the afterburner, and in the afterburner transfer duct carrying the combustion gases to the pollution control system. The Soups contain compounds of a variety of boiling points requiring sampling with a variety of procedures including the volatile organic sampling train (VOST).

In many ways the operation at the CRF is very different from the normal procedures in that immediately after the VOST sample has been taken, it is removed from the train, capped and delivered to the laboratory for analysis. This unusual manner of operation has resulted in a number of variations from the usual manner of using the VOST system and it is these variations that will be the subject of

this paper. In addition, the use of the VOST in a water saturated gas stream (the exit gases from the scrubber are saturated at 81°C) introduces peculiar analytical problems which are also treated below. The nature of these problems and the solutions introduced at the CRF are seen in Table 1.

The dry gas meters have been calibrated on site and showed a low and varible average bias of 7% to 9%. Recalibration using a wet test meter shows a consistently low average bias of 5%.

Thermal Desorption System - NuTech

TABLE 1. MODIFICATIONS TO VOST PROTOCOL[2]

PROBLEM	The time consuming nature of sample tube preparation and blanking especially when many samples will be taken in a given experiment.
SOLUTION	Tenax® is aspirated into the tube, weighed, and thermal conditioning takes place on an easily constructed 24-port manifold located in a forced draft oven. Cleaning is accomplished by steam stripping requiring approximately four hours.
PROBLEM	The need to transfer large volumes of water/steam (derived from the saturated combustion gases) during analytical thermal desorption of sample tubes leads to low and variable Principle Organic Hazardous Constituent (POHC) recoveries.
SOLUTION	Bulk of water entrained in the tubes is transferred during a preheating step without purge gas flow.
PROBLEM	Breakage of glass sample tubes during analysis and field sampling may easily exceed 30%.
SOLUTION	Stainless steel (S.S.) tubes of several designs have shown good POHC recoveries in extensive trials.

It is recognized that the solutions listed in Table 1 represent deviations from and/or expansions of the most recently enunciated[2] VOST sampling and analysis protocol. To support and validate these changes extensive QC data will be given when these and other elements of the CRF investigations with VOST techniques are discussed below.

APPARATUS

The VOST sampling and analysis equipment is listed in functional order below, along with comments identifying specific problems encountered in its use.

Sampling System-NuTech Model 280B - Model 320 - This is <u>not</u> the Model 320 probably familiar to most current NuTech users: (1) it has no provision for cryo-trapping; (2) it can desorb only two sample tubes (I/I design) at a time; (3) tubes are no longer sealed into the system with duck-bill valves, but connected with SWAGELOK® reducers, ceramic-filled TEFLON® ferrules and stainless steel capillary tubing; (4) this tubing looses its flexibility after a period of service and becomes a source of glass sample tube breakage; (5) the thermal desorption chamber itself is of improved design, more accessible and more convenient to use and (6) the Valco® 6-port valve and associated tubing are of

narrow bore, keeping instrument dead volume to a minimum but causing problems in wet sample processing.

Purge and Trap System - Tekmar Model LSC-1 - This equipment, familiar to many in the analytical community, has given the dependable performance that users have come to expect.

Gas Chromatograph - Hewlett Packard Model 5880A - This system, configured for packed column[5] use with FID, has given predictably dependable performance.

VOST Sorbent Cartridge (sample tube) Conditioning Equipment - This apparatus was constructed on site from materials, largely, on hand. A twenty four-port manifold was assembled from Swagelok®, 1/4 inch straight-run tees and elbows of #316 stainless steel. Fittings as well as connecting lengths of 1/4 inch #302 seamless stainless steel tubing were sonicated through three changes of 1:1, acetone: methanol (Burdick and Jackson) and oven dried before assembly. The manifold configuration is such that it supports VOST tubes at a 45° angle above the horizontal and was installed in a forced draft oven capable of maintaining 250°C. The oven itself is placed in a forced draft laboratory hood for safety reasons. The manifold is supplied with UPC grade nitrogen which receives final polish through a bed of activated carbon and silica gel.

OVERVIEW OF VOST QA/QC

As staff skills in VOST techniques have grown, the QA/QC program has matured in the direction of more realistic mimicry of incinerator operation and sampling conditions. While the work of many investigators has been valuable, only two [3,4] are cited here. The progression of our investigations naturally divided itself into phases, and will be discussed in that fashion.

Phase 1 - Calibration of the Analytical System

Since purge and trap (P&T) methodology[5] has established performance criteria and VOST methodology does not[2], the former was used as the standard of performance of the latter. Thus, a stock standard solution was prepared containing four compounds of current interest - Freon®113, carbon tetrachloride, trichloroethylene and chlorobenzene - in methanol. The concentration of each compound in this solution was 1.0 µg/µl. Dilutions of this stock standard were made to contain 0.10 µg/µl and 0.010µg/µl of each compound in methanol. The sparger of the P&T was charged with 5 ml of organic free water (OFW) and spiked with 3µl of the stock standard i.e. 3.0µg of each compound. The P&T analysis was then conducted in accordances with reference (5) and a calibration table at 3.0 µg for each compound was created. This process was repeated for each of the diluted standard solutions described above, thus creating a P&T calibrator for each of the four compounds at three levels, i.e., 3.0 µg, 0.30 µg and 0.030µg. Next, the VOST Thermal Desorption System (TDS) was connected and spikes were placed on the entry end of tube #2 with respect to desorb gas flow direction. Analysis of these spikes using different combinations of desorb temperature, time and gas flow rate identified a set of TDS operating conditions (180°C, 15 minutes and 40 ml/min helium) whereby P&T and TDS analyses of the same standard solutions gave nearly identical resutls (see Table 2).

Phase 2 - Effect of Spike Location on POHC Recovery

With respect to the direction of desorb gas flow, there are four physical locations on a pair of VOST tubes at which a spike of known amounts of authentic compounds may be placed. Table 3 compares the TDS data for several POHC spiked at these locations with the P&T values for the same

TABLE 2. COMPARISON OF P&T AND TDS ANALYSES OF IDENTICAL STANDARD SOLUTIONS (values in µg)

	P&T	TDS	P&T	TDS	P&T	TDS
Freon® 113	3.00	3.01	0.300	0.282	0.0300	0.0370
Carbon tetrachloride	3.00	3.05	0.300	0.327	0.0300	0.0906*
Trichloroethylene	3.00	3.04	0.300	0.279	0.0300	0.0353
Chlorobenzene	3.00	3.03	0.300	0.274	0.0300	0.0354

*Value exaggerated by high and variable blank

TABLE 3. COMPARISON OF P&T AND TDS SPIKES PLACED AT SEVERAL POINTS IN A PAIR OF VOST TUBES (values in µg)

	P&T	TDS tube #2 exit	TDS tube #2 entry	TDS tube #1 exit	TDS tube #1 entry
Freon® 113	3.00	3.04	3.01	3.00	-0-
Carbon tetrachloride	3.00	3.07	3.05	3.00	0.023
Trichloroethylene	3.00	3.13	3.04	3.01	-0-
Chlorobenzene	3.00	3.12	3.03	2.97	-0-

standard solution. It is of interest to note that TDS and P&T data are virtually identical for all locations except tube #1-entry. POHC recovery at this location (the charcoal portion of the Tenax®/charcoal tube) is virtually zero. This experiment has been repeated several times with the same results, and no explanation can be given.

Phase 3 - Flash Evaporation Spikes

The current VOST protocol[2] requires the preparation and anlysis of standards generated by the flash evaporation technique. Suffice it to say that these exercises have limited relevance as a diagnostic procedure for VOST sampling and analysis validity. The results of CRF performance are displayed in Table 4.

Phase 4 - VOST Spike and Recovery by Incinerator Mimicry

In an effort to lend more relevance to VOST QA/QC, a practice has been initiated at the CRF. Periodically several pairs of VOST tubes are inoculated with various amounts of POHC and products of incomplete combustion (PIC) of current interest. In pairs, these tubes are installed in a full dress sampling train and 20 dry standard liters (dsl) of steam-laden ambient air are drawn through them from a flask of boiling OFW. Routine analysis of these tubes allows calculation of spike and recovery data (see Table 5). This QC device may represent a practical compromise between the somewhat sterile approach of the protocol[2] and the quite complex apparatus used[3] by

TABLE 4. RESULTS OF ANALYSIS OF FLASH EVAPORATION STANDARDS

	% Recovery @ Spike = 3.0µg	% Recovery @ spike = 0.30µg	% Recovery @ spike = 0.030µg
Methylene chloride	91	62	95
Chlororform	91	87	106
Freon® 113	101	86	102
Carbon tetrachloride	86	93	68

(continued)

TABLE 4. (continued)

	% Recovery @ Spike = 3.0µg	% Recovery @ spike = 0.30µg	% Recovery @ spike = 0.030µg
Trichloroethylene	92	89	95
Benzene	93	90	97
Toluene	93	109	114
Chlorobenzene	93	91	104

TABLE 5. ANALYTICAL RESULTS FOR INCINERATOR MIMICRY SPIKED SAMPLES

	% Recovery @ spike = 30.0µg	% Recovery @ spike = 3.0µg
Chloroform	104	115
Freon® 113	72	65
Carbon tetrachloride	97	97
Trichloroethylene	105	100
Benzene	105	101
Toluene	106	102
Chlorobenzene	101	94

some other workers.

Phase 5 - Rapid Packing and Blanking of Sorbent Cartridges

Sampling tubes of the I/I design may be rapidly and uniformly packed as follows: (1) a glass wool plug is placed in one end of the tube, (2) this end is connected to a water aspirator while the other end is placed in a container of Tenax GC and tapped gently; (3) when the tube is filled, the resin is held in place by a second plug of glass wool.

Contaminant levels for carbon tetrachloride, benzene and toluene may be reduced to values $\leq$ 0.005 µg per pair of tubes as follows: (1) packed tubes are washed by percolation with 25-30 ml of OFW and allowed to soak 15 min. or more, (2) tubes are then connected to the manifold in the cold oven with nitrogen set at ~ 30 ml/min/tube or 40 psig when all 24 tubes are in place; (3) oven is set for 180°C and turned on; (4) temperature increases rapidly to set point in ~ one hr. where it is held for $\geq$ 3 hrs.; (5) tubes are cooled with nitrogen flow and put into immediate service or sealed for storage. It should be pointed out that the compounds listed above are the major contaminants routinely found, and that scant other material is found using the analytical method of reference (5). Also, glass wool, glass sampling tubes, Tenax® GC, charcoal, Swagelok® fittings and Teflon® ferrules are given no pre-treatment but are used as received from their various suppliers.

Phase 6 - Analysis of Wet VOST Samples

A pair of packed sampling tubes may easily contain 6 ml. of entrained condensate after use in stack sampling at the CRF. The NuTech Thermal Desorption System in use at the CRF cannot accomodate this volume of liquid in a prompt or reproducible fashion due to the very narrow bore valve and tubing of which it is constructed. If thermal desorption with purge gas flow is attempted, the results are low, erratic, sometimes zero recovery of POHC and PIC. A simple remedy for this problem is as follows: (1) the bulk of the

entrained condensate is removed by several sharp bursts of vacuum charcoal filtered air is used) over a period one min.; (2) the remaining liquid is vaporized during a 15 min. pre-heating period during which the tubes are connected in the thermal desorption chamber but no purge gas is flowing, (3) during pre-heating much of the liquid transfers, as steam, to the sparger where it condenses again and thus carries out no sparing; and (4) after pre-heating, the analysis is conducted normally, starting with the desorb purge flow cycle. This seemingly radical departure from protocol has been validated by saturating tubes with water, spiking them with known quantities of authentic POHC and PIC, removing the water pneumatically/ thermally and conducting their analysis to measure recovery of the spikes. Table 6 displays the average recoveries of each of eight compounds, determined in triplicate, at each of three spiking levels. The analytical system was calibrated using purge & trap methodology as the performance standard.

TABLE 6. VALIDATION OF PROPOSED PROTOCOL MODIFICATION FOR ANALYSIS OF WET VOST SAMPLES

	% Recovery @ spike = 30.0µg	% Recovery @ spike = 3.0µg	% Recovery @ spike = 0.30µg
Methylene chloride	98.0	99.5	138.5
Chloroform	94.3	100.2	102.7
Freon ® 113	99.8	103.4	108.5
Carbon tetrachloride	107.2	104.1	92.1
Trichloroethylene	102.1	103.2	104.3
Benzene	101.9	102.8	107.2
Toluene	102.5	99.9	102.1
Chlorobenzene	99.8	92.4	97.7

Phase 7- Excessive Breakage of VOST Tubes

In field sampling applications, workers generally concede that a breakage rate of 30% is not unusual for glass VOST tubes of the I/I design. CRF experience parallels that of other workers and the cost here in lost analytical data is considerable. As a result of these considerations, tubes of two different designs were assembled/fabricated locally and evaluated in spike and recovery studies (see Table 7).

Swagelok® design - *#302 seamless* S.S., 1/4" o.d. x 5.5", usable internal volume ~ 1.8 cm^3 containing ~ 0.30 gm Tenax® GC.

Welded design - #302 seamless S.S., 5/8" o.d.x 3.0", fabricated by welding 5/8" - 1/4" reducers on either end of S.S. tube, usable internal volume ~ 11.5 cm^3 containing ~ 1.8 gm Tenax® GC.

The results listed in Table 7 were encouraging to the point that a third design, a S.S. replica of the I/I glass design, was fabricated locally and field tested at the CRF.

This third design was constructed as follows: a 2 3/4" length of 5/8" o.d. #302 seamless S.S. tubing was provided with female threads at each end; end fittings were machined from rod stock of the same material with matching male threads, wrench flats and a taper to 1/4" o.d. tube size; end fittings were installed on the 5/8" tube with Teflon® tape seals; the assembled unit was demonstrated leak free @ 80 psig helium; it was weighed, charged with TENAX GC®, weighed again and inscribed with an identifying number.

It is important to note that each of the prior experimental designs suffered from serious defects which have been eliminated in the most recent one. The Swagelok® design could only contain ~ 20% the amount of resin required by protocol[2], and exhibited high

TABLE 7. RECOVERY DATA FOR METAL VOST TUBES OF TWO DESIGNS

	% Recovery @ 3.0µg		% Recovery @ 0.30µg	
	Swagelok®	Welded	Swagelok®	Welded
Methylene chloride	105	100	122	96
Chloroform	105	111	122	88
Freon®	106	108	122	90
Carbon tetrachloride	105	102	126	46
Trichloroethylene	105	110	120	78
Benzene	105	114	121	91
Toluene	102	107	122	76
Chlorobenzene	98	100	120	79

pressure drops when tested in the sampling train. The welded design rusted badly at the butt seals and, in fact, spit rusty water during thermal conditioning.

After steam stripping, thermal conditioning and demonstration of analytical blank, these S.S. replica tubes were evaluated in recovery studies involving 19 compounds at 3 spike levels (Table 8). These levels were 3.0µg and 0.30µg, and 0.03µg for each compound per pair of VOST tubes. In addition, 1 ml of water was placed in each tube of every pair and the analytical system was calibrated using P&T methodology. It is worth noting that among the several chemical compound classes included in these data, the results are good. The abrupt threshold effect shown by acetonitrile is not surprising in view of its miscibility with water, while the high recoveries shown by readily polymerizeable styrene at least suggest that catalytic effects exerted by the steel walls of these

TABLE 8. RECOVERY DATA FOR STAINLESS STEEL REPLICA VOST TUBES

	% Recovery @ spike = 3.0µg	%Recovery @ spike = 0.30µg	% Recovery @ spike = 0.030µg
Acetonitrile	116	110	-0-
Methylene chloride	102	106	105
Chloroform	105	107	108
1,2-Dichloroethane	101	104	95
1,1,1-Trichloroethane	103	104	105
Carbon Tetrachloride	97	92	90
Trichloroethylene	103	104	107
Benzene	103	105	102
Tetrachloroethylene	104	104	91
Iso-octane	104	105	100
Toluene	103	104	106
Chlorobenzene	99	94	114
Ethylbenzene	100	88	110
Octane	106	105	110
Styrene	104	88	86
Ortho-xylene	105	99	99
1,3-Dichlorobenzene	105	82	95
1,4-Dichlorobenzene	104	73	94
Nonane	104	104	113

tubes may not be marked.

Additional evidence of a low order of catalysis exerted by the walls of the S.S. replica VOST tubes may be drawn from limited studies with additional compounds at the spiking levels indicated:
1,1-dichloroethylene (0.20µg); trans-1,2-dichloroethylene (0.60µg); bromodichloromethane (0.60µg); 1,2-dichloropropane (0.20µg); trans-1,3-dichloropropene (0.60µg); and bromoform (0.60µg). Each of these compounds was recovered at 88% or better except bromoform whose recoveries ranged from 42-113% with 71% as the average.

Table 9 displays the results of a study undertaken to demonstrate recovery by incinerator mimicry (see phase 4 section above) as well as compound stability in S.S. replica VOST tubes. This investigation was conducted as follows. Initially, three sets of VOST tubes were prepared. Each set was made up of one blank pair of tubes plus two spiked pairs. Each spiked pair contained 18 compounds at 0.30µg per compound per tube pair. On day #1, 20 dsl of steam-laden air were drawn through every pair of tubes which were then sealed, and the tube pairs in set 1 were analyzed. On day #2, the tubes of set 2 were analyzed, while set 3 tubes were analyzed on day #5.

TABLE 9. RECOVERY AND STABILITY DATA FOR S.S. REPLICA VOST TUBES EVALUATED BY INCINERATOR MIMICRY

	% Recovery @ *TET=0 hrs.	%Recovery @ TET=48 hrs.	% Recovery @ TET = 120 hrs
Acetonitrile	-0-	4	-0-
Methylene chloride	7	55	37
Chloroform	82	90	87
1,2-Dichloroethane	93	96	92
1,1,1-Trichloroethane	88	93	94
Carbon Tetrachloride	88	90	85
Trichloroethylene	98	97	96
Benzene	99	98	98
Tetrachloroethylene	96	93	92
Iso-octane	88	104	103
Toluene	103	106	98
Chlorobenzene	100	99	98
Ethylbenzene	100	98	99
Octane	106	112	106
Styrene	99	101	96
Ortho-xylene	103	101	102
1,3-Dichlorobenzene	87	93	86
1,4-Dichlorobenzene	71	79	69

*TET = Total Elapsed Time Since Spiking

SUMMARY AND CONCLUSIONS

VOST techniques are invaluable in the characterization of volatile emissions from hazardous waste incinerators. Practitioners of these techniques, the CRF among them, have identified several nagging operational problems that are frequently encountered. This report presents validated solutions to some of these problems in the hope that fewer VOST pitfalls may lead to wider VOST usage, and the harvesting of more and better

data on volatile emissions.

It must be emphasized here that none of the remedies suggested is infallible. For example, S.S. replica VOST tubes possess certain unmistakable advantages over their glass counterparts. Nonethless, investigators contemplating the use of such steel tubes should demonstrate that compounds of interest to them are well behaved in these devices.

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NOTICE AND ACKNOWLEDGEMENT

This document has been reviewed in accordance with U. S. Environmental Protection Agency policy and approved for publication. Mention of trade names or commercial products does not constitute endorsement or recommendation for use.

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