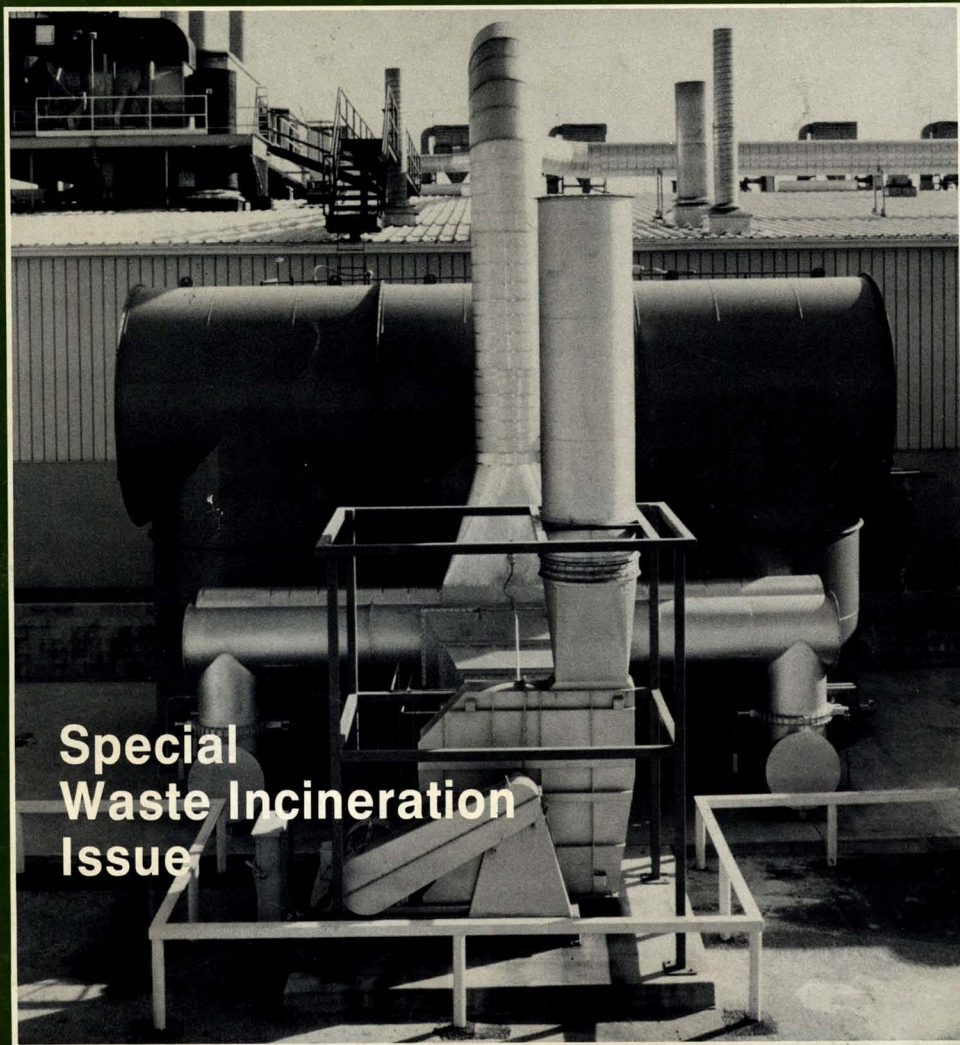


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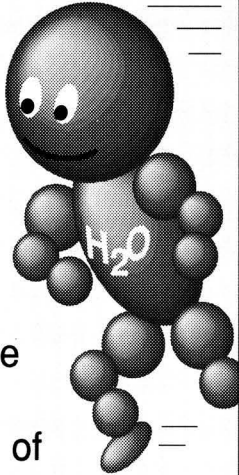
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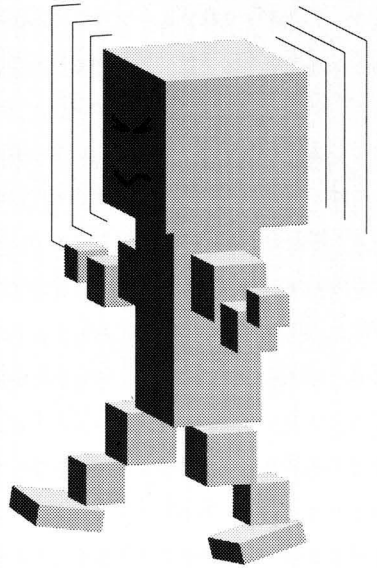
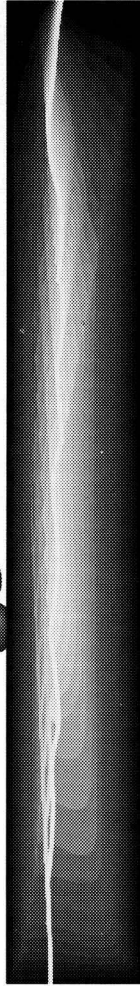
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Regenerative fume oxidation system.
Photo courtesy of Huntington Energy Systems, Union, N.J.

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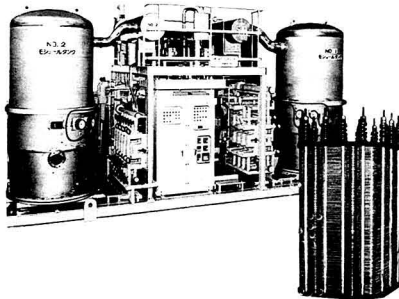
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Volume 8

Number 3

Special Issue Featuring
WASTE INCINERATION
Charles A. Wentz, editor

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From the Editor

This special issue of *Environmental Progress* is devoted to waste minimization—the cost-effective reduction of hazardous waste. Everyone is supportive of waste minimization that may best be achieved through innovative chemical engineering. Most of the papers in this issue have been presented at AIChE national meetings. All of them have been peer reviewed.

The broad scope of waste minimization exemplifies interests from industry, government, and academia. This issue is representative of this dynamic growth field and includes federal government regulations, tracking and audits, manufacturing and marketing strategies, industrial case histories, economic evaluation, state government assistance, and opportunities for future research programs.

We would like to thank all of the authors for preparation of their manuscripts and the reviewers for their contributions to the quality of the papers.

Charles A. Wentz, Editor
Special Waste Minimization Issue

Washington Environmental Newsletter

EPA to Sponsor Workshops on QA/QC Procedures for HW Incineration

EPA's Center for Environmental Research Information will present three workshops in August to introduce the "Handbook on QA/QC Procedures for Hazardous Waste Incineration." Primary audience is EPA RCRA permit writers and applicants for hazardous waste incinerators, but will also be of interest to engineers, chemists, environmental scientists and plant managers. Workshops will involve explanations of, and exercises in, process monitoring, sampling and analytical activities, after first defining the Data Quality Objectives (DQOs) needed for testing and sampling HW incinerators, including procedures during trial burns. Quality Assurance and Quality Control procedures will be defined for pollutants normally associated with incinerator emissions such as POHC's, PIC's, metals, particulates, dioxins, furans, acid gases and combustion gases.

Workshops will be held in San Francisco, Kansas City and Atlanta. There is no registration fee. For more information call Trisha Fasch at EPA Region I (617) 648-7811.

SARA Waste Material Remediation Through Incineration

The preliminary EPA interpretation of SARA requirements is that incineration becomes the preferred alternative. However, since incineration costs are so high, alternatives such as bio-remediation may be examined as alternatives. Conventional liquid incineration technologies typically do not apply to Superfund sites unless the primary waste source is containerized. Because the predominant waste form at Superfund sites is contaminated soils; rotary-kiln incineration technology or, moving grate infrared technology, are the most practical alternatives. The application of extraction technologies to remove and concentrate contaminants from soils may be a feasible intermediate to reduce the cost of ultimate incineration. Heavy metal recovery in secondary smelters is also under consideration, pending removal of potential RCRA barriers.

Love Canal Wastes Targeted for Incineration

A partial consent order has been signed between Occidental Chemical and state and federal governments obligating the company to store and destroy wastes from the Love Canal site. These include the remedial wastes from Black and Bergholtz creeks, contaminated sediments taken from area sewers, material stored in barrels at Love Canal, and the sludge resulting from the treatment of leachate by Love Canal's on-site treatment plant. Occidental will dewater the collected wastes at a nearby facility, then place them in polypropylene bags and transport them to their Niagara Falls plant. They will remain in storage until Occidental receives approval for and builds a rotary-kiln incinerator on site. The incinerator will thermally treat the solid wastes from Love Canal as well as from other company sites. Sludge from the Love Canal leachate treatment plant will be destroyed in Occidental's existing liquid incinerator at its Niagara Falls plant. The company will also be allowed to use the new rotary-kiln to burn wastes from its other western New York sites, but will not accept out-of-state or other company wastes.

Related New Legislation

Representative Mrazek (D.-NY) has introduced H.R. 2052 which would set strict limits on dioxin emissions from resource recovery plants and municipal waste incinerators.

*This material was prepared by AIChE's Washington Representative, Siegel • Houston & Associates, Inc.
Suite 333, 1707 L Street, N.W., Washington, D.C. 20036. Tel. (202) 223-0650*

Hazardous Waste Incineration: A Preferred Treatment Technology

Calvin R. Brunner

CH2M Hill, Reston, Virginia

Over the past ten to fifteen years the annual expenditure on pollution control in the United States as a percent of industrial capital equipment investment has risen from less than one percent to almost six percent. By the end of the century this figure is expected to more than double. This does not include pollution control for automobiles, or the cost of disposal of municipal solid waste or sewage.

The most effective means of dealing with waste disposal is to reduce the amount of waste generated. In industry this means process modifications, or establishing new markets for generated streams. In the public sector waste reduction translates to source separation, recycling and resource recovery.

Waste reduction is a goal, and a goal that will be driven forward by economic conditions. As the cost of waste disposal increases, new methods of waste reduction will become economically attractive, and will be implemented. It is difficult to imagine, however, a time when there will be no waste generation. For the foreseeable future, while waste reduction may reduce the amount of waste that must be disposed of, there will be hundreds of millions of tons of waste that must be destroyed or controlled to protect the public health and the sanctity of the environment.

While industry is struggling with the mechanisms of waste reduction, the avenues open for waste disposal are becoming fewer and fewer, particularly in the area of hazardous wastes. Incineration is becoming more attractive when looking at alternative disposal methods. Through incineration the hazardous organic component of the waste is destroyed, the volume and weight of the waste is reduced to a fraction of its original size and waste reduction is immediate; it does not require long-term residence in a land disposal system. Waste can be incinerated on-site, without being carted to a distant area. Of particular concern, air discharges can be effectively controlled for minimal impact on the atmospheric environment. The ash residue may be subject to declassification as a hazardous waste and with this the case, incineration becomes, essentially, a final disposal method as well as treatment.

Other features of the incineration process are that it requires a relatively small disposal area, not the acres and acres needed for land disposal, and that incineration is easily terminated. A cessation of incineration activity will remove any liability for the generator or operator as compared with land burial where liabilities are indefinite and uncertain. Using heat recovery techniques the cost of operation can be reduced or offset by the use or sale of energy.

Although incineration is becoming more and more attractive as a waste treatment option, it is not universally applicable to waste disposal. Not all materials are incinerable. For example, high aqueous wastes or non-combustible soils will not sustain combustion. Certain organic materials, particularly those containing a chlorine component, tend to generate products of incomplete combustion that are the subject to continuing study for their toxicity and the means necessary for their destruction. Incineration represents a high capital cost and skilled operators are required compared to land disposal techniques. Supplemental fuel is required to bring up an incinerator to operating temperature and, with some materials, to maintain combustion temperatures.

The incineration option is, on balance, an attractive option for a growing number of waste streams. The trend today is an increase in the use of incineration for a wider profile of wastes.

With more and more exposure given to the features and uses of incineration technology, the public will see it as a new and sophisticated technology, not an anachronism of past practice where incineration was synonymous with smoke and odor. Increased use of incineration will promote safe and effective environmental clean-up and maintenance. This issue deals with hazardous waste incineration, as well as, non-thermal destruction, and issues concerning incinerator ash.

Calvin R. Brunner, P. E., is Chief Engineer, Incineration Systems, for CH2M Hill in Reston, VA. He has over twenty years experience in the thermal disposal of wastes and has written numerous textbooks on the subject.

Whazan: A Software for Chemical Hazards Analysis

Ashok Kumar and Sushant Agarwal

Department of Civil Engineering, University of Toledo, Toledo, Ohio 43606

Recent industrial accidents, involving episodic releases of hazardous or toxic materials are drawing considerable attention from the regulators, public and researchers. A recent article by Egol [1] discusses the role of computers in environmental management of hazardous materials and the availability of softwares to perform various tasks required by recent regulations. One activity which is important during an emergency involving chemicals is the calculation and prediction of concentration as a result of a chemical release. In this article, a software (WHAZAN) developed by Technica International, 1440 N. Harbour Blvd., Suite 800, Fullerton, CA 92635, USA is discussed.

The WHAZAN (World Bank Hazard Analysis) [2] software consists of a series of computer programs and is available on diskettes for the use on the IBM PC-XT or PC-AT or PS/2 or on the IBM compatible computers. The program requires the use of PC-DOS version 3.0 or higher. You will need a minimum of 512 Kbytes of memory to load/run the software. Without sufficient memory the programs will not run at all. Moreover, care should be taken while choosing the color graphics adapter during program installation for display of graphical output.

The following steps were taken in order to test the software:

1. All individual models were run for various release conditions,
2. An attempt was made to obtain information on chemicals already stored in the software,
3. Adding information on new chemicals, and
4. Linked models were tried.

The software comes with a manual which is divided into two parts consisting of the user guide and a theory manual (1988). The guide is divided in five chapters and an appendix. The guide is virtually error free and minor editing will improve the manual. The theory manual consists of four chapters and four appendices.

Chapters 1 and 2 of the user guide covers the basics of installation and running the computer program. Hardware requirements are included in Chapter 2. The procedure to load the program is fairly simple. The instructions given in the users guide are straight forward and no difficulties were encountered during this process. Chapter 3 describes the chemical properties and structure of the chemical data base, which contains data on a total of 20 commonly encountered hazardous chemicals. It also describes the basic definitions of the chemical properties for easy reference. A maximum of 100 chemicals can be stored for hazard analysis.

The procedure for running 13 individual models is given in Chapter 4. The various models cover the following areas:

- i. Outflow of either a liquid, gas or a two phase flashing mixture,
- ii. Behavior immediately after release. The various models incorporated into the system calculate the plume rise in case of gaseous release and pool size and evaporation rate in case of liquid release,
- iii. Dispersion in the atmosphere. The calculations for fatality probability are included for toxic chemicals, and,
- iv. Fire and explosions due to ignition of a pool or cloud of flammable material.

Chapter 5 discusses the concept of linked consequence models. The appendix gives conversion factors for the parameters used in WHAZAN. This would be particularly helpful to industrial users of the software. A good feature about the manual is the use of actual on-screen display, along with program explanation.

The Chapter 1 of the theory manual discusses the difference between the work done by Technica Ltd. for World Bank in 1985 and current version of the software. Chapters 2 and 3 describe most common release scenarios in an industrial complex. Chapter 4 provides the theoretical framework for each model discussed above. Appendix A gives the typical velocity head losses due to flow through various valves and fittings which in turn are used to calculate the discharge coefficient for an orifice. Such information can prove to be quite handy while using this package. A discussion on atmospheric stability and surface roughness is included in Appendix B. Problems associated with the choice of consequence levels in hazard analysis are explained in Appendix C.

Overall the program gave satisfactory results. Some minor difficulties may be encountered by the user in the area of adding information on new chemicals. The information should be selected with care otherwise the program may not run and the computer may lock up requiring rebooting. The package can be made more flexible if data could be read from a data file for production runs.

The software WHAZAN is a useful tool for performing hazard analysis of toxic releases. It is menu driven and user-friendly.

REFERENCES

1. Egol, L., Hazardous Materials Trigger a Software Explosion, Chemical Engineering, pp. 179-182, April 1989.
2. *WHAZAN User Guide and WHAZAN Theory Manual*, Technica International Ltd., March 1988.

Book Reviews

How to Respond to Hazardous Chemicals Spills by W. Unterberg, R. W. Melvold, S. L. Davis, E. J. Stephens, and F. G. Bush III, Noyes Data Corporation, Park Ridge, NJ (1988), 274 pages, U.S. List Price: \$39.00

This book is a reference manual of the countermeasures designed to assist responders to spills of hazardous substances. The book begins with two short introductory sections dealing with how to use the manual and how to assess the spill situation.

Using the techniques described in Chapter 2 and the situation Assessment Flow Charts and the Site Assessment Checklist which accompanies it, the responder should be able to identify the chemical involved in the spill. Also, the photoreproduction of the flowchart is not good and the size of the chart is so small it is hard to see.

The lists of chemicals in Chapter 3 contain 700 hazardous substances designated by the Comprehensive Environmental Response Compensation and Liability Act (CERCLA) of 1982. For each chemical, the following data are given: (Table A) name, chemical class, CAS Registry No., hazards (i.e., flammable, toxic, etc.), and behavior in water (soluble, sinks, etc.). The second table (Table B) gives countermeasure actions which are technically feasible for the various chemical classes following their recommended process. Finally one consults the third table (Table C) which contains descriptive values of each of the selected criteria; development, time, cost, and cleanup efficiency. Further refinement of countermeasure selection is available through the use of the fourth chapter in which countermeasure-mechanical containment and displacement; physical, chemical, and biological treatment; and ultimate disposal/destruction, are listed together with detailed, distinguishing characteristics.

The book ends with an excellent 30-page reference list and three appendices: (1) Guidelines for site assessment, entry, and control, (2) Suggested guidelines for selecting chemical protective clothing, and (3) Personnel and response equipment decontamination.

This book will be quite useful to those involved with the management and response to hazardous chemical spills at industrial facilities.

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How to Prevent Spills of Hazardous Substances by W. Unterberg, R. W. Melvold, K. S. Roos, and P. A. Scofield, Noyes Data Corporation, Park Ridge, NJ (1988), 185 pages, U.S. List Price: \$39.00

Of all the areas of hazardous materials, I am most keenly interested in spill prevention. So, when I picked up this book, it was with real enthusiasm and with much expectation. Unfortunately, I was totally disappointed as there was little information in the book that was of any use and virtually nothing new. The first 80 pages were simply a listing of 700 chemicals designated as hazardous substances by the Comprehensive Environmental Response Compensation and Liability Act (CERCLA). The data given included chemical class, CAS registry number, hazard, and behavior in water.

What I thought would be the heart of the book: (1) facilities spill prevention, practices, and (2) preventive engineering practices was limited to approximately 20 pages. It is not that the right concepts are not covered within these 20 pages; those topics are not covered in enough detail. I wished for much more.

The book ends with a long (70 page) appendix, describing fixed facilities, chemical process equipment components, such as pumps, piping, heat exchangers, etc. Why the authors included a description of commonly used process equipment is not clear to me at all.

In summary, a great book title, but disappointing because of many unfulfilled expectations.

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Introduction to Hazardous Waste Incineration by Louis Theodore and Joseph Reynolds, John Wiley & Sons, New York, New York (1987), 463 Pages, U.S. List Price: \$49.95

This book examines basic principles, equipment, and applications for hazardous waste incineration. It is the only textbook to date that covers both scientific and engineering aspects of hazardous waste incineration.

It is an excellent textbook for engineering students who are interested in this field. The text has been well conceived and is written to provide an introduction to hazardous waste incineration concepts, design, and operations. Numerous illustrative examples and problems have been included to assist the reader.

In addition to its obvious utility as an engineering textbook it should also be a useful engineering reference for practicing engineers and scientists. The writing style of the authors is easy to follow for readers who have some prior knowledge of science and mathematics.

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Breakthrough Excavation-Free Hazardous Waste Treatment Process

Weston, Westchester, PA, has signed an exclusive licensing agreement with the IIT Research Institute (IITRI) to offer a new hazardous waste treatment process on a commercial basis. Developed by IITRI, this patented process, called In situ Radio-Frequency (IRF) decontamination, treats the waste in place without excavation. This new process represents a significant breakthrough in reducing the cost of treating many of the nation's hazardous waste sites.

The low cost process is estimated to cost between \$50 and \$90 per ton of soil treated, according to John W. Noland, vice president of Weston Services, Inc. (WSI). WSI is a major construction company with proven environmental expertise. In the past five years, WSI pioneered the development, design, permitting, construction, performance testing and operation of several new thermal systems for hazardous waste removal.

IRF decontamination is accomplished by inserting tubular electrodes (hollow pipes) into contaminated soil. By exciting the electrodes with radio-frequency energy, the soil is heated to between 200 degrees fahrenheit and 1,000 degrees fahrenheit, thereby vaporizing the hazardous contaminants. The vapors are collected in the hollow electrode pipes and removed under negative pressure to a vapor treatment system designed by Weston.

"This process is similar to the heating accomplished within a microwave oven, although the volume heated is much larger, up to 5,000 tons of soil at a time, and the frequencies are much lower. Radio frequency energy is an efficient and cost-effective method of heating the

soil without digging it up. Collection and treatment of the vapors is accomplished using the vapor extraction technology Weston developed under a contract with the U.S. Army Toxic and Hazardous Materials Agency. The IRF process is best described as thermally enhanced vapor extraction," said Noland.

The IRF process is an extension of the technology developed by IITRI to extract useful fuels from oil shale and tar sand deposits. In this application, massive blocks of oil shale or

tar sand at depths of thousands of feet are heated by radio-frequency energy. Conversion of the technology to decontaminate hazardous waste sites was funded in part by the U.S. Air Force and the U.S. Environmental Protection Agency.

Weston is headquartered in West Chester, PA, and operates through a network of four analytical laboratories and 45 offices, including Los Angeles, Houston, Chicago, Atlanta, Boston, New York and Washington, D.C.

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Continued from page A8

Hazardous Waste Minimization Handbook by Thomas E. Higgins, Lewis Publishers, Chelsea, Michigan (1989), 250 pages, U.S. List Price: \$49.94

This is a handbook that would be helpful for a waste minimization program with industrial processes. It is probably the most current book in this field that is on the market today. There are numerous case studies, for example, that lead the reader through "how to do it" exercises in waste minimization.

The book emphasizes economics as the major criteria in determining waste minimization priorities. A variety of industrial processes including metal working, solvent cleaning and degreasing, metal plating and surface finishing, painting and coating, and paint removal are covered in the book. There is also a

discussion of waste treatment to minimize the quantity of waste requiring disposal.

In summary, this book is useful in expanding knowledge in the field of hazardous waste minimization. It should be of general interest to managers, operators, and engineers who are involved in the industrial processes that are addressed.

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Hazardous Waste Management, Volume I by George Dominguez and Kenneth G. Bartlett, CRC Press, Inc., Boca Raton, FL 33431 (1986), 207 pages, U.S. List Price: \$110.00

This is a well written book that provides an overview of the legal aspects of hazardous waste management. The individual chapters have been written by various contributors, who are knowledgeable in their field. It provides a ready reference and understanding of important aspects of laws and their application in the environmental field with particular emphasis on the Resource Conservation and Recovery Act. It could be useful to a broad audience ranging from lawyers to practicing engineers who desire to better understand hazardous waste legislation in an integrated manner.

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Incineration of Solid Waste

C. C. Lee and George L. Huffman

U.S. Environmental Protection Agency
Office of Research and Development
Office of Environmental Engineering and Technology Demonstration
Risk Reduction Engineering Laboratory
Cincinnati, OH 45268

The concern over solid waste disposal and dump-site clean-up resulted in the passage of three major U.S. environmental laws. They are the Resource Conservation and Recovery Act (RCRA) of 1976, Public Law 94-580, the Toxic Substances Control Act (TSCA) of 1976, Public Law 94-469, and the Comprehensive Environmental Response, Compensation and Liability Act (CERCLA) of 1980, Public Law 96-510. The implementation of these three laws has intensified incineration research, because incineration represents the highest degree of destruction and environmental control possible for various waste types. This paper reviews the fundamentals of incineration and provides an incinerator design example to show how combustion fundamentals are applied to an incineration system.

INTRODUCTION

Conventional combustion (of coal, oil, and gas) has been a subject of research for many decades. However, incineration research for solid waste destruction was fairly minimal until the mid-1970's when incineration was found to be effective for the disposal of various wastes. In responding to the numerous environmental catastrophes resulting from the improper waste disposal practices of the past, the Congress enacted RCRA, TSCA, and later, CERCLA. The purpose of these laws is to assure the reliable management of hazardous/toxic waste disposal operations and dump-site clean-up. Because incineration is very popular for waste disposal, the enactment of these laws considerably intensified incineration research within EPA and private industry.

Scientifically, the terms "combustion" and "incineration" have the same definition: a process of burning, resulting from the rapid oxidation of substances. Both of these terms have been used interchangeably in waste incineration documents. Combustion, however, is generally used more often in the area of fossil-fuel burning for steam or power generation and incineration is used more often when referring to waste destruction. Nevertheless, incineration uses many of the terminologies originally defined in the field of conventional combustion.

This paper includes:

- A review of combustion fundamentals and terminologies often used in the field of waste incineration;
- A description of incineration phenomena in a typical rotary kiln incinerator; and
- An incinerator design example to show how combus-

tion fundamentals are applied to an incineration system.

The purpose of this paper is to help those interested in waste incineration understand its basics and thereby, hopefully, improve the outlook for the incineration processes of the future.

Incineration can destroy a variety of wastes including medical, hazardous and municipal wastes and residues from dump-site clean-up. EPA's research data and industry's operating experience indicate that incineration, when compared to the other alternative technologies, has the highest overall degree of destruction and control for the broadest range of waste streams [1].

Definition of Hazardous Waste

A substance is defined as a hazardous waste by the EPA if it meets the definition of solid waste under 40 CFR 261.2, and either meets one or more of the hazardous waste characteristics (ignitability, corrosivity, reactivity, or toxicity), or is listed as a hazardous waste in Part 261. Incinerators that burn hazardous waste must meet the requirements of the RCRA incineration standards [2], which are summarized below:

1. An incinerator must achieve a destruction and removal efficiency (DRE) of 99.99% for each principal organic hazardous constituent (POHC) designated for the waste feed. For PCB (polychlorinated biphenyls) and dioxin-listed wastes, the DRE requirement is 99.9999%. POHCs are to be designated based on compound incinerability and concentration in the waste feed. EPA initially suggested that heat of combustion be used as the measure of compound incinerability in its guidance manual to permit writers [3].
2. The DRE for an incinerator/air pollution control system is defined by the following formula:

$$\text{DRE (\%)} = 100 \times (W_{in} - W_{out}) / W_{in}$$

where DRE = destruction and removal efficiency, percent

W_{in} = mass feed rate of POHC to the incinerator

W_{out} = mass emission rate of POHC to the atmosphere (as measured in the stack prior to discharge)

3. An incinerator burning hazardous waste must remove 99% of the hydrogen chloride (HCl) from the exhaust gas or have no more than 4 lbs/hr of HCl in the emissions.
4. An incinerator burning hazardous waste must not emit particulate matter exceeding 180 mg/dscm corrected to 7% O₂ in the stack gas.
5. A trial burn (or data equivalent to a trial burn) is generally required to demonstrate the ability of a hazardous waste incinerator to comply with the above performance standards.

LITERATURE REVIEW

The earliest available literature on chlorinated compound research was in 1929, when Fredenhagan [4] observed that chlorine-fluorine mixtures could produce a flame as they were sparked. In 1956, Garner, *et al.*, [5] examined the inhibitory effects of chlorinated methanes on the burning velocities of propane/air mixtures when present in quantities of less than 1 mole percent. They concluded that the order of effectiveness in reducing burning velocity was in the order of CH₄ < CH₃Cl < CH₂Cl₂ < CHCl₃ < CCl₄. Fletcher, *et al.*, [6] measured the spatial velocities of chlorine-fluorine flames over the flammable

range. The results were compared with theoretical flame temperatures and equilibrium compositions, and a simple, plausible rate expression was developed. They concluded that although the spatial velocities did not correlate well with temperature, they correlated with equilibrium fluorine atom concentration in the products.

Wolfhard (and co-workers) [7, 8] was one of the pioneers to study the flammabilities of substances. He used the oxygen index as the parameter to compare flammabilities of some light fuels. Fenimore [9] used the same concept to study the flammability of polymers and concluded that the oxygen index seemed to be a useful measurement of polymer flammability. It was easy, reproducible, and numerical.

Barnard, *et al.*, [10] and Hoare, *et al.*, [11, 12] studied the thermal oxidation of ketones. They concluded that oxidation of ketone-related compounds, such as acetone, methyl-ethyl-ketone, and diethyl ketone, followed the same patterns that they had found earlier, *i.e.*, that hydrogen abstraction could take place from the methyl group or from the α or β position of the alkyl group.

The implementation of the RCRA, TSCA, and CERCLA laws has resulted in publication of a large quantity of incineration information since 1976 [13-22]. In addition to reviewing this incineration information, this paper also reviews combustion fundamentals [23-28] and related incineration subjects [29-34].

UNDERSTANDING THE COMBUSTION PROCESS

Combustion or incineration is a very complicated subject. It is so complicated that many consider it as an art rather than a science. Understanding the combustion process is, however, essential in order to effectively design, operate, and regulate incinerators. Key areas requiring the understanding of the combustion process include:

- Mass balance (it determines the amounts of the products formed by the reactants);
- Energy balance (it determines the energy transferred within a combustion system or how much auxiliary fuel is needed for an incinerator to reach a certain temperature);
- Thermodynamic analysis (it reveals information about the changes of the chemical components of a combustion system. However, it does not reveal how rapidly these changes will occur);
- Kinetic analysis (it provides information on how quickly changes can occur, but does not predict the extent of change that is ultimately possible);
- Heat transfer (it determines the temperature distribution within a combustion system);
- Turbulent mixing (it determines whether the waste compounds are effectively put in contact with oxygen for reaction); and
- Residence time (it determines the volumetric size of a combustor).

The last three items, *i.e.*, temperature, turbulence, and time, are called "the three t's" of waste incineration.

Combustion or incineration basically refers to the burning of substances during an extremely rapid chemical oxidation process. In contrast, rusting is a very slow chemical oxidation. When oxidation is rapid, the temperature of the material rises rapidly due to the inability to transfer the heat to the surroundings as rapidly as it is produced by the oxidation reaction. As a result, the material emits visible radiation, which is referred to as a flame.

Fundamentally, there are four major components in an incineration system. They are: 1. fuel; 2. oxidizer; 3. diluent; and 4. waste.

Fuel

A fuel is a mixture of hydrocarbons containing energy-rich bonds such as the carbon-carbon and carbon-hydrogen bonds. These hydrocarbons are a common source of chemical potential energy.

Oxidizer

The second component of an incineration system is the oxidizer. The oxidizer is the chemical species that reacts with the fuel or waste compounds during incineration. Its function is to transform the chemical potential energy stored in the fuel into thermal energy or to convert heavy-molecule waste compounds into light, simple compounds such as CO_2 , H_2O , and HCl . Most commonly, the oxidizer is molecular oxygen, a constituent of air.

Air, the natural source of oxygen for incineration, is considered an ideal gas in many incineration calculations. It is a mixture of oxygen, nitrogen, and small amounts of water vapor, carbon dioxide, argon, and other elements. For the purpose of combustion calculations, the last four items are usually included with the nitrogen. Accordingly, the volumetric and gravimetric analyses of air, along with its density and standard volume, are as follows:

Volumetric Analysis of Dry Air

Oxygen: 21 percent or 0.21 mole/mole of air
 Nitrogen: 79 percent or 0.79 mole/mole of air
 $0.21 \text{ O}_2 + 0.79 \text{ N}_2 = \text{air}$ (1)
 or $\text{O}_2 + 3.76 \text{ N}_2 = 4.76 \text{ air}$ (2)

Gravimetric Analysis of Dry Air

Molecular weight of dry air = $0.21 \times 32 + 0.79 \times 28$
 = 28.84 lbs/mole
 Oxygen mass fraction = $0.21 \times 32/28.84 = 0.23$
 Nitrogen mass fraction = $0.79 \times 28/28.84 = 0.77$

Thus, one pound of air can be expressed by:
 $0.23 \text{ lb O}_2 + 0.77 \text{ lb N}_2 = 1 \text{ lb air}$ (3)
 or $1 \text{ lb O}_2 + 3.35 \text{ lb N}_2 = 4.35 \text{ lb air}$ (4)

Air Density

Air density at standard conditions = weight/volume
 = $28.84/359$
 = 0.0808 lb/ft^3

Standard Volume of Gases

A mole of any gas at standard conditions has a volume of 359 ft^3 . EPA's standard conditions are: temperature 25°C and pressure 760 mm Hg (29.92 in. Hg).

Diluent

The third component that may be present in an incineration system is the diluent. A diluent is a substance that does not participate chemically in the combustion reaction either as a fuel substance or as an oxidizer. It is physically present and often does influence the combustion process. For example, diluents have heat capacity and while they do not make a positive contribution to the total energy released, they do act as a thermal sink and limit the temperature rise achieved by combustion. A diluent can be thought of as a substance that participates principally in the physical aspects of the combustion process.

There are several possible diluents in an incineration system:

- Nitrogen, which comprises almost 79% of air, is the most common diluent.
- Excess amount of oxygen. Incineration normally takes place at about 150 to 200% of the amount of theoretical air needed for combustion. The excess oxygen (the amount over 100% of theoretical air) will act as a diluent.

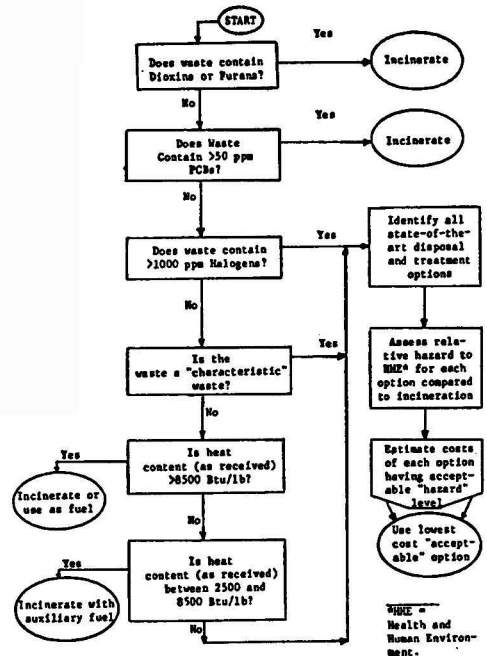


Figure 1. Conceptual strategy for determining waste burnability.

- Water vapor contained either in combustion air or in the waste feed, or the amount formed during the incineration process.
- Inorganic ash compounds present in the waste or in the fuel.
- Trace heavy metals present in the waste or in the fuel.

These diluents are neither fuels nor oxidizers. However, when they are involved in incineration, they may alter the process physically by virtue of their behavior as a thermal sink and by alteration of the high temperature equilibrium distribution of the reacting gas mixture.

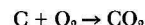
Waste

Incineration has been used for waste disposal for many decades. The waste streams that are incinerable include hazardous waste, municipal waste, toxic substances (PCB), medical waste, spent pesticides, sludges from both municipal and industrial wastewater treatment processes, and other unclassified waste such as non-hazardous military waste. However, some wastes can be more efficiently incinerated than others. Figure 1 [19] shows a strategy to determine what wastes should be incinerated. Also, in evaluating RCRA's waste streams (40 CFR 261), EPA has rated candidate waste streams as to their potential for incineration [32].

THE COMBUSTION AND INCINERATION PROCESS

Combustion Process

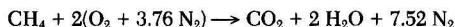
Combustion is a process of rapid oxidation that involves heat and light. Consider the oxidation of carbon:



This equation states that one mole of carbon reacts with one mole of oxygen to form one mole of carbon dioxide. This also means that 12 lbs of carbon react with 32 lbs of

oxygen to form 44 lbs of carbon dioxide. All feed substances that undergo the combustion process are called the reactants, and the substances that result from the combustion process are called the products.

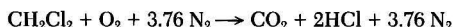
Obviously, combustion has to follow the law of mass conservation and law of energy conservation. Therefore, during combustion, chemical elements can react with each other but the mass and the energy level of the entire combustion system must remain the same. Consequently, the combustion of methane can be represented as:



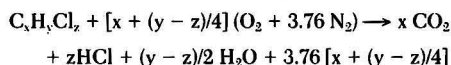
Incineration Process

Incineration of wastes in general involves three simultaneous chemical reaction modes: strong oxidation; weak pyrolysis; and weak radical attack.

Strong oxidation: The oxidation of waste is shown in the following example for which dichloromethane is oxidized to produce harmless products:



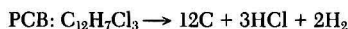
A generalized formula for the complete combustion of a typical waste, $\text{C}_x\text{H}_y\text{Cl}_z$ (i.e., "theoretical air combustion"), can be expressed as follows for $y \geq z$:



where: x , y , and z represent the relative number of atoms of carbon, hydrogen, and chlorine respectively.

Pyrolysis: Pyrolysis is a thermal degradation process, wherein carbonaceous materials are destroyed or chemically rearranged in the absence or near absence of oxygen or air. It uses heat to break the bonds of the elements contained in a compound.

Although incineration requires about 50%–150% excess air to ensure enough oxygen in the combustion chamber to effectively contact with the waste, some small fraction of the waste still may not have a chance to contact the oxygen. These small waste fractions that remain in the high-temperature environment may undergo pyrolysis. For example, the pyrolysis of cellulose and PCB would be as follows:



The degraded compounds will generally produce simpler compounds such as CO , CH_4 , and H_2O , which will be in the gaseous phase, and carbon (C), char, which will be in the solid or liquid phase.

Radical attack: During incineration, flames are characterized by temperatures usually in the neighborhood of 1,000°C and a radical-rich gas flow. This gas flow consists primarily of atomic hydrogen (H), atomic oxygen (O), atomic chlorine (Cl), hydroxyl radicals ($\text{OH} \cdot$), possibly methyl radicals ($\text{CH}_3 \cdot$) in carbon-hydrogen-oxygen systems, and chloroxy radicals ($\text{ClO} \cdot$) in chlorine-containing systems. The radical attack on waste compounds facilitates the decomposition of the waste.

During incineration, there are at least three possible situations:

- A majority of the waste can be easily oxidized and totally destroyed in the primary combustion chamber. Or, if a small fraction of the waste is pyrolyzed in the primary chamber, the pyrolysis products are totally destroyed in the secondary combustion chamber, the afterburner.
- A very small amount of waste, for some reason, may escape from the incineration process and is not de-

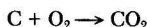
stroyed or is only partially destroyed. In this case, POHC emissions will generally be too high.

- Waste compounds may produce intermediate compounds and may result in the emission of unwanted products of incomplete combustion that may be more hazardous than the parent compounds. In this case, the emission of PICs (products of incomplete combustion) may well be beyond desired levels.

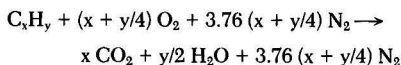
COMPLETE COMBUSTION AND COMPLETE INCINERATION

Complete Combustion

To obtain the optimum temperature during combustion, it is desirable to convert all the chemical energy stored in the reactants into thermal energy. To reach this goal, all carbon and hydrogen elements in a combustion system must be fully oxidized and become only carbon dioxide and water. When all carbon and hydrogen elements are converted into only carbon dioxide and water, the process is referred to as complete combustion. The conversion of carbon and hydrogen can be expressed as follows:



A generalized formula for complete combustion of a conventional fuel, C_xH_y ("theoretical air combustion"), can be expressed as:



where: x and y represent the relative number of atoms of carbon, and hydrogen, respectively.

Complete Incineration

The ultimate goal of the incineration of waste is to convert the waste materials into harmless combustion products so that they can be safely emitted to the environment. When a waste is completely incinerated, the elements in the waste are generally assumed to follow reaction patterns shown in Table 1:

TABLE 1. ASSUMPTIONS OF COMPLETE INCINERATION [31]

Waste Elements	Conversion	Products
Hydrogen, H	→	H_2O
Carbon, C	→	CO_2
Chloride, Cl	→	HCl or Cl_2
Fluoride, F	→	HF or F_2
Sulfur, S	→	SO_2
Nitrogen, N	→	N_2
Alkali metals	→	hydroxides
Sodium, Na	→	NaOH
Potassium, K	→	KOH
Non-alkali metals	→	oxides
Copper, Cu	→	CuO
Iron, Fe	→	Fe_2O_3

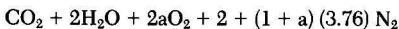
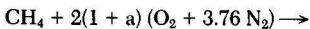
However, complete incineration is solely a theoretical concept. In actual practice, partially oxidized products of incomplete combustion (PICs) are formed. These PICs may include carbon monoxide (CO), soot, and a whole myriad of other organics. It is always possible to over-design an incinerator or to use extra fuel for higher flame temperatures to ensure sufficiently complete combustion. However, either of these corrective measures increase the cost of incineration.

SPECIAL COMBUSTION TERMINOLOGIES FOR INCINERATION APPLICATIONS

Air is a natural oxygen source. The exact amount of air required to burn a given amount of a fuel or a waste compound is defined as the Theoretical Air or Stoichiometric Air requirement.

Excess air is the air supplied in excess of that necessary to burn the compound completely and it appears in the products of combustion. The amount of excess air is normally expressed as a percentage of the theoretical (stoichiometric) air required for complete combustion of the compound.

For example, for the combustion of methane, CH₄:

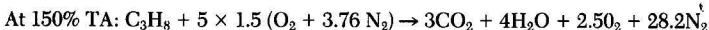
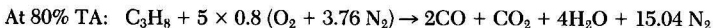
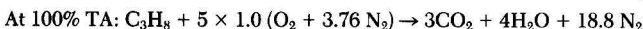


where: *a* is the fraction of excess air (EA) and the fraction of excess air = (*aa* - *ta*)/*ta*

where: *aa* = moles of air used in the actual combustion process

ta = moles of air used at 100% of stoichiometric combustion
= theoretical air (TA)

Combining these principles with the use of the generalized formula for the complete combustion of a conventional fuel, C_xH_y, presented earlier, we have:



Consequently, the 150% of theoretical air is equivalent to 50% excess air.

Air/Fuel Ratio

The air/fuel is defined by the following two options:

$$\text{AF}_m = (\text{Air/Fuel}) = n (1 + 3.76)/nf$$

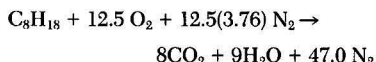
by mole

$$\text{AF}_w = (\text{Air/Fuel}) = n (1 + 3.76) 29/(nf \times \text{Mf})$$

by weight

where: *n* = moles of oxygen
nf = moles of fuel
Mf = molecular weight of fuel
29 = molecular weight of air (actually 28.84)

To calculate the theoretical air/fuel ratio for the combustion of octane, C₈H₁₈, the combustion equation is:



The theoretical air/fuel ratio on a mole basis is:

$$\text{AF}_m = (12.5)(4.76)/1 = 59.5 \text{ moles air/mole fuel}$$

The theoretical air/fuel ratio on a mass basis is found by introducing the molecular weights of the air and fuel. That is:

$$\text{AF}_w = 59.5(28.84)/114.2 = 15 \text{ lb air/lb fuel}$$

Combustion Efficiency (CE)

Combustion efficiency is defined as:

$$\text{CE} = \text{CO}_2/(\text{CO}_2 + \text{CO})$$

where: CO₂ = carbon dioxide
CO = carbon monoxide

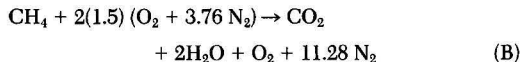
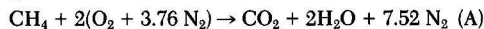
Correction Factor (CF)

For comparison purposes, it is sometimes necessary to correct a measured value of a compound's concentration at the stack to a certain desired ("standard") concentration. The way to make such a correction follows.

The correction factor (CF) for oxygen is defined as:

$$\text{CF} = (21 - \text{desired O}_2)/(21 - \text{measured O}_2)$$

Examples of CF calculations:



Equation (A) depicts combustion at 0% excess air and equation (B) shows 50% excess air combustion. The following calculation shows how CO₂ measured at 150% of theoretical air combustion (50% excess air) is converted to 0% excess air combustion.

O₂ measured at the wet condition of Equation (B)

$$= 1/(1 + 2 + 1 + 11.28) = 6.5\%$$

O₂ measured at a dry condition of Equation (B)

$$= 1/(1 + 1 + 11.28) = 7.5\%$$

To correct the measured (dry) O₂ value to a desired standard concentration of 0% O₂:

$$\text{CF} = (21 - 0)/(21 - 7.5) = 1.55$$

CO₂ measured at a dry condition (Equation (B))

$$= 1/(1 + 1 + 11.28) = 7.5\%$$

To correct the measured CO₂ to a standard O₂ level of 0% excess air (i.e., at the theoretical air condition):

$$7.5\% \times 1.55 = 11.625\%$$

This figure can be checked with the dry CO₂ level from the theoretical air combustion of CH₄ from Equation (A). That is:

$$\text{CO}_2 = 1/(1 + 7.52) = 11.73\%$$

The discrepancy between the 11.625% and 11.73% values is probably due to rounding off certain values; in any case, the values are very close.

Combustion—Lean and Rich

A combustible mixture that contains excess oxidant for the complete combustion of the available fuel is considered lean. A combustible mixture that contains insufficient oxidant for the complete combustion of the available fuel is considered rich.

Equivalence Ratio

It is often desirable to compare the richness or leanness of combustion for different fuels. The equivalence ratio (ER) is convenient for this type of comparison, and it may be defined as the actual fuel-air ratio divided by the stoichiometric fuel-air ratio.

$$\text{ER} = \frac{(\text{F/A}) \text{ actual}}{(\text{F/A}) \text{ stoichiometric (theoretical)}} \quad (\text{C})$$

or, alternatively, it is sometimes defined in terms of air-fuel ratios. In that case:

$$ER = \frac{(A/F) \text{ actual}}{(A/F) \text{ theoretical}} \quad (D)$$

By either definition, for a stoichiometric mixture, $ER = 1.0$. However, it should be recognized that even though the equivalence ratios defined above have identical values at stoichiometric conditions, they are not identical for off-stoichiometric (rich or lean) mixtures because (F/A) and (A/F) ratios are reciprocals. This is illustrated in Table 2.

Adiabatic Flame Temperature

For a given combustion process that takes place adiabatically and with no work or changes in kinetic or potential energy involved, the temperature of the combustion products is referred to as the "adiabatic flame temperature." With the assumptions of no work and no changes in kinetic or potential energy, this is the maximum temperature that can be achieved for the given reactants because any heat transfer from the reacting substances and any incomplete combustion would tend to lower the temperature of the products.

For a given fuel and given pressure and temperature of the reactants, the maximum adiabatic flame temperature that can be achieved is with a stoichiometric mixture.

FLAMES

Because combustion or incineration will result in flames, there are several kinds of flames which need to be understood. They are: premixed flame versus diffusion flame; and laminar flame versus turbulent flame.

Premixed Flame Versus Diffusion Flame

As the term implies, a premixed flame is the flame resulting from the combustion of premixed fuel and oxidant (fuel and oxidant are mixed before combustion). Otherwise, the type is the diffusion flame. Premixed flame combustion is largely applied to relatively small devices such as automobile engines and laboratory burners, and is usually limited to fuels that are gaseous at ambient temperature or to those that vaporize at relatively low temperatures.

Diffusion flame combustion, which primarily occurs in such large-scale devices as incinerators, boilers, and furnaces involves very complicated processes involving pre-combustion, mixing, volatilization, vaporization, combustion, and post-flame reactions.

Laminar Flame Versus Turbulent Flame

A laminar flame represents a situation in which the transport of heat, mass, and momentum occurs by molecular conductivity, density, and viscosity gradients. Under these relatively quiescent conditions, diffusion occurs only by the driving forces of the concentration gradients.

A turbulent flame is defined as a flame propagating through a turbulent stream. The stream is an irregular three-dimensional flow in which the transport of heat, mass, and momentum is several orders of magnitude greater than that by molecular conductivity, diffusivity, and viscosity (i.e., greater than that which occurs in a laminar flame). Turbulence causes significant changes in flame speeds, flame stability, and pollutant formation rates. Past scientific investigations have proposed several conceptual models to qualitatively describe turbulent flame characteristics. However, there is currently no com-

TABLE 2. EQUIVALENCE RATIO

	Mixture	Value
Per Equation (C)	Rich	$ER > 1$
	Stoichiometric	$ER = 1$
	Lean	$ER < 1$
Per Equation (D)	Rich	$ER < 1$
	Stoichiometric	$ER = 1$
	Lean	$ER > 1$

plete fundamental theory that can be used to quantitatively calculate the effects of turbulence on combustion.

FLAME AND NON-FLAME MODE DESTRUCTION

Incineration processes involve two fundamental modes: the flame mode and the non-flame mode of thermal decomposition. The high temperatures required to promote flame or non-flame mode reactions may be generated from actual combustion of the organic constituents in the waste or of co-fired auxiliary fuel. The oxidant may be the oxygen in the waste stream or in the air.

The flame and non-flame modes of thermal destruction are interrelated. The flame mode involves reaction and destruction within the flame itself, while for the non-flame mode, the flame serves as the heat source for the hot combustion gas to continue decomposition beyond the flame. A flame is a chemically reacting, radical-rich gas flow that propagates through space at temperatures generally above 1000°C. This gas flow may consist of atomic hydrogen (H), atomic oxygen (O), atomic chlorine (Cl), hydroxyl radicals ($\text{OH}\cdot$), and methyl radicals ($\text{CH}_3\cdot$) in carbon-hydrogen-oxygen systems, and chloroxy radicals ($\text{ClO}\cdot$) in chlorine-containing systems. There are always several sequential reaction pathways with the reaction rate controlled by many chemical and physical factors such as chemical kinetics, mixing, air-fuel ratio, etc.

The non-flame zone of an incinerator surrounds and extends beyond the flame. This non-flame zone is characterized by temperatures generally between 650°F and the flame temperature. It is also a reacting gas flow consisting of a mixture of nitrogen, oxygen, carbon dioxide, water, hydrogen chloride, chlorine, organic compounds, intermediates, and radicals. Although the reaction conditions are much less severe compared to flame conditions, the time spent by the reactants under the non-flame thermal decomposition conditions is much greater than the time spent in the flame (a few seconds versus milliseconds).

INCINERATION SYSTEMS

Although there are several types of incinerators such as rotary kilns, liquid injection incinerators, fluidized beds, and multiple hearths, their process principle is about the same. A typical incinerator is shown in Figure 2 [33]; it

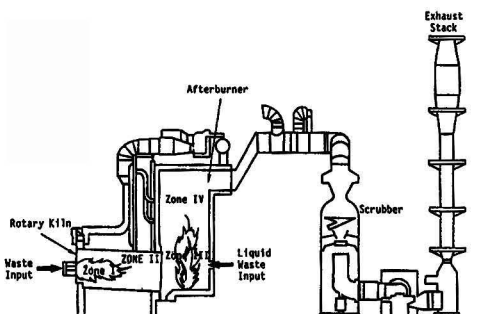


Figure 2. Simplified diagram of an incineration system consisting of a rotary kiln and an afterburner.

shows a rotary kiln followed by an afterburner. A rotary kiln is, in general, designed to handle drums or cartons of solid waste or dewatered sludges and an afterburner is designed to incinerate any unburned compounds from the kiln.

The overall incineration process can be divided into four destruction zones:

- Zone I. Rotary kiln flame zone
- Zone II. Rotary kiln non-flame zone
- Zone III. Afterburner flame zone
- Zone IV. Afterburner non-flame zone

Incinerating Solid Wastes

Zone I is for the purpose of incinerating *solid* wastes. If the afterburner is used for liquid waste incineration alone, the liquid waste is injected directly into Zone III for incineration. If the afterburner is used to further incinerate any unburned compounds coming from the rotary kiln, auxiliary fuel is generally injected into Zone III to assist in the incineration process. Zones II and IV have the same function, i.e., for non-flame thermal degradation. In general, the mean temperature of the afterburner is 200° to 400°F higher than that of the rotary kiln.

The range of solids burned in an incinerator is much more diverse with respect to waste composition and state of aggregation than that of liquid wastes. The state of aggregation of solid wastes may range from finely-divided particles to objects as large as a 55-gallon drum. This wide range of particle size adds further complication to the combustion of solid fuels.

What possible pathways are available to solid wastes when they are fed into an incinerator? Numerous physical and chemical processes can occur as shown in Figure 3 [33]. The solid wastes must be gasified before incineration can occur. Much of the gasified waste will mix with air and undergo combustion directly.

Solid wastes contain a variety of chemical constituents, not all of which are combustible. Non-combustible components of the solid wastes are often referred to as inerts.

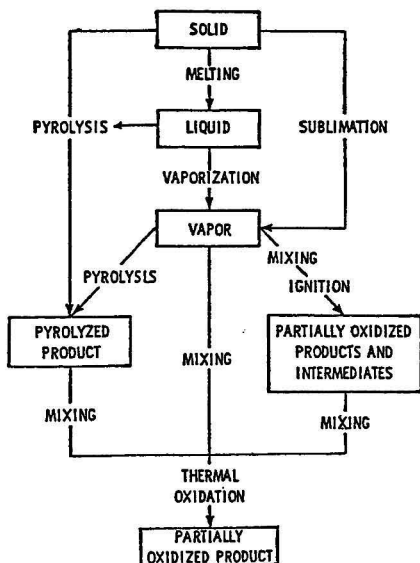


Figure 3. Schematic diagram of processes occurring during the thermal destruction of a solid waste.

They act as a thermal sink and influence the peak temperature achieved during combustion. The inert substances in the waste feed may include:

- Moisture.
- Mineral substances such as silicates, sulfides, halogen salts, etc. When such substances are oxidized in the flame, the resulting ash is either retained in the combustion bed itself or entrained in the effluent.
- Oxides of certain metals such as mercury, selenium, and cadmium, which have relatively high vapor pressures. When they are liberated in the combustion zone, a disproportionate fraction is present in the post-flame as a vapor. This vapor later condenses as the post-flame gases cool and appears as ash, particulate, or a colloidal suspension in the effluent.

If high enough combustion temperatures are achieved, the ash may melt or fuse to form a slag. For example, silicates melt when the temperatures rise above 1,800°F. The molten globules may coalesce to form larger particles. This may be desirable because it is generally easier to remove larger particles from the effluent gases. However, the formation of slag may be undesirable because it may act as a solvent for the chamber materials. Also, when the particles do coalesce, they may envelop other small particles of combustible material. If this occurs, the coated combustible material is generally lost to the combustion process and will not be consumed even if the slag particles are recycled to the combustion zone.

Incinerating Liquid Wastes

Zone III is usually for the incineration of liquid waste (droplets). Liquid wastes are often prepared for combustion by dispersing them as a spray of droplets. New efficient nozzles are capable of producing aerosol distributions with droplets smaller than 100 microns in diameter [13] for effective incineration.

In general, the field of droplets is not arrayed in a uniform fashion. The distance between some of the droplets will be greater than that separating others. Furthermore, these distances will be constantly changing as the droplets change position in both space and time. This constant change will be due to differences in the way different droplets, particularly ones varying in size, interact with the flowing air.

For those droplets with small spaces in between, combustion may occur under locally fuel-rich conditions which may result in partial oxidation. Perhaps if conditions are rich enough, unburned or even unvaporized fuel will remain after the flame around the droplet has died out due to lack of oxygen. The products from this partial oxidation will be enveloped in the hot combustion gases generated by that portion of the fuel that did burn. Vaporization and pyrolytic conversion of these products will continue. Thus, an inefficient process such as this has the potential of producing large amounts of particulate matter and pyrolytic products.

For those droplets with large spaces in between, combustion may occur under locally fuel-lean conditions. Complete combustion is likely because of enough oxygen being locally present.

AN INCINERATOR DESIGN EXAMPLE

The following example calculation shows how the incineration fundamentals discussed previously are applied to the design of an incineration system. The example uses data from one of Ciba-Geigy's tests performed in 1984 [34].

Given:

Waste feed rate = 4 gpm
 1 gallon = 10 lbs
 Waste feed rate = 2400 lbs/hr
 Excess air = 0%
 Reference (ambient) temperature = 70°F
 Humidity = 80%
 Waste content:

For C₂Cl₄, M = 166

C	0.14578	0.007272
Cl	0.855421	0.043027

For C₆H₅Cl, M = 112.5

C	0.640000	0.188928
Cl	0.315555	0.093152
H	0.044444	0.013112

For C₇H₈, M = 92

C	0.913043	0.553121
H	0.086956	0.052678

Mass Fraction	Mass Feed Rate (lbs/hr)
0.0487	117
0.0503	121
0.2952	708
0.6058	1454
1.0000	2400

Hexachloroethane, C₂Cl₆
 Tetrachloroethene, C₂Cl₄
 Chlorobenzene, C₆H₅Cl
 Toluene, C₇H₈

M = Molecular Weight

Total C	= 0.754 lbs/lb of waste
H	= 0.066 lbs/lb of waste
Cl	= 0.180 lbs/lb of waste
	1.000 lbs/lb of waste

Find:

The mass flow rates of the incinerator products (at 100% of theoretical air or the Theoretical Combustion Products, TCP)

Calculation of Incinerator Products

Chemical analysis

	lbs/lb of Compound	lbs/lb of Waste
For C ₂ Cl ₆ , M = 237		
C = 2 C/M	0.101265	0.004931
Cl	0.898734	0.043768

Chemical analysis summary

Elemental Analysis	Weight Fraction	lbs/hr in feed
C	0.754	1810
H	0.066	158
O	0.000	0
Cl	0.180	432
N		0
S		0
H ₂ O		0
ash		0
	1.000	2400

Calculation of oxygen needs

C + O₂ → CO₂
 O₂ = C*32/12 = 2.67*C = 2.67 × 1810 = 4827 lbs/hr
 H left over after Cl's reaction = HLO
 HLO = H - Cl/35.5 = 145.75 lbs/hr
 H₂ + 0.5O₂ → H₂O
 O₂ = HLO*0.5*32/2 = 145.75 × 8 = 1166
 S + O₂ → SO₂
 Bound O₂ = 0
 Theoretical oxygen = TO = 5993 lbs/hr
 Theoretical nitrogen =
 TN = TO × 3.76 × 28/32 = 19718
 Theoretical dry air = TO + TN = TDA = 25711

At 70°F dry bulb temperature and 80% relative humidity, the humidity ratio or # H₂O/# dry air = 0.0127 (From the Psychrometric Chart in Gordon & Sonntag)

H₂O in combustion air = 0.0127 × 25711 = 327
 Actual theoretical air = ATA = TDA + its H₂O = 26038
 Theoretical reactants = TR = 28438 lbs/hr
 = ATA + feed

Theoretical combustion products (TCP)

CO₂ = C*44/12 = 1810 × 44/12 = 6637 lbs/hr
 SO₂ = S*64/32 = 0
 H₂O = HLO*18/2 = 145.75 × 9 = 1312
 N₂ = TN = 19718
 HCl = Cl*36.5/35.5 = 432 × 36.5/35.5 = 444
 Unburned carbon = 0
 H₂O in feed = 0
 Ash in feed = 0
 H₂O from the combustion air = 327

∴ TCP = 28438 lbs/hr

CONCLUSION

Incineration has been shown to be one of the best treatment technologies for hazardous/toxic waste destruction. Both flame and non-flame mode studies indicate that most organic wastes can be destroyed to greater than 99.99% destruction efficiency if the incinerator is operated under optimum conditions. However, the fact that these optimum conditions do not always exist and the excursions from these optimum conditions often result in the formation of products of incomplete combustion (PICs) has led to increased concern over incineration operations. At the same time, the increased need for and regulation of incineration has intensified efforts to understand and predict what happens during the combustion of organic wastes. Specific terminology has evolved over the years to characterize the incineration process. This paper discusses that terminology and some basic principles regarding incineration.

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Relationships Between Laboratory and Pilot-Scale Combustion of Some Chlorinated Hydrocarbons

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Factors governing the occurrence of trace amounts of residual organic substance emissions (ROSEs) in full-scale incinerators are not fully understood. Pilot-scale spray combustion experiments involving some liquid chlorinated hydrocarbons (CHCs) and their dilute mixtures with hydrocarbons (HC) were undertaken at the USEPA's Center Hill Laboratory. Individual droplet-burning characteristics of CHCs and HCs were also studied at the University of California, Davis on a more fundamental level to isolate and identify potentially important phenomena. The practical implications of the experimental observations on incinerability ranking, formation of ROSEs, and strategies for reducing ROSEs are discussed.

INTRODUCTION

Waste incineration can be conceptualized as a two-stage process (see Figure 1). In the flame zone, very high temperatures (near adiabatic), extremely rapid reactions, and high concentrations of reactive species (radicals) characteristic of flames, convert reactants introduced with the fuel/waste mixture on relatively short time scales (<0.1 second). In the post flame, high temperature, thermal decomposition zone (characterized by slower reaction rates, lower concentrations of reactive species, but longer residence times of the order of 1 second), appreciable conversion of reactants persists. Several possible reasons for the failure of a liquid injection combustor to completely destroy organic compounds have been set forth [10].

In spray combustion incinerators, a possible explanation for the escape of some reactants from the flame zone can be described by the "rogue droplet" hypothesis [14]. According to the hypothesis, the inertia of an oversize droplet of fuel/waste carries the droplet out of the fuel-rich core of the flame zone before it completely evaporates. In such a circumstance, the oversize droplet may

or may not be ignited as it passes through the flame. Having exited the primary flame, its behavior might then correspond to that of an isolated gasifying droplet. The term "gasifying" is used to encompass the evaporation of the droplet with or without accompaniment by a rapid exothermic reaction, e.g. a flame. It is known that individual droplets that have been ignited can also spontaneously extinguish in a cooler post-flame environment before complete consumption of the reactants [9, 12]. In such cases, only one out of a multitude of droplets need escape the flame to account for the low levels of residual organic substance emissions* (ROSEs) observed in poorly operat-

* The term "residual organic substance emissions" (ROSEs) is being used to this paper to refer to those organic compounds which are in the feed, e.g. principal organic hazardous constituents (POHCs), but not completely destroyed by the combustion process, those compounds which are possibly reformed or newly formed in the incinerator (but not limited to the USEPA definition of product of incomplete combustion, PIC, which requires appearance in "Appendix VIII"), and those compounds which represent products other than inorganic combustion products such as CO, CO₂, H₂O, HCl, or Cl₂.

ing incinerators. On the supposition that the conceptual models described above are realistic representations of physical processes that occur during the initial phases of spray combustion, a study was undertaken of both single droplet and spray combustion of oversize droplets. One goal was to determine whether a correspondence could be obtained between spray atomization failure in a turbulent flame reactor (TFR) and single droplet burning results. A second goal was to determine whether a "flame" ranking scale of incinerability, based on droplet burning characteristics (burning-rate and/or flame extinction), might be developed to complement the University of Dayton Research Institute's (UDRI) non-flame, gas-phase thermal stability (TS) ranking [5]. The logic in applying such rankings would be that those compounds highly ranked on both scales would be difficult to destroy in liquid-injection incinerators. Therefore they would be suitable surrogate compounds to be used in testing the ability of an incinerator to destroy the POHCs of a waste.

DESCRIPTION OF RESEARCH CONDUCTED

The research program was carried out under Cooperative Agreement with the U.S. Environmental Protection Agency (USEPA) at its Center Hill Laboratory (CHL) in Cincinnati, Ohio and under California Air Resources Board (CARB) sponsorship at the University of California, Davis (UCD). The CHL study involved spray combustion of mixtures of chlorinated hydrocarbons (CHC) in a pilot-scale turbulent flame reactor (TFR) while those at UCD consisted of measurements of isolated droplet burning in a lab-scale, laminar flow combustor. Details of the experimental procedures have been presented elsewhere [3, 4, 18, 20, 24]. This paper relates the results of the two studies to one another. A brief synopsis of the apparatus used and experiments follows.

DESCRIPTION OF OVERSIZE SPRAY EXPERIMENTS

The primary goal of the experiments performed at the CHL was to determine the relative destruction efficiency (DE) under simulated atomization failure conditions (oversize droplets) of five compounds: 1-chloropentane

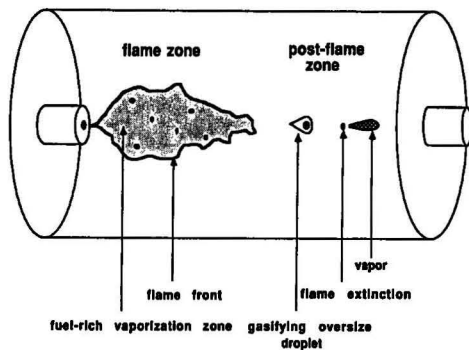


Figure 1. Conceptual diagram of incinerator illustrating penetration of an oversize droplet through the flame and nonflame zones during spray atomization failure condition. Adapted from Chang et al., 1988a.

(CP), 1,1,2,2-tetrachloroethane (TECA), trichloroethene (TCE), tetrachloroethene (PERC), and 1,2,4-trichlorobenzene (TCB). These surrogate POHCs were burned as pairs and blended with heptane (HEPT) to determine relative DE. To reduce variability in stoichiometry, the mixtures were concocted such that equimolar amounts of each POHC were blended with HEPT to yield an overall H:Cl ratio of 100:1 (about 5.3% by weight Cl). The composition of the "cocktails" is shown in Table 1. In order to maintain the thermal environment in the TFR as close to the same as possible, identical fuel feed rate, stoichiometry, and turbulent mixing (swirl setting) were used. A 1.5 gph, Delavan WDA 60° hollow-cone nozzle operated at 40 psig was used to produce the oversized droplets, whereas a 1.0 gph, WDA 90° hollow-cone nozzle operated at 120 psig was used for nominally "optimum" droplet atomization.

Kramlich, et al. [11] have performed cold-flow, light-scattering measurements of droplet size distribution with similar nozzles and demonstrated that oversize droplets could be produced by reducing the pressure supplied to a nozzle. No measurements were made of droplet size dis-

TABLE I. POHC PROPERTIES AND MIXTURE COMPOSITIONS

Compound	b.p. [°C]	density [g/ml]	M.W.	C atoms per mole	H atoms per mole	Cl atoms per mole
CP	107.8	0.882	106.6	5	11	1
1,1,2,2-TECA	146.0	1.590	167.9	2	2	4
1,2,4-TCB	231.5	1.454	181.5	6	3	3
PERC	121.0	1.623	165.8	2	0	4
TCE	87.0	1.464	131.4	2	1	3
HEPT	98.4	0.684	100.2	7	16	0

Mixture	Average composition			Cl conc. wt.%
	C	H	Cl	
CP:TECA:HEPT	1.00	2.27	0.023	5.3%
TECA:TCB:HEPT	1.00	2.24	0.022	5.3%
PERC:TCB:HEPT	1.00	2.24	0.022	5.3%
TCE:TCB:HEPT	1.00	2.23	0.022	5.3%

CP—chloropentane
 PERC—tetrachloroethene
 TECA—tetrachloroethane
 TCB—trichlorobenzene
 TCE—trichloroethene
 HEPT—heptane (technical grade)

TABLE 2. SUMMARY OF TEST CONDITIONS OVERSIZE DROP STUDY

Test Mix	Pressure [psig]	Fuel Flow [ml/s]	S.R.	CO @ 0% O ₂ [ppm]	Swirl	Temp [°C]
HEPT	40	0.92	1.22	702	1.1	
CP:TECA:HEPT	40	0.92	1.27	969	1.1	489
HEPT	40	0.92	1.22	426	1.1	
TECA:TCB:HEPT	40	0.92	1.26	886	1.1	482
HEPT	40	0.91	1.22	405	1.1	
PERC:TCB:HEPT	40	0.91	1.25	787	1.1	504
HEPT	40	0.93	1.26	582	1.1	
TCE:TCB:HEPT	40	0.93	1.26	875	1.0	476
HEPT*	120	0.99	1.18	27	1.1	
TCE:TCB:HEPT*	120	0.99	1.20	40	1.1	507

* Optimum atomization pressure.

tribution in this study. However, it was evident from the flame pattern (much longer and lazier in appearance) and from observation of the spray during cold fuel-flowrate measurements that considerably larger droplets were present. The conditions for the tests are summarized in Table 2. Combustion gases were sampled for the POHCs by drawing known volumes of combustion effluents over multi-sorbent tubes. Gas chromatography with flame ionization detection (GC/FID) was the primary means of quantitation of the desorbed samples. Two sorbent tube samples were also analyzed by mass spectrometry on a chromatograph equipped with an identical analytical column. By careful matching of identified peaks and retention times, certain ROSEs were also tentatively identified and quantified relative to the internal standard.

DESCRIPTION OF SINGLE DROPLET EXPERIMENTS

There were four major goals to the study carried out at UCD: 1) to quantify single droplet gasification characteristics such as burning rate, vaporization rate, and extinction diameter, for a variety of pure and multicomponent mixtures of CHCs and HCs; 2) to determine factors which govern the extinction of the flame surrounding a burning droplet, e.g. the role of chlorine containing species or bulk heating value effects; 3) to determine if droplet extinction could account for the DE of POHCs observed in full and pilot-scale studies; 4) to investigate the development of a single droplet incinerability ranking methodology which could complement existing incinerability ranking methodologies.

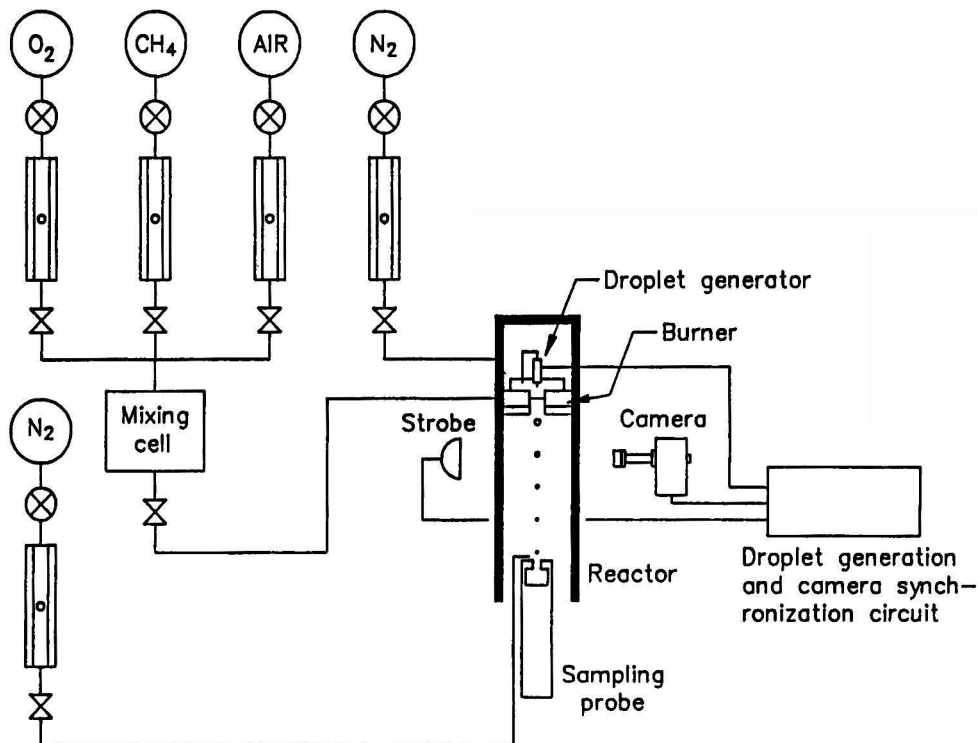


Figure 2. Schematic diagram of droplet combustion system. Adapted from Sorbo et al., 1988b.

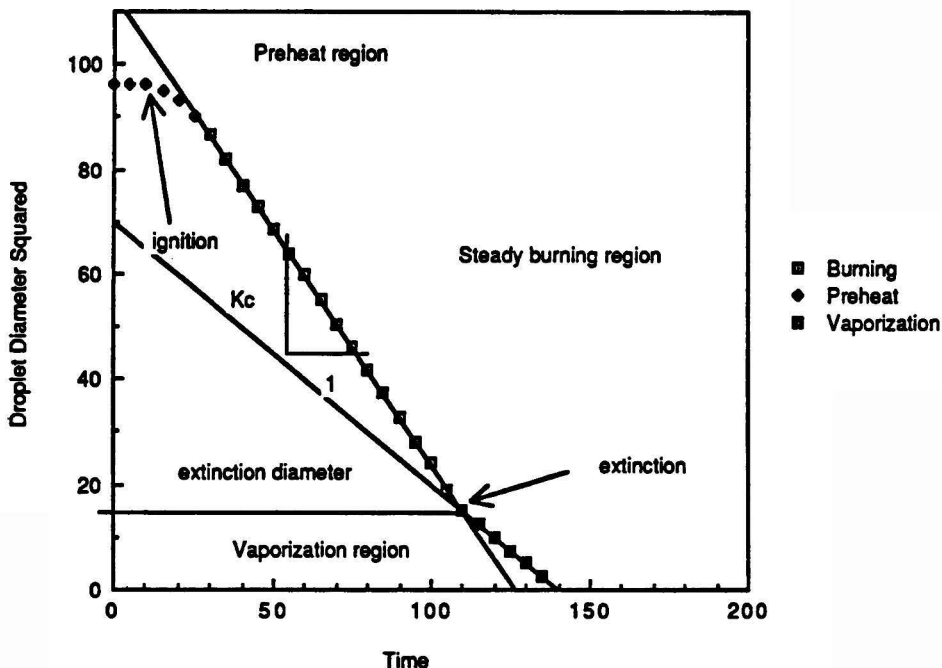


Figure 3. Example of a typical droplet gasification profile. Adapted from Sorbo et al., 1988a.

The experimental apparatus used, shown in Figure 2, was a laminar down-flow reactor. Individual droplets of fuel/POHC mixtures were injected into the post combustion region of a laminar flat-flame burner. The monodisperse droplets were created by a droplet generator based on the ink-jet printing technique [1]. A square wave pulse was applied to a cylindrical piezoelectric crystal causing it to contract and force the liquid through a glass nozzle. The droplet size and spacing were controlled by the frequency, pulse width, and voltage on the droplet generation circuit and the nozzle size. The droplets, with diameters varying between 200 and 300 μm and droplet Reynolds numbers of about 1, were injected into a chamber, heated by combustion products of a methane/ O_2/N_2 flat-flame burner. The burner was operated to produce two different environments: 1. an oxidizing environment with an O_2 concentration of about 18.5% (21% O_2 dry basis), and 2. an "inert" environment with no oxygen. The size history of the droplets was determined by use of photomicrography. Liquid-phase samples of the droplets were obtained using a sample probe inserted into the reactor.

Measurements of droplet diameter squared, D^2 , were plotted versus time to yield a droplet gasification profile. A hypothetical profile with arbitrary units is shown Figure 3. The example profile consists of a non-linear preheat region, a linear steady burning region, and a linear vaporization region. In the preheat region, a droplet undergoes heating and an increasing rate of vaporization, followed by fuel vapor ignition. After ignition, the gasification rate increases until a steady-state condition is reached. The steady-burning region is characterized by a linear gasification profile.

A theory developed in the 1950s [7, 8] called the "D-squared law" (D^2 -law) describes the steady-state behavior of droplet gasification. Droplet gasification is never truly steady-state because the droplet is continually losing mass and its diameter is shrinking. A quasi-steady

state assumption can still be made, since the characteristic time for changes in the liquid phase occur about 1,000 times slower than those in the gas phase. The gasification profile in the vaporization region of Figure 3 is also linear. Thus, droplet vaporization and droplet gasification can be thought of as similar processes occurring at different rates, but described by the same D^2 -law. In the burning region of the gasification profile the droplet surface experiences heat transfer from the flame, which causes a higher gasification rate. In the vaporization region, there is no flame surrounding the droplet. The lower ambient temperature results in a slower rate of heat transfer and a flatter gasification profile.

Liquid-phase sampling of droplets at various stages of their gasification history was also carried out. Mixtures of TECA/heptane, TECA/nonane, and TECA/hexadecane were sampled to provide a lower, equal, and higher volatility component in comparison to the surrogate POHC, TECA. The samples were subsequently analyzed by GC/FID. These measurements provided insights into the effects of volatility differentials.

Selected Results

A complete description of all test results from the CHL and UCD studies is not given here in the interests of brevity. Our purpose is to highlight those results which may have significance to the actual testing or operation of liquid-injection combustors burning wastes.

Oversize Spray Results

Clear differences in the DE of the fuel/POHC cocktails were observed. The differences were smaller for the most refractory compounds TCB and PERC, but were several orders-of-magnitude between the most and least refractory POHCs tested, TCB and CP, respectively. A relative

TABLE 3. COMPARISON OF OBSERVED POHC DE WITH VARIOUS RANKING METHODS

Compound	Relative Penetration	TFR	Rank based upon:			
			H _c *	TSHiO ₂ *	TSLoO ₂ *	TFMKLoO ₂
TCB	1.0E + 00	1	4 (64/272)	3 (12/23)	1 (1/43)	1
PERC	6.0E - 01	2	1 (11/272)	1 (2/23)	2	2
TCE	3.8E - 02	3	3 (22/272)	2 (9/23)	3	3
TECA	7.6E - 02	4	2 (16/272)	4 (21/23)*	4 (6/43)*	4#
CP	9.3E - 04	5	5 (NA)	NA (NA)	NA (NA)	4#
HEPT	5.2E - 04	6	6	NA	NA	6##

* Values in parentheses are the ranks reported in the reference sources below and the total number of compounds ranked by the source. A ranking for 1,1,2,2-TECA was not given, but it was assumed that 1,1,1-trichloroethane would yield a similar ranking because of a common thermal decomposition pathway, i.e., molecular elimination of HCl. In the case of the TFMKLoO₂ ranking, the methodology described in the reference was applied.

A low energy decomposition pathway for molecular elimination of HCl exists for both TECA and CP. TECA and CP can also be attacked by Cl-atom abstraction of H. No attempt was made to determine the fastest route of attack, so a relative order is not assigned for these two compounds.

Heptane is subject to Cl-atom attack under the fuel-rich condition which was used as the basis for this ranking.

References—

H_c—(CARB, 1986)

TSHiO₂—(Dellinger, 1985b) observed T₅₀

TSLoO₂—(Taylor, 1987)

TFMKLoO₂—(Tsang, 1982; 1988)

ranking of compounds was constructed from the observed absolute penetrations (Pt = 1 - DE). (No physical significance should be attached to the numerical values of the relative Pt reported.) The ranking is shown in Table 3 along with a ranking based on heat-of-combustion (H_c), gas phase thermal stability high O₂ environment (TSHiO₂), low O₂ environment (TSLoO₂), and theoretical flame mode kinetics (TFMK). The observed order of difficulty of destruction was TCB > PERC > TCE > TECA > CP > HEPT.

A relatively small number of chlorine atoms in comparison to hydrogen atoms in the mixture, 1:100 (5.3% Cl by weight), can produce noticeable effects on the combustion process, as evidenced by increased CO production (several hundred ppm above heptane alone—see Figure 4). This difference in CO production is believed to have resulted primarily from chemical effects since the reduced specific energy of the POHC/heptane mixtures caused overall exhaust temperature decreases of only 10 to 15°C. The corresponding change in theoretical adiabatic

Increase in CO from Heptane to POHC Mix
At Constant Heat Release Rate

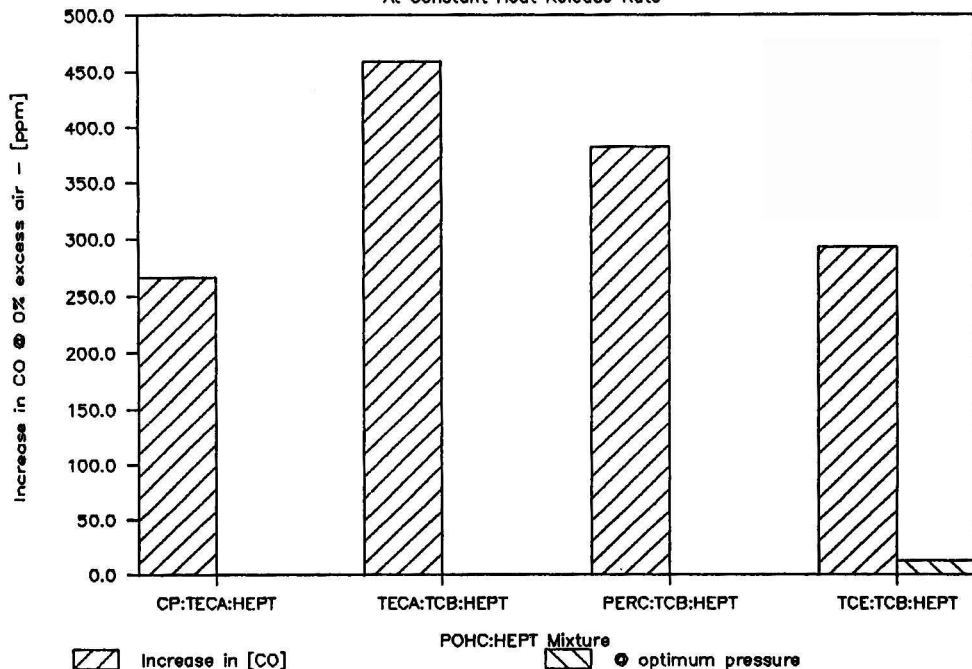


Figure 4. Increase in [CO] above baseline heptane [CO] corrected to 0% excess air during simulated atomization failure for four test mixtures and during optimum atomization for one test mixture. Adapted from Chang et al., 1988b.

TABLE 4. SELECTED PIC SUMMARY

POHC Mix	GC/FID Relative Area Count						
	DCM	CHCl ₃	EDC	BZ + CCl ₄	TCE	TOL	CLBZ
CP:TECA:HEPT	0.61	0.86	0.55	44.63	2.52	0.62	1.29
TECA:TCB:HEPT	0.14	0.36	0.33	22.91	1.41	0.33	1.09
PERC:TCB:HEPT	0.12	1.36	0.35	14.20	0.15	0.28	0.78
TCE:TCB:HEPT	NA	NA	NA	21.29	0.33	NA	1.37
HEPT*	0.04	0.67	0.44	3.26	0.04	0.17	N.D.
TCE:TCB:HEPT*	0.05	0.87	0.42	2.68	0.02	0.26	N.D.

* Optimum nozzle atomization pressure

DCM—dichloromethane

CHCl₃—trichloromethane

EDC—dichloroethane

BZ—benzene

CCl₄—tetrachloromethane (minor constituent of unresolved peak)

TOL—toluene

CLBZ—monochlorobenzene

tic flame temperature, assuming the same amount of air supplied to the POHC/fuel mix as for fuel alone, was calculated to be less than 35°C. It was qualitatively noted that the formation of soot was increased at this level of chlorine content in the waste as well.

By using a retention time correlation constructed from comparison of GC/FID and GC/MS analyses it was possible to tentatively identify some peaks observed in the chromatograms. The concentrations of selected products of incomplete combustion (PIC), tabulated as GC/FID area of the PIC normalized by area of the internal standard bromofluorobenzene (BFB), is shown in Table 4. When burning TECA-containing mixtures, a chromatographic peak assigned to TCE was clearly present. The

ratio of TCE to TECA in those cases ranged from about 1.5 to 2.5. TCE concentrations were observed at levels about an order-of-magnitude lower when TCE was a POHC in the mixture and TECA was absent. Formation of PICs that are specific to certain POHCs does appear to occur in the oversize droplet model. On the other hand, benzene was observed in every POHC mix as well as in the HEPT-only sample. Benzene was apparently formed from one or more of the components of the fuel, possibly from cyclic alkanes present in abundance in the technical grade heptane. Whenever substantial amounts of benzene were formed, a smaller amount of chlorobenzene was observed, independent of the POHCs contained in the mixture. No chlorobenzene was observed when burn-

CO VS Benzene (+ Carbon Tetrachloride)

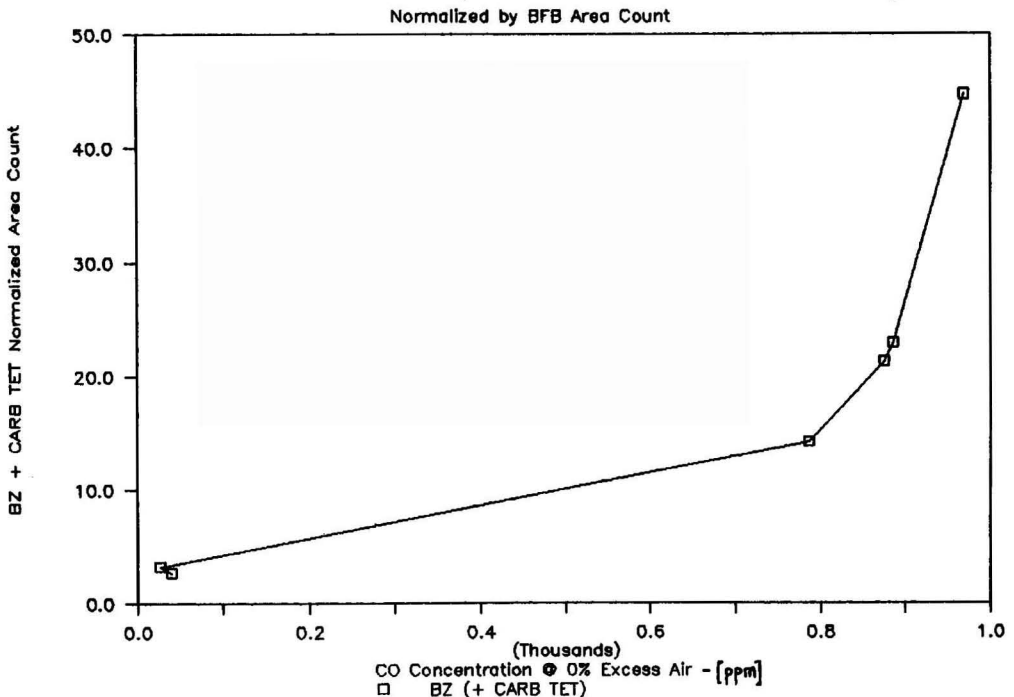


Figure 5. Relative increase in benzene concentration as a function of [CO] corrected to 0% excess air under optimum and simulated atomization failure. Adapted from Chang et al., 1988b.

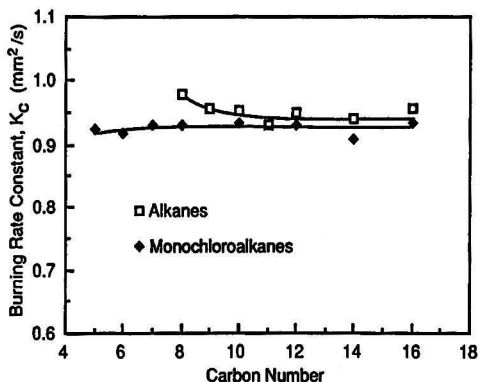


Figure 6. Gasification rate constants for n-alkane and 1-chloroalkane droplet studies. Adapted from Sorbo et al., 1988b.

ing heptane alone. This was interpreted to mean that common recombination chemistry was probably occurring, e.g. substitution of a hydrogen atom on a ring by a chlorine atom.

With the limited data available, concentrations of PICs were compared with CO concentrations. A consistent relationship was observed for CO and benzene and is shown in Figure 5. This suggests that the residual levels of CO and benzene observed in the exhaust gases were related through a common physical mechanism, poor atomization, in conjunction with a common chemical mechanism, interference of CO oxidation by chlorinated species. The surrogate POHC mixture that yielded the highest benzene level (CP:TECA:HEPT) was not the most difficult to destroy, but rather, relatively the easiest.

SINGLE DROPLET RESULTS

The first series of experiments examined the effects of substitution of a single chlorine atom on the isolated droplet gasification of alkanes. A graphical summary of burning and vaporization rates of n-alkanes and monochloroalkanes is presented in Figure 6. For monochloroalkanes, a slight increase in K_C for C_5 to C_7 was observed and the burning rate for the C_5 to C_7

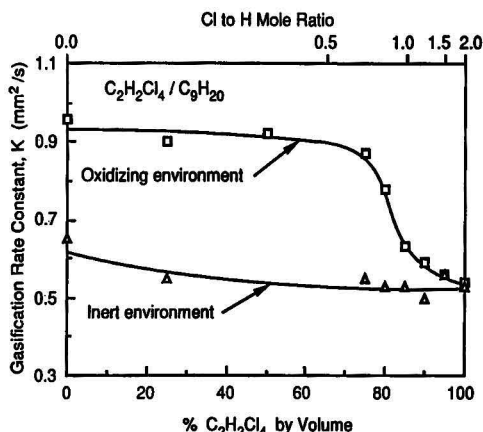


Figure 7. Effect of TECA concentration on gasification rate of equal volatility mixtures of TECA/nonane. Adapted from Sorbo et al., 1988b.

monochlorinated alkanes was less than similar values for n-alkanes. However, the occurrence of one atom of chlorine substituted on an alkane molecule of 5 carbons or longer did not cause early flame extinction under the conditions tested. For a carbon number of 8 or greater, both the n-alkane and monochlorinated alkanes had similar burning rates. Furthermore, the vaporization rate results for both the n-alkanes and the monochloroalkanes were between 0.5 and 0.6 mm²/s.

The next series of droplet experiments involved the gasification of equal volatility mixtures of TECA and nonane. Figure 7 compares the burning rate constant, K_C , for TECA/nonane mixtures of various concentrations. The curve can be divided into two distinct regions, a burning rate plateau with a relatively constant K_C for TECA/nonane mixtures between 0% and 75%, and a region in which the droplets are not burning, TECA/nonane mixtures >90%. It is significant that a mixture of 75% TECA by volume ($K_C = 0.85$ mm²/s) burns almost as rapidly as pure nonane ($K_C = 0.96$ mm²/s) despite a very large difference in mixture heating value; 2.80 kcal/g (LHV) for the 75% TECA/nonane mixture versus 11.41 kcal/g for pure nonane. This apparent anomaly can be understood by recognizing that the calculation of heating value of a highly chlorinated molecule (Cl:H > 1:1), in air, normally assumes formation of some molecular chlorine. However, in a system such as the one used, an excess of hydrogen atoms was present in the form of water vapor from combustion of methane. Therefore, hydrogen chloride was formed. Furthermore, the Cl atoms oxidized hydrogen atoms in the fuel/waste molecules to HCl, thereby reducing the stoichiometric requirement for oxygen. Following this reasoning, the theoretical adiabatic flame temperature of a highly chlorinated mixture of CHC and HC undergoes a relatively small change when compared to the HC alone as can be demonstrated by thermochemical calculations.

A possible exception would be the use of coke or low volatility coal as the primary fuel, in which case excessive amounts of chlorine would result in Cl₂ in the effluent. In practical liquid-injection incinerators, an excess of hydrogen to chlorine will normally be present as long as the fuel/waste mixture has been adequately blended. This is one reason why the heat of combustion, H_c , incinerability ranking does not correlate with observed DE.

For mixtures containing greater than 75% TECA, the burning rate dropped rapidly to the vaporization rate with increasing concentration of TECA. Despite the relatively rapid burning rate of the 75% TECA/nonane mixture, early droplet extinction was noted when the ambient temperature was in the range of 1,000°C or lower (Dext = 117 ± 9 μm). For an 80% TECA mixture, flame extinction occurred at a droplet diameter of about 190 μm compared to less than 50 μm for pure nonane. Hence the mass of unburned fuel was about an order of magnitude greater. The decrease in burning rate could be due to a heat of combustion effect and/or a kinetic effect. Our current thinking is that the burning rate is governed by the heat of combustion of the mixture to first order, whereas the extinction of the flame may be a kinetic effect, which is species dependent. It is interesting to note that the Cl/H mole ratios were 0.66, 0.79, 0.96, and 1.19 for the 75, 80, 85, and 90% TECA mixtures respectively (21% O₂ dry basis). While these results exhibit a weak oxygen dependence, they suggest that for TECA/nonane mixtures, droplet combustion was inhibited when the Cl/H mole ratio becomes larger than unity.

Mixtures of TECA and n-alkanes (TECA/alkanes) were also examined to determine the effect of volatility differential on the burning of TECA in droplet form. To facilitate the comparison of the effects of mixture volatility on gasification rate, the average K_C 's of TECA/alkane mix-

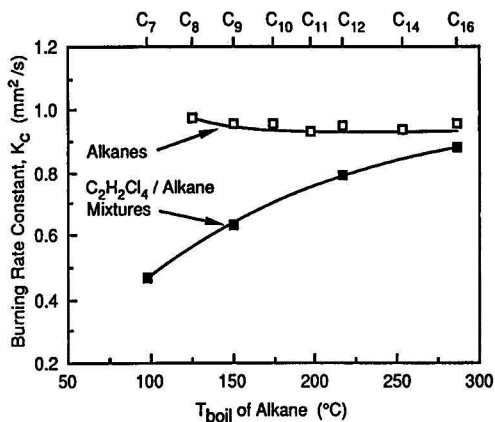


Figure 8. Effect of volatility differences on burning rates of TECA/n-alkane mixtures. Adapted from Sorbo et al., 1988b.

tures are contrasted with the average K_C 's of n-alkanes in Figure 8. The K_C for the TECA/alkane mixture increases with increasing number of carbon atoms in the added alkane. By comparing the relatively flat n-alkane burning-rate curve to the steeper TECA/alkane burning-rate curve, we conclude that the increase in the TECA/alkane burning-rate with increasing alkane chain length was not due to differences in the burning-rates of the alkanes added to TECA.

Based on the work of Randolph, et al. [15] and Makino and Law [13], the change in the TECA/alkane burning curve is hypothesized to be the result of differential distillation processes, liquid-phase diffusional resistance, and gasification rate. To verify this hypothesis, liquid-phase droplet sampling of TECA/HEPT, TECA/nonane, and TECA/hexadecane mixtures was conducted. Droplets were sampled at various stages in their lifetimes and analyzed by gas chromatography. The results, presented in Figure 9, show the variation of TECA droplet concentration as a function of non-dimensional D^2 -time ($1 - (D_s/D_{s0})^2$), where D_{s0} is the ignition diameter. The TECA/HEPT curve rises to 100% TECA very rapidly. The TECA/hexadecane curve drops off steadily throughout the droplet lifetime, until a rapid drop occurs near flame extinction. The TECA/nonane curve shows a slight rise in the TECA concentration from 85% to 90% during

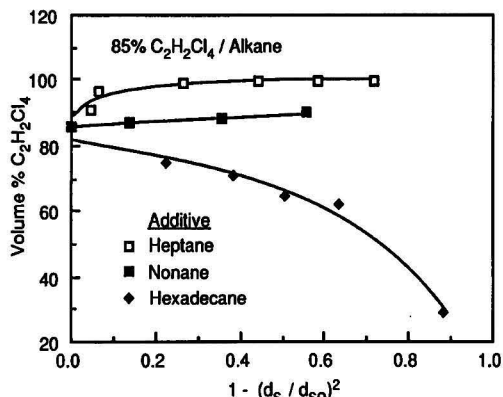


Figure 9. Sampling history of droplets initially containing 85% TECA (by volume) in an oxidizing environment. Adapted from Sorbo et al., 1988b.

the sample period. Because the TECA/nonane mixture was an equal volatility mixture, it was not expected that the TECA/nonane mixture would change significantly. Non-ideal solution behavior of the TECA-nonane mixtures is a probable explanation for the observed results.

The sampling results presented in Figure 9 are in agreement with the current state of understanding that multicomponent droplet gasification is controlled by liquid-phase mass diffusion, droplet surface regression rate (gasification rate), and volatility differential between components [13, 15]. After the start of gasification, much of the volatile component in the surface layer is preferentially gasified because of the short diffusion distance to the surface of the droplet. Subsequent behavior depends on the surface regression or gasification rate. If the surface regresses rapidly, then the volatile component in the droplet interior remains trapped because of the relatively slow rate of mass diffusion. Therefore, for fast gasification rates or slow liquid phase diffusion, a "diffusion limit" is approached. However, for a slower rate of surface regression or gasification, there is more time to transport volatile components to the droplet surface. Thus, the droplet continually loses the more volatile component. In the limit of zero surface regression rate, the volatile components have an infinite amount of time to reach the surface, independent of the liquid-phase diffusion, and a "distillation limit" is approached.

To more clearly evaluate the effect of gasification rate on the history of TECA/HEPT droplets, a mixture of 50% TECA in HEPT droplets was sampled in an oxidizing environment. The mixture burned well ($K_C = 0.86 \text{ mm}^2/\text{s}$), but had a rather large extinction diameter of $158 \mu\text{m}$. The results showed that the concentration in the TECA/HEPT droplets did change throughout the droplet lifetime. When TECA/HEPT droplets were injected into the chamber, the higher volatility heptane rapidly left the droplet. Therefore, the droplet became enriched with the non-burning TECA and, ultimately, burning was inhibited. As the droplet diameter became smaller, flame extinction was more likely due to a reduced droplet diameter and a decreased chemical reaction rate resulting from the enrichment of TECA in the droplet. Both of these effects increased the extinction Damkohler number [12] and extinction was promoted.

Upon injection of TECA/hexadecane droplets into the combustion chamber, TECA was preferentially gasified resulting in enrichment of the droplet with the rapidly burning hexadecane. The gasification of large quantities of TECA early in the TECA/hexadecane droplet lifetime explained the observed ignition delay of TECA/hexadecane droplets. The enrichment of the droplet with hexadecane further explains why the burning-rate of a TECA/hexadecane droplet was almost as large as the burning-rate of the pure hexadecane droplet over the range of compositions tested. At the end of the lifetime of a TECA/hexadecane droplet, it had become enriched with hexadecane, which delayed extinction and promoted more complete burnout of the droplet. Thus for the mixtures tested, TECA/HEPT, TECA/nonane and TECA/hexadecane, droplet composition curves confirmed the results of Randolph, et al. [15], that the more volatile component left the droplet preferentially. These results confirm that batch-distillation processes, and not liquid phase diffusional resistance, governed the burning of TECA/alkane droplets. This effect may be important in formulating blending strategies for hazardous waste incineration. That is, to reduce the adverse affects associated with production of oversize droplets in a spray combustor, a higher and a lower volatility alkane could be blended to promote the ignition and complete burnout of any oversize droplet in the combustion chamber.

PERC/OCTANE GASIFICATION RATE CONSTANTS

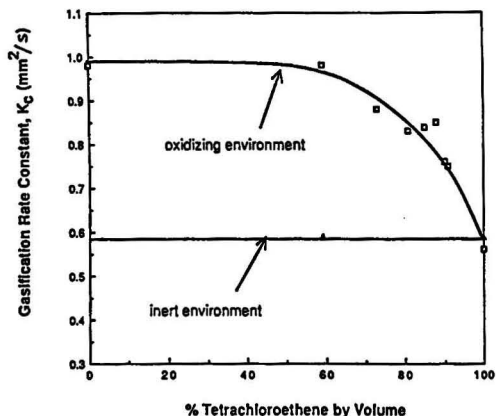


Figure 10. Effect of PERC concentration on gasification rate of PERC/octane. Adapted from Sorbo et al., 1988b.

To burn droplets of PERC, it must be mixed with a fuel that burns well. In order to control the gas phase mixture composition and eliminate differential volatility effects, octane (OCT) was blended with PERC to form an equal volatility mixture. Gasification rates were plotted as a function of volume percent PERC and presented in Figure 10. The shape of the oxidizing branch of Figure 10 is similar in shape to the TECA/nonane gasification rate constant curve shown in Figure 7 with the following exceptions: a) PERC/OCT mixtures burned strongly under the same ambient conditions until a critical concentration of 88% PERC was reached, while the critical TECA concentration was 75% by volume, b) the Cl/H ratios at the critical PERC and TECA concentrations were 2.5 and 0.66, respectively, and c) the heats of combustion at the critical PERC and TECA concentrations were 1.79 and 3.13 kcal/g, respectively. These observations suggest that PERC and TECA behave differently from one another in an oxidizing flame environment. A hypothesis for the difference in behavior in flames for PERC and TECA is formulated below.

PERC molecules are difficult to thermally decompose [21]. Thus PERC molecules can approach the flame zone, from the fuel-side, quite closely before they begin to decompose. Once decomposition begins, the chlorine spe-

cies liberated can scavenge H radicals and inhibit flame propagation as illustrated in equations (a), (b), and (c):



However, at high temperatures in, or very near the flame, chain branching reactions (d), (e), and (f) dominate the radical scavenging reactions.



Thus, once in the flame, the high flame temperatures (adiabatic flame temperature of about 2300 K) are sufficient to destroy PERC efficiently.

In contrast, TECA, like all chloroalkanes (except perchlorinated alkanes), is subject to an endothermic decomposition reaction via a four-center elimination of HCl molecules [16, 22] at a relatively low temperature. (The four-center elimination reaction can occur when there are adjacent Cl and H atoms which do not share the same carbon atom. The products of this reaction are a chlorinated ethene and HCl.) The molecular elimination reaction requires about 20 kcal/mol and has been calculated to occur at temperatures as low as 373 K [27]. If we follow the TECA molecule as it leaves the droplet surface, it is subject to an endothermic decomposition early in its gas-phase history. This breakdown could inhibit the flame in two ways: a) by cooling down the reactants, thereby slowing down the rate of reaction, or b) scavenging H radicals with HCl the primary decomposition product [see Equation (c)]. Crude calculations of HCl concentration profiles in the flame and back-diffusing toward the droplet surface appear to rule out the second possibility.

The final group of compounds examined were the chlorobenzenes: monochlorobenzene (MCB), 1,2-dichlorobenzene (DCB), and 1,2,4-trichlorobenzene (TCB). A summary of the chlorobenzenes droplet gasification results is presented in Table 5. The K_c results indicate fairly strong burning with the expected decrease in K_c with increasing chlorine substitution of the benzene ring. The flames observed for these droplets were very sooty, so much so that a soot trail could be seen in the wake of the droplet. The extinction diameters for both MCB and DCB were at the limit of the optical system's ability to distinguish the droplet from the background. The extinction diameter of TCB droplets was larger, at 70 μm .

TABLE 5. SUMMARY OF CHLOROBENZENE DROPLET GASIFICATION RESULTS

Compound	Cl/H (mole ratio)	HHV (kcal/g)	K_c (mm^2/s)	K_v (mm^2/s)	Dext (μm)	MOD (μm)
chlorobenzene	0.2	6.60	0.92	—	—	46
			0.89	—	—	43
			0.90	—	—	38
			$0.90 \pm .02$	—	—	—
1,2-dichlorobenzene	0.5	4.57	0.85	—	—	35
			0.85	—	—	29
			0.86	—	—	43
			$0.85 \pm .01$	—	—	—
1,2,4-trichlorobenzene	1.0	3.40	0.78	—	—	96
			0.79	—	70	36
			—	0.50	—	168
			$0.79 \pm .01$	0.50	—	—

MOD = minimum observed diameter, micrometers.

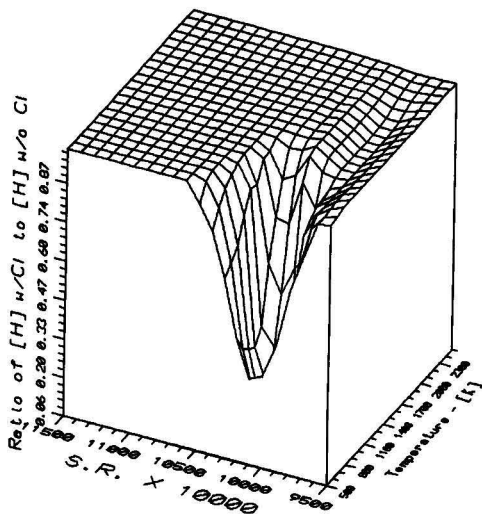


Figure 11. H-atom concentration ratio (with and without presence of chlorine) as a function of temperature and stoichiometric ratio.

DISCUSSION

Our spray studies showed that even in low concentrations, CHCs measurably increased CO and benzene concentrations above the baseline resulting from oversize droplets of HEPT alone. However, the CHCs produced minimal effects on droplet burning rate when mixed with HEPT until relatively high concentrations were reached. It is difficult to reconcile the increased CO, benzene and POHC penetration with reduced efficiency of in-flame processes. Flame extinction or post-flame thermal decomposition may better explain the observations. The droplet experiments suggest that volatility differentials could have led to an increasing concentration of POHCs in the oversize droplets (at least one POHC in each mixture had a boiling point substantially greater than heptane). As mentioned previously, such increases in the liquid-phase could lead to earlier flame extinction because of endothermic decomposition reactions, i.e. HCl elimination, or inhibition of chain-branching reactions, i.e. H-atom scavenging. (H-atoms are needed to regenerate OH radicals which in turn are needed to oxidize CO and benzene. It is well documented that H-atom formation can be the rate-limiting step in OH formation.)

The equilibrium H-atom concentration for the fuel/POHC composition in the TFR has been computed for the system in order to illustrate the possible effect of chlorine on H-atom concentration. The ratio is shown in Figure 11 as a function of stoichiometric air-to-fuel ratio (S.R.) and temperature. There is a narrow region near S.R. = 1.0 in which the presence of chlorine reduces H-atom concentration up to an order of magnitude compared to chlorine's absence as the temperature falls below about 1,300 K. At higher temperatures, or higher or lower S.R., H-atom concentration was not appreciably affected by the presence of chlorine. Thus, if oversize droplets penetrated the flame region and extinction occurred as hypothesized, H-atom scavenging could explain the increased level of CO and benzene observed. As a practical consequence, the droplet results suggest that blending of easily burned fuels of lesser volatility than the CHCs present in a waste may lead to reduction of flame extinction residues and improved DE in thermally quenched systems.

A limited comparison of "incinerability rankings" is presented in Table 3 for the oversize droplet results obtained in the TFR. It shows that the "best" agreement was obtained with low O₂ rankings, in agreement with an earlier comparison with field test data [5]. Nevertheless, excess oxygen was supplied in the primary combustion air to the TFR (S.R. = 1.25). As hypothesized below, the finding of correlation under low oxygen conditions is consistent with the occurrence of oversize droplet residues in the TFR.

When a flame extinguished around a droplet, the remaining fuel/waste mixture continued to vaporize. The dimensions of the droplet and the time scale associated with completion of this process indicate that a "fuel-rich," microscopic cloud of vapor formed. The vapor cloud underwent thermal decomposition while oxygen from the ambient gas diffused into it, because the cloud was much smaller than the length scale of micro-scale turbulence. The TFR acted as a strongly "quenched" system because of its water-cooled walls, thus by the time oxygen diffused into the "micro-cloud," thermal degradation reactions of the refractory CHCs had slowed considerably. Therefore the DE was dominated by the thermal degradation of the POHCs remaining in the droplet residue under oxygen-deficient conditions. The reader should recognize that in an incinerator with refractory-lined walls, the temperature in the post-flame region may be sufficiently high such that thermal degradation continues even after oxygen has diffused into the "micro-cloud."

Although pure 1,2,4-TCB was capable of self-sustained droplet burning, unlike TECA or PERC, TCB was ranked more highly as a difficult to destroy CHC under low O₂ conditions on the bases of its thermal stability (TSloO₂), slow kinetics of reaction (TFMK), and slow burning rate. It has also been observed to yield the lowest DE of several compounds in full-scale POHC mixture tests [2]. Its high boiling temperature ensures that it is among the last species to gasify from droplets. The above results establish the utility of TCB in surrogate POHC mixtures. It has the drawback (or advantage) that it could also be a precursor of 2,3,7,8-TCDD. Thus if it is to be used in an incinerator test, the unit should have a demonstrated capability of high DE for other compounds.

The TCB example points out a difficulty with the use of pure liquid droplet burning characteristics to rank incinerability. Pure compounds having a high degree of chlorination are difficult to burn or will not sustain combustion at all. In order to sustain combustion these compounds must be burned in mixtures. To avoid the complications of compounds concentrating in the liquid-phase, equal volatility mixtures must be burned. Thus we conclude that a practical flame-ranking of incinerability based upon pure compound droplet burning characteristics is not feasible.

CONCLUSION

This study determined the relative DE of 5 CHCs for the case of spray atomization failure (oversize droplet production) in a thermally quenched TFR. The observed compound incinerability was consistent with rankings based upon low oxygen conditions, even though an excess of oxygen was present in the system on average. Single droplet burning experiments have illuminated plausible mechanisms for degraded POHC DE. We observed that many pure CHCs could burn alone, and that the addition of small amounts of vigorously burning fuels to the CHCs could greatly enhance their burning.

As a practical matter, the studies suggest that with appropriate blending of fuels, improved DE should be ob-

tained even for relatively high concentrations of CHCs. Furthermore, the droplet experiments indicate the possibility for increased liquid-phase concentration of low volatility CHCs in gasifying droplets. In such cases, ignition and extinction may be more sensitive to the manner of introduction of excess air than for conventional HC fuels.

Experiments are currently underway to determine the composition of gases immediately following flame extinction and in the atmosphere surrounding isolated burning droplets. With such data, it should be possible to conclusively determine the efficiency of flame processes in bringing about high CHC DE. Furthermore, it should also be possible to isolate whether post-flame thermal decomposition or flame extinction governs the composition of the "micro-cloud" produced by droplet residues. Lastly, spray combustion of trinary mixtures of POHCs and high and low volatility HCs are being undertaken with oversize droplets to test the droplet burnout hypothesis.

Future experiments which should be conducted include examining the effect of ambient oxygen concentration on the ignition of the droplets as they emerge from a flame. The single droplet studies suggested that as concentration of a CHC in a droplet increases, ignition becomes more difficult. Similarly, the effect of ambient temperature on flame extinction of droplets needs to be characterized. There were indications in the single droplet studies of larger extinction diameters as ambient temperatures dropped, while for vigorously burning fuels, e.g., a normal alkane, the ambient temperature played little or no role in flame extinction. It may be that complete combustion of difficult to burn fuels like CHCs is sensitive to the manner of introduction of excess air, in real incinerators as well on a lab-scale.

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Industrial Sludge Waste Incineration

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*A fluidized bed incinerator was installed to handle sludge disposal.
Construction and the permit process is discussed.*

INTRODUCTION

Primary and waste activated sludge are generated at an industrial on-site wastewater treatment plant. The manufacturing facility produces plastics additives, catalysts, surfactants, and animal feed intermediates. Since the early 1970s, the plant had been disposing of its wastes in its own landfill on the plant site. Concerned with the adequacy of this method of disposal for the future, the decision was made to incinerate the sludges. Spent solvents with a relatively high heating value, which are also generated at the plant, would be fired in the incinerator to produce the heat required for incineration of the sludge cake. In late 1985, after evaluating several types of sludge burning systems, it was decided to purchase a fluidized bed incinerator. This case study documents the successful efforts to obtain permits and construction. The incinerator is currently in operation, disposing of the designated waste streams.

WASTE STREAMS

Sludge and liquid wastes are generated at the wastewater treatment plant and at other locations in the facility. Three waste streams are defined: spent waste solvents,

high solids sludge, and low solids sludge with characteristics as follows:

- Spent waste solvents with heating values in the range of 12,000 to 17,000 Btu/lb; predominantly organic with trace amounts of sulfur and less than 1% solids content.
- High solids sludge—predominantly activated sludge from the secondary treatment of plant wastewater; thickened sludge is conditioned with lime and alum and filtered by a plate and frame press to approximately 35% solids.
- Low solids sludge having similar conditioning as high solids, except filtration by a vacuum filter, yielding approximately 16% solids.

In an effort to reduce ash generation and increase incinerator operating efficiency, plant trials are now in progress to determine suitable polymer conditioning chemicals to replace lime and alum conditioning, which contributes to increased ash loads and higher energy consumption.

WASTE GENERATION

Two to four times a week, solvents are brought by tank truck to the incinerator facility and are stored in a solvent

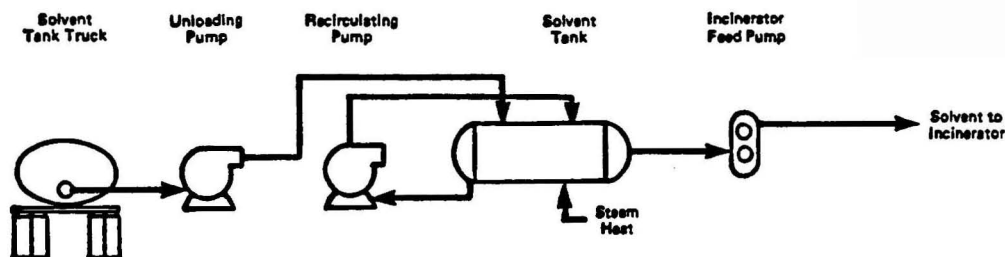


Figure 1. Solvent feed to incinerator.

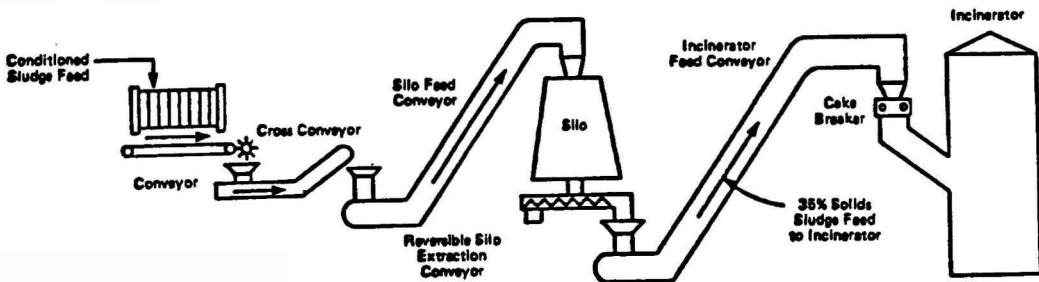


Figure 2. High solids sludge feed to incinerator.

storage tank provided with a recirculation pump and heaters, as shown in Figure 1. The solvents tend to be viscous at ambient temperature, particularly in winter months. To address this, steam heaters control solvent temperature to reduce viscosity to below 750 SSU, allowing smooth pumping to the incinerator. The recirculation pump encourages mixing and uniform heating of the solvent and reduces the tendency of entrained solids to settle.

High solids sludge originates in the secondary wastewater treatment system. Thickened secondary sludge solids are conditioned with lime and alum and directed to a plate and frame press that dewateres the sludge to a 35% solids consistency. This press is a batch device, generating sludge 20 minutes on a 2-hour batch cycle. An incinerator requires a consistent flow to operate properly to avoid temperature swings and minimize the need for operator attention. As shown in Figure 2, high solids sludge is collected in a storage silo, which holds up to a one-day accumulation of sludge. It receives sludge on a cyclical basis, but discharges to the incinerator at a uniform rate.

Low solids sludge is usually primary wastewater treatment sludge, conditioned with both lime and alum. One of two vacuum filters (one is operating, the other is a spare) generates a 16% solids cake. This stream is continuous and is fed directly to the incinerator, shown in Figure 3.

HIGH SOLIDS FEED

Sludge cake from the plate and frame press is dropped onto a belt conveyor that feeds a series of drag chain conveyors. A major concern during the selection of this equipment was the transfer of sludge through the conveyors without a sludge buildup on the walls or severe caking or adhesion between the flights and the conveyor. Therefore, drag-chain conveyors with thin tubular flights were used. The flights have relatively little surface area, which helps prevent adhesion of sludge. An additional

feature of the conveyor design is the internal lining of basalt. Basalt tends to prevent adhesion of sludge and will encourage the smooth transfer of sludge along conveyor surfaces, minimizing wear (erosion).

A major component of the high solids sludge-feed system is the sludge silo. The silo is fed at the top by a drag-chain conveyor. Sludge accumulates within the silo until it is discharged by an extractor arm (a thin, long, metal bar), which rotates slowly over a single longitudinal opening. The movement of the arm encourages the sludge to drop into the opening. This opening feeds the silo extractor screw that drops sludge cake into the incinerator feed conveyor, another drag-chain conveyor. The extractor screw is turned by a variable speed drive that is controlled to move faster when more sludge is desired or slower when less is needed.

Another area of concern during design was the potential for sludge to build up and cake within the silo. For example, if the sludge accumulated in the hopper for 48 hours, would it harden to the point that it could not be removed by the extractor? It was found, by accident, that sludge can be retained in the silo for several days without adverse effects.

The facility design includes an alternate discharge at the opposite end of the silo extractor screw, which is reversible. If the sludge is not to be incinerated for a protracted period of time, it can be discharged to a container for eventual reinsertion into the system. This system is also used for calibration checks of the extractor screw.

Concern with the caking of the sludge leaving the silo and incinerator feed conveyor resulted in provision of a cake breaker at the incinerator feed. This is a slow speed breaker with dual shafts, each turning a set of thin fingers. Sludge is reduced to uniform size by this equipment, eliminating any clumps.

INCINERATOR

The incinerator is a fluid-bed furnace system, shown in Figure 4. The heart of the furnace is the reactor, a vertical

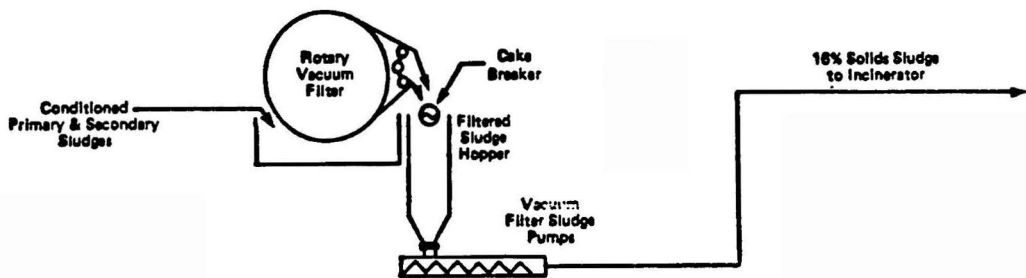


Figure 3. Low solids sludge feed to incinerator.

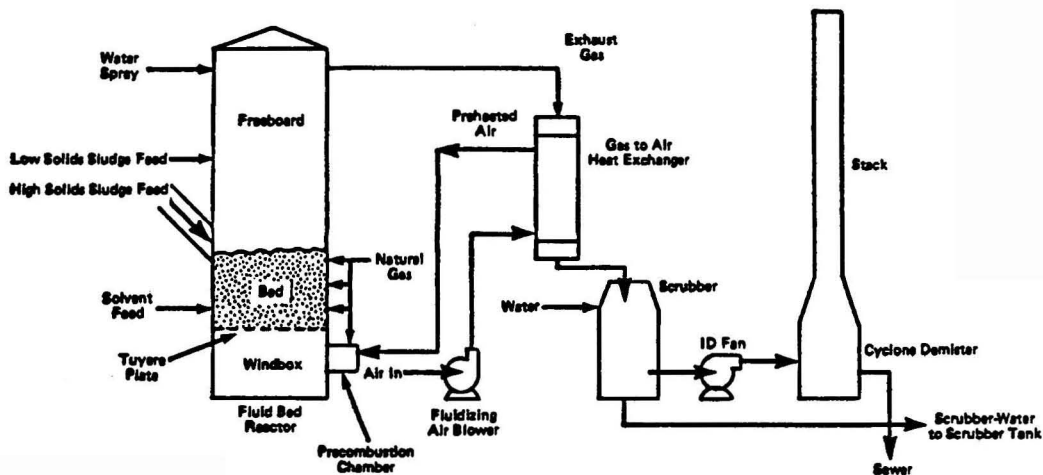


Figure 4. Fluid bed incinerator.

refractory-lined chamber approximately 9 feet outside diameter and 35 feet high. This unit is designed to incinerate 4,000 lb per hour of high solids (35%) sludge, with a heat input of 225,000 Btu per hour per square foot of bed area. Flue gas exits the top of the incinerator at approximately 1,600°F and is cooled to approximately 1,000°F through a gas-to-air heat exchanger. Air entering the cold side of the heat exchanger is heated from near ambient temperature to approximately 1,100°F. The heated air stream is directed to the lower chamber of the furnace, the windbox. A precombustion chamber at the entrance of the windbox raises the temperature of the entering air at startup, until the temperature at the hot side of the heat exchanger is hot enough to bring the air temperature to 1100°F.

From the windbox, the heated air stream passes upward through openings (tuyeres) in a refractory grate (tuyere plate) that supports a sand bed, which is 18 to 24 inches deep at rest. Upon fluidization, the sand bed expands in volume by 30 to 60%.

The injection of hot air into the sand bed creates a high degree of turbulence and the top of the bed appears as a fluid in motion. With the high temperature of the air and the intense turbulence, moisture in sludge introduced into the bed will evaporate practically instantaneously. Combustion will occur with less than 50% excess air at design load, which is an indication of the good burning efficiency of this unit.

Off-gas from the bed will pass into the volume above the bed, the freeboard, which is normally maintained at a temperature of 1,600°F. Residual organics in the gas stream will be destroyed at this temperature based on a residence time in excess of 5 seconds.

Residual solids, including ash, will be elutriated in the gas stream exiting the reactor. Along with the ash load, some sand from the bed will also be carried by the gas. A critical concern with bed operation is the possibility of agglomeration. If the feed contains materials with a relatively low melting point (such as salts), sand particles can grow in size and eventually seize the bed, preventing air flow and forcing shutdown. Sludge is generated in the plant from many different sources, and the presence of salts is always a possibility. To identify and control this potential problem, periodic size analyses of sand samples are made. If the sand particles show an increase in mean diameter, agglomeration may be developing. To control inorganic buildup (or sand agglomeration) routine (con-

tinuous) bed tapping and clean sand makeup may be necessary.

A fluidizing air blower provides the air required to maintain fluidization of the sand bed. The blower is sized to provide sufficient pressure to overcome the resistance of the air side of the gas-to-air heat exchanger, the windbox, the sand bed, and associated ducts and dampers.

An induced draft (ID) fan maintains a negative pressure within the reactor freeboard. It is sized to draw hot combustion gases through the furnace (the freeboard), the gas side of the gas-to-air heat exchanger, the scrubber, and associated flues and dampers. The discharge of the ID fan is through the cyclone demister, the stack, and into the atmosphere.

The scrubber is of radial design and scrubs flue gas exiting the heat exchanger with plant process water. No additives (such as lime or caustic) are used in the scrubber system. The saturated gas stream is cooled below 200°F, and entrained water droplets are removed in the cyclone demister downstream of the scrubber.

The water/ash slurry discharge leaving the scrubber is discharged to the surface impoundment on the plant site that is permitted for hazardous waste disposal.

WASTE BURNING

The moisture content of the sludge is too high to allow autogenous burning. Waste solvent maintains the required furnace temperature after the furnace is brought to operating temperature. Natural gas is used for startup and to supplement the heat required to maintain required combustion temperatures if sufficient solvent is not available.

The system is designed to burn either high solids sludge or low solids sludge at any time, not both feeds at once. Solvent is used as a fuel for either sludge feed or it can be fired by itself. If fired without sludge, the temperatures generated will probably exceed the 1,600°F maximum temperature limitation in the freeboard. A water spray in the freeboard, indicated in Figure 4, is used to control temperature.

Solvent and natural gas are injected within the bed. Low solids sludge feed is introduced into the freeboard, and high solids sludge feed is dropped into the furnace immediately above the bed.

REGULATORY ACTIVITY

The operation of the incinerator is regulated by two environmental permits: state air and hazardous waste. The air permit requires that air emissions from the incinerator be maintained below regulated limits. The hazardous waste permit, issued under the aegis of RCRA, requires that inspection and operating records be maintained for the life of the facility, that training programs in the operation of the facility be implemented, and that certain operating conditions be maintained. These permits were issued after the filings were complete and a public hearing was held, subject to performance of a successful emissions test.

Startup and Training

Hazards and Operability (HAZOP) reviews were conducted at the end of the design phase in 1985 and again in the closing period of construction in November 1986, along with an operational readiness review. These reviews were performed to determine the ranges of safe operation of the incinerator facility and the proper response to conditions outside normal operating ranges. Construction was completed on the incinerator in December 1986. The startup and checkout procedures began with curing of the refractory, followed by a detailed and rigorous check of the instrumentation and control systems.

Waste was first fed to the incinerator in January 1987, and commissioning and operational testing were completed over the next four months. This time was spent in on-the-job training for operators, testing the control system and all setpoints, and defining the operational ranges of the process.

The trial burn, which is required as part of the hazardous waste management permitting process, was conducted in May 1987. The results of the trial burn demonstrated a destruction and removal efficiency (DRE) of 99.99% for the principal organic hazardous constituent, which is toluene.

Operator training is required as part of RCRA permitting requirements. All incinerator operators and supervisory personnel must receive formal training in the operation of the equipment and in safety procedures. Operator training began in November 1986 and was completed as the incinerator was ready to go on line. An examination was included in each training session to add credibility to the program and to impress upon the operators the importance of formal training. These training sessions were recorded on videotape for the future training of new employees, for retraining of operators who have been away from the facility for six months or more, and for annual retraining of operators at the facility.

CONCLUSION

A solution to a potential waste disposal problem was identified and implemented. Landfills are becoming obsolete in all parts of the country. Incineration, which had been seen as an expensive alternative, has now become a reasonable answer to the disposal of these industrial wastes.

LITERATURE CITED

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Chemical Demilitarization: Disposing of the Most Hazardous Wastes

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This country's aging stockpile of chemical warfare munitions require safe and economical disposal. These munitions present a unique challenge for demilitarization, since handling of both explosives and toxic material is required. The first full-scale munitions disposal facility is presently undergoing testing and systemization on Johnston Island. The technology developed for incorporation into the Johnston Atoll Chemical Agent Disposal System maximizes the use of automated equipment, provides the containment necessary to protect the worker and environment, and thermally destroys both the toxic fill and explosives from the munitions.

INTRODUCTION

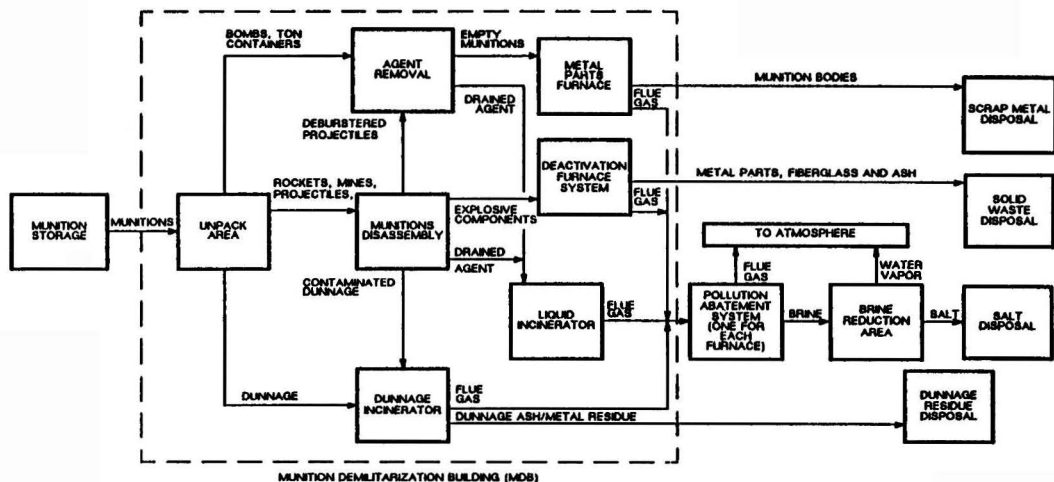
This country's policy on chemical warfare (CW) can be stated succinctly. The objectives of the U.S. CW policy are to eliminate the threat of chemical warfare by achieving a complete and verifiable ban on chemical weapons; and until such a ban is obtained, to deter the use of chemical weapons against the U.S. or its allies. A necessary adjunct to this policy is the maintenance of a credible retaliatory stockpile. Although manufacturing of unitary CW munitions was halted in the late 1960's, large quantities of these items remain stored in ammunition magazines at eight US Army installations. In 1986, the U.S. Congress mandated that the unitary chemical stockpile (less 10%) be destroyed as part of a modernization effort for the entire U.S. chemical capability.

The munition types that make up this stockpile include bombs, rockets, land mines, spray tanks, cartridges, projectiles, and bulk containers. Disposal of these munitions presents a unique challenge, since these items may contain both energetic materials (explosive components) and an extremely toxic fill (chemical agent). Not all CW munitions are explosively configured; many munitions are stored separately from the explosive components. The special hazards associated with chemical demilitarization operations require considerable safeguards in order to dispose of this material in a safe and environmentally acceptable manner. In response to these requirements, the Army has developed methods and procedures on the leading edge of technology for hazardous waste disposal.

The munitions and bulk containers are each filled with one of the following lethal chemical agents: GB, VX, or mustard. These lethal chemical agents are liquids at room temperature and are not corrosive. The agents do not exist

in the munitions or bulk containers as pure compounds; they are stabilized with various compounds to prevent acid formation. The Army believes it is reasonable to presume that none of the agent decomposition products due to aging, degradation, or decontamination will be more difficult to destroy by incineration than the agents, and that the decomposition products are less hazardous than pure agents.

CW munitions presently in storage were not designed to facilitate their eventual disposal; early disposal efforts were primarily accomplished by burial at sea, the last being Operation Chase X, in August 1970. Rising worldwide environmental concern led the Department of Army (DA) to commission a study by the National Academy of Sciences (NAS) to investigate disposal alternatives for CW munitions. The NAS concluded: "... that all such agents and munitions will require eventual disposal and that dumping at sea should be avoided. Therefore, a systematic study of optimal methods of disposal on appropriate military installations, involving no hazards to the general population and no pollution of the environment, should be undertaken. Appropriately, large disposal facilities should be a required counterpart to existing stocks and planned manufacturing operations. As the first step in this direction, we suggest the construction of facilities for gradual demilitarization and detoxification" [1]. The NAS recommendations for chemical demilitarization were supplemented by DA guidance to insure absolute safety and security rather than cost or time, maximum protection for operating personnel, absolute assurance of total containment of agent, and collection of incontrovertible data to support personnel safety, security, and community safeguard.



NOTES:

1. MDB IS KEPT UNDER NEGATIVE PRESSURE.
2. MUNITION DISASSEMBLY PERFORMED IN EXPLOSION CONTAINMENT ROOMS.

Figure 1. JACADS—process flow diagram.

The first full-scale destruction facility, called the Johnston Atoll Chemical Agent Disposal System (JACADS), is currently undergoing equipment testing and systemization. The facility was built on Johnston Island, one of four small land bodies that make up Johnston Atoll (JA), located 717 nautical miles west southwest of Honolulu, Hawaii. JA is an unincorporated U.S. possession under joint management by the Defense Nuclear Agency (DNA) and the Department of Interior (DOI). Johnston Island, the largest body in the Atoll, is approximately 2 miles long and 1/2 mile wide, and covers 630 acres. The Atoll is both a wildlife refuge monitored by the Fish and Wildlife Service, and a contingency site maintained by DNA for resumption of above-ground nuclear testing.

The CW stocks stored at JA came originally from Okinawa in 1971 as a result of their prohibition from being returned to the United States by Public Law 91-672. When the Army initiated planning in March 1981 for disposal of the obsolete munitions on JA, environmental considerations were given priority. A public meeting was held in Honolulu in March 1983 and a final EIS published in November 1983. Of the viable alternatives, con-

struction of a state-of-the-art disposal facility on JA was determined to offer the best solution. The technology selected was that demonstrated by the Chemical Agent Munitions Disposal System (CAMDS) prototype facility located at Tooele Army Depot, Utah. The key elements of this technology are illustrated in Figure 1; they served as the basis for the design of the JACADS process and facility.

MUNITIONS

Chemical munitions are maintained in storage in a variety of configurations; some include fuzes, explosive burster charges, and propellant. Lethal chemical agents currently available for military application include mustard and nerve agents. Table 1 illustrates the various munitions that the JACADS disposal process will handle.

TOXIC AGENTS

Chemical warfare agents are extremely toxic compounds that produce lethal or incapacitating effects on

TABLE 1. U.S. CHEMICAL WARFARE MUNITIONS

Designation	Description	Fill	Explosives	Propellant	Fuze
M55	115mm rocket	10.7 lb GB or 10.2 lb VX	3.2 lb	19.3 lb	Yes
M23	Land Mine	10.5 lb VX	0.9 lb	None	Yes
M2/M2A1	4.2" Cartridge*	6.0 lb H/HD	0.14 lb	0.6 lb	Yes
M60	105mm Cartridge*	3.0 lb H/HD	0.26 lb	2.8 lb	Yes
M360	105mm Cartridge*	1.6 lb GB	1.1 lb	2.8 lb	Yes
M110	155mm Projectile	11.7 lb H/HD	0.83 lb	None	No
M104	155mm Projectile	11.7 lb HD	0.83 lb	None	No
M121A1	155mm Projectile	6.5 lb GB or VX	2.45 lb	None	No
M122A1	155mm Projectile	6.5 lb GB	2.45 lb	None	No
M426	8" Projectile	14.5 lb GB or VX	7.0 lb	None	No
MC-1	750 lb Bomb	220 lb GB	None	None	No
MK-94	500 lb bomb	108 lb GB	None	None	No
TC	Ton Container	1600 lb GB/VX/H	None	None	No
TMU-28	Spray tank	1356 lb VX	None	None	No

*A projectile, burster, fuze, cartridge casing, propellant, and primer comprise a cartridge.

TABLE 2. PHYSICAL & CHEMICAL PROPERTIES OF CW AGENTS

Chemical Name	GB	VX	HD
	Isopropyl methyl phosphono fluoridate	O-ethyl 5-(2-diisopropylaminoethyl) methyl phosphonothiolate	Bis(2-chloroethyl) sulfide
Common Name	Sarin	—	Distilled Mustard
Molecular Wt	140.1	267.4	159.1
Liquid Density (4°C)	1.09	1.006	1.27
Freezing Point (°C)	-56	-39	14
Vapor Pressure at 20°C (mm Hg)	2.2	.0007	.072
Boiling Point (°F)	316.0	568.0	423.0
Heat or Vaporization (BTU/LB)	144.0	141.0	169.0
Flash Point (°F)	—	318.0	221.0
Heat of Combustion (BTU/LB-HHV)	8,709	13,148	7336
Liquid Specific Heat (BTU/LB°F)	0.416	0.484	0.333
Vapor Density (Relative to Air)	4.8	9.2	5.5
Decomposition Temp. (°C)	400-560	700-800	149-177
LD ₅₀ (mg-min/m ³)	100	*	1500
Chemical Formula	CH ₃ P(O)(F)OCH(CH ₃) ₂	CH ₃ P(:O)(OC ₂ H ₅)SC ₂ H ₄ N(iso-C ₃ H ₇) ₂	(ClCH ₂ CH) ₂ S

* Exposure is primarily via skin penetration. Medium lethal dose is 2.5 mg (equivalent of 0.56 mg intravenous dose).

man, depending upon the degree of exposure. Excluded from this definition are riot control agents, chemical herbicides, and smoke and flame materials. Table 2 provides data on the toxic agents.

The term nerve agent refers to two groups of highly toxic chemical compounds that are generally organic esters of substituted phosphoric acid. Nerve agents affect body functions by inhibiting cholinesterase enzymes, permitting accumulation of acetylcholine and subsequent paralysis. Two general categories of nerve agents are currently stockpiled: G agents and V agents.

The G agent used in munitions is GB (Sarin); it is a liquid under ordinary atmospheric conditions, with a relatively high vapor pressure. GB is colorless and odorless. It is readily absorbed into the body by inhalation, by ingestion, and through the skin and eyes without producing any irritation prior to onset of symptoms. It hydrolyzes slowly in water at neutral or slightly acidic pH, and rapidly under strong alkaline or acidic conditions.

Other nerve agent munitions are filled with VX. This agent is amber in color and odorless. A liquid at normal ambient temperatures, it has an extremely low vapor

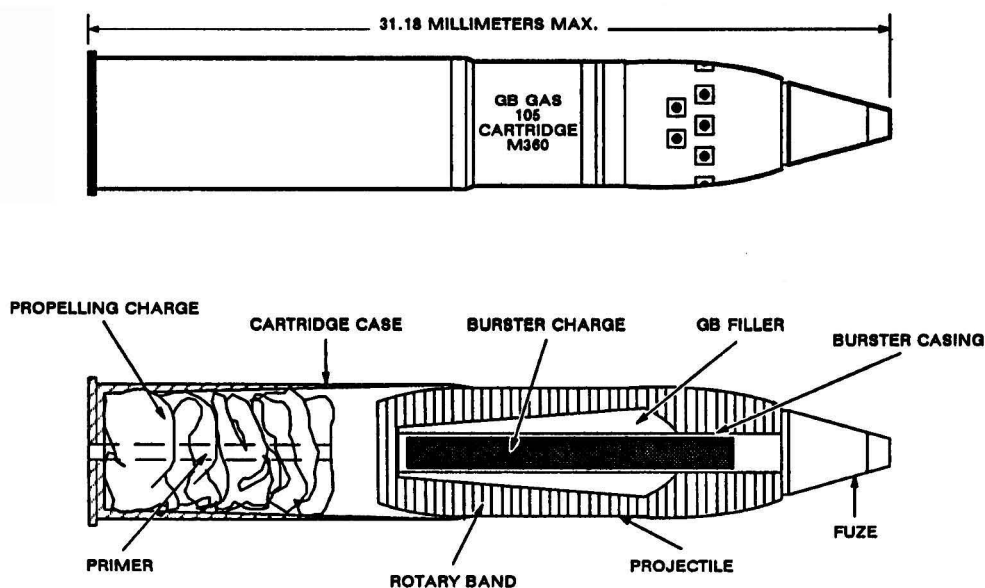


Figure 2. Cartridge, 105 millimeter: agent GB, M360.

pressure. Consequently, it is dispersed as an aerosol, and exposure is primarily via skin penetration. The toxicity of VX is 3-10 times that of GB. Exposure to either nerve agent can result in death within minutes.

Blister agents, such as mustard, are systemic poisons, attacking the eyes and lungs and blistering the skin as the result of either liquid or vapor contact. Most blister agents cause little or no pain on contact. Symptoms of exposure do not usually appear for several hours. Mustard blister agents include Levinstein Mustard (H), and Distilled Mustard (HD). Pure mustard is a colorless, oily liquid; impurities impart a characteristic garlic odor. It is sufficiently volatile to present a vapor hazard in warm weather.

DEMILITARIZATION CRITERIA

As was shown in Table 1, each agent is contained in a variety of munitions. Figure 2 illustrates a typical chemical filled munition, an M360 cartridge. A projectile, burster, fuze, cartridge casing, propellant, and primer comprise a cartridge. Disposal poses significant challenges for the following reasons:

1. Safe disassembly of the explosives.
2. Disposal of the removed explosive components and propellants.
3. Accessing the agent cavity.
4. Disposal of the toxic agent.
5. Disposal of the munition bodies.
6. Disposal of the process generated wastes.

In addition to these considerations, the Army has estab-

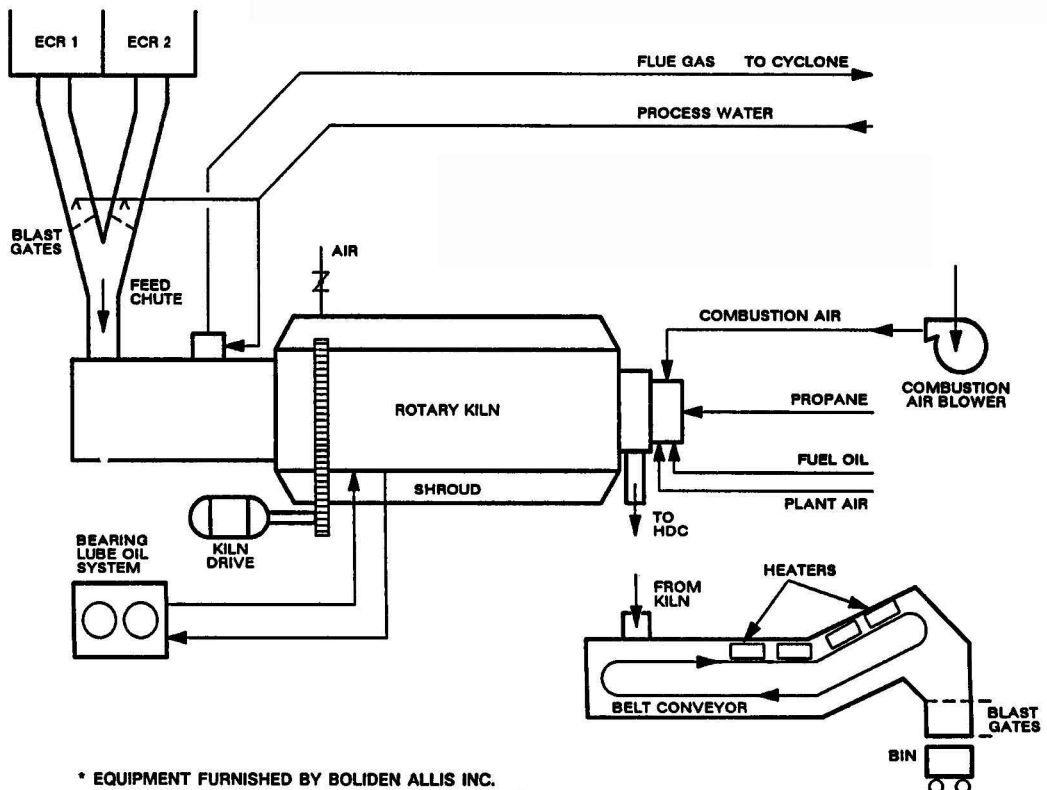
lished criteria for the storage, transportation, and disposal of CW material. These criteria address the following areas, and influence selection of disposal alternatives:

1. Restrictions on total quantity of explosives within the process building.
2. Agent emission limitations.
3. Process effluent standards.
4. Personnel safety requirements.

The overriding facility design criteria is agent containment [2]. By maintaining negative pressure within all processing areas, air flow is always from areas of lesser contamination potential to areas of greater potential; this scheme results in agent containment for all processing steps. The resulting ventilation air is scrubbed by redundant High Efficiency Particulate Air (HEPA) and charcoal filters. These filters are designed to prevent the release of detectable agent to the atmosphere. Containment of both the overpressure and fragments resulting from an accidental detonation is provided for those process steps involving explosively configured munitions. This total containment is accomplished by use of a reinforced concrete structure contained within the building. Blast valves and containment dampers isolate this structure from the rest of the building in the event of an accidental detonation.

CAMDS

In September 1979, the Chemical Agent/Munitions Disposal System (CAMDS) at Tooele Army Depot, Utah, became operational. This \$67 million dollar prototype



* EQUIPMENT FURNISHED BY BOLIDEN ALLIS INC.

Figure 3. DFS Kiln system.

plant serves as a test facility to evaluate various processes for possible incorporation into future large-scale production demilitarization facilities. To support the development of the process design for JACADS, the Army initiated a comprehensive testing program at CAMDS in 1982. Results of this program, and experience gained during actual disposal operations in the late 1970's, assisted with development of the JACADS design criteria.

PROCESS TECHNOLOGY

The specific process steps and equipment required for demilitarization are dependent upon the munition type. Generically, all munition types fall into one of three categories:

Rockets and Mines. These thin-walled munitions are processed without removal of their explosive components, except for a small booster in the M23 mine.

Projectiles and Cartridges. Removal of explosives from these heavy-walled munitions is the first processing step. **Bulk Items.** This category includes bombs, spray tanks, and ton containers; they do not contain explosives in their storage configurations.

For all three munition categories, the demilitarization process involves two distinct operations: preparation for thermal treatment, followed by thermal processing. Agent destruction is accomplished by incineration. Figure 1 illustrates the JACADS processing steps.

The JACADS facility has been designed with the capability to process all three munition categories. The primary process building comprises 73,000 sq ft on two levels. The second floor houses the equipment required for preparation of the munition for thermal processing. Munition processing is accomplished by machines designed and built for specific chemical demilitarization operations. This equipment includes the rocket shear machine for shearing rockets and explosives, the projectile/mortar disassembly machine for removing explosive components by reversing the assembly process, the multipurpose demil machine for draining agent from projectiles, and the bulk drain station for punching and draining bombs, ton containers, and spray tanks.

The process's four furnaces are located on the ground level, facilitating gravity feed of munition components into the furnaces. The four process furnaces: the liquid incinerator (LIC), the deactivation furnace system (DFS), the metal parts furnace (MPF), and the dunnage incinerator (DUN) are the heart of the demilitarization operation. All furnaces and afterburners are fired with propane for

TABLE 3. AGENT INCINERATOR DESTRUCTION REQUIREMENTS (200% EXCESS AIR)

Agent	Discharge Std (mg/m ³)	Required Destruction Efficiency (%)
GB	0.0003	99.999999
VX	0.0003	99.999999
H	0.03	99.99995

warmup, and use JP-5 fuel oil during operations. The following sections discuss the design and the role of each of these furnaces in the disposal process.

Liquid Incinerator (LIC)

In the design of an agent incinerator, the overriding criteria is destruction efficiency [3]. Table 3 illustrates the degree of destruction required for each agent. Test results from past and current disposal systems verify the capability to meet these values.

Chemical agent, drained as a liquid from all munitions and pumped to intermediate holding tanks, is incinerated in the LIC. Design criteria for the LIC are tabulated in Table 4.

Agent pumped from the intermediate holding tanks is atomized by a spray nozzle into the primary chamber of the two-chamber furnace. The resultant combustion

TABLE 4. LIC DESIGN CRITERIA

	Primary Chamber	Secondary Chamber
Chamber Temperature (°F)	2,700	2,000
Agent Destruction Time (Sec.)	0.42	—
Flue Gas Residence Time (Sec.)	0.90	2.06
Agent Mean Droplet Size (u)	50	—
No. of burners	1	2
GB Rate (LB/HR)	1,050	—
VX Rate (LB/HR)	700	—
H/HD Rate (LB/HR)	1,330	—
Decontamination Solutions* (LB/HR)	—	2,000
Salt Collection Efficiency (%)	—	99
GB Heat Release (BTU/HR)	9,145,000	—
VX Heat Release (BTU/HR)	9,204,000	—
H/HD Heat Release (BTU/HR)	9,757,000	—
JP-5 Fuel Heat Release (BTU/HR)	2,500,000	4,800,000

* When processing GB, 99.5% H₂O and 0.5% NaOH; when processing VX or HD, 97.5% H₂O and 2.5% NaCl.

TABLE 5. DFS DESIGN CRITERIA

	Rotary Kiln	Heated Discharge Conveyor	Afterburner
Chamber Temperature (°F)	1,000*	1,000	2,000
Munition Residence Time (Min.)	12 @ 1 RPM	15 @ 1,000°F	—
Flue Gas Residence Time (Sec.)	—	—	0.5
Rockets per Hour	40	1,340**	—
Mines per Hour	59	690**	—
Bursters/Fuzes per Hour	400	—	—
Kiln Speed (RPM)	0.5-2.0	—	—
No. of Burners	1	—	2
Explosives Heat Release (BTU/HR)	416,000	—	—
Propellant Heat Release (BTU/HR)	2,474,000	—	—
JP-5 Fuel Heat Release (BTU/HR)	10,000,000	—	16,000,000
Heating Load (KW)	—	150	—
Conveyor Speed (FPM)	—	1.4-2.8	—

* Measured at the burner end.

** LB/HR of scrap metal.

products are further incinerated in the secondary chamber (fume burner). In addition, spent decontamination solution is injected into the system to completely burn any organic constituents present and reduce the solution to molten salt and water vapor. Molten salt is removed from the system for ultimate disposal. T-Thermal Inc. furnished the LIC equipment, but certain proprietary aspects of the design preclude the inclusion of a LIC schematic here.

Deactivation Furnace System (DFS)

Disposal of the munitions' explosive and propellant components is accomplished by incineration in the DFS kiln. Table 5 summarizes the DFS design criteria. Bursters and rocket propellants are preprocessed through a mechanical shear. This shear reduces the size of the material and exposes additional surface area to facilitate controlled combustion rather than detonation. Fuzes, booster pellets, and supplementary charges are fed to the furnace intact.

The deactivation furnace consists of a 310 stainless steel rotary kiln, controlled at 1,000°F at the burner end, and a heated discharge conveyor, operated at 1,000°F. Figure 3 illustrates the DFS. Residence time of the explosives inside the kiln is at least 12 minutes—sufficient to allow complete burning of all energetic material. Upon exiting the kiln, the non-combustible components travel on the heated discharge conveyor for an additional 15 minutes to insure complete thermal decontamination of any residual agent. The DFS is capable of processing approximately 150 lbs/hr of explosives.

The exhaust of the deactivation furnace exits through a blast attenuation duct prior to entry into an afterburner. The DFS afterburner has been designed to the same criteria as the LIC secondary chamber (fume burner) [4].

The deactivation furnace room was designed to provide containment of all fragments, overpressure, and agent in the event of an accidental detonation during the incineration process.

Metal Parts Furnace (MPF)

In addition to the agent and explosives, the munition metal parts constitute a third category of hazardous waste. Metal that has been in contact with liquid agent has been shown to release agent vapors when subjected to elevated temperatures, even after the metal has been chemically decontaminated. For this reason, all metal parts are thermally decontaminated to a criteria of 15 minutes at 1,000°F prior to discharge from the process areas. Metal parts from projectiles and bulk items are processed through a separate metal parts furnace (MPF) for thermal decontamination. The throughput rates of this furnace are a function of the munition types, as shown in Table 6. This roller hearth type furnace is designed to process metal parts through the furnace on reusable 3 feet × 10 feet trays with a residence time of approximately 60 minutes [5]. Figure 4 is a schematic of the MPF. In addition to the decontamination of metal parts, this furnace has been designed to incinerate a residual agent "heel" of 5% by

TABLE 6. MPF MUNITION AVERAGE PROCESSING RATES

Munition Type	No./Hour	Lbs/Hour (Metal)
105 mm Projectile	352	23,200
4.2" Mortar	352	16,000
155 mm Projectile	181	25,800
8" Projectile	97	27,500
Bomb	7	9,900
Ton Container	2	6,100

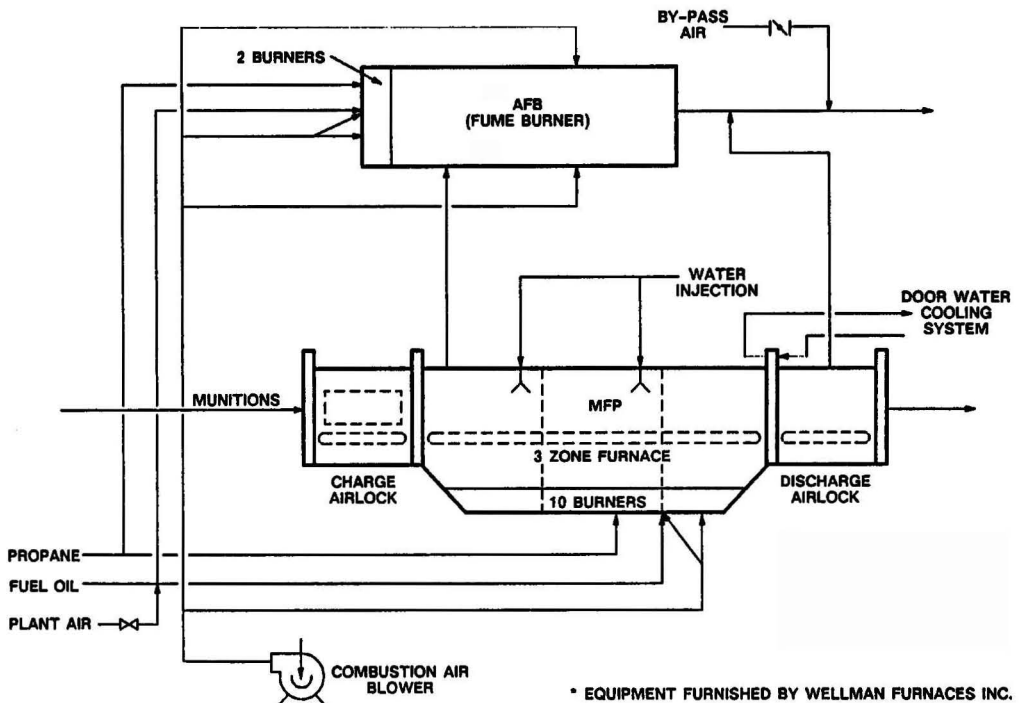


Figure 4. Metal parts furnace system.

weight of the agent fill of each munition. Exhaust gases from the MPF are incinerated in an afterburner. Table 7 shows the design criteria for the MPF.

TABLE 7. MPF DESIGN CRITERIA

	Primary Chamber	Afterburner
Chamber Temperature (°F) ⁶	1,600*	2,000
Flue Gas Residence Time (Sec.)	—	0.5
Munition Residence Time (Min.)	60	—
No. of Burners	10	2
JP-5 Fuel Heat Release (BTU/HR)	15,142,000	6,432,000
Water Injection (GPM)	4.8	—
Conveyor Speed (FPM)**	20.6	—

* 1400°F when processing ton containers

** Two speed motor—oscillation speed is 10.3 FPM.

Dunnage Incinerator (DUN)

The fourth furnace system within the JACADS facility is the dunnage incinerator (DUN). Table 8 summarizes the DUN design criteria. This incinerator is designed to burn all process dunnage, including agent contaminated wood, wooden pallets impregnated with PCP preservatives, contaminated protective clothing, and other packaging materials. In addition, the DUN thermally decontaminates mine drums. The DUN is illustrated in Figure 5. The primary chamber is a refractory lined furnace operated at approximately 1,600°F when processing combustibles in the starved air mode. A ram feeder pushes materials into the furnace, simultaneously discharging ash from the opposite end. An afterburner assures complete incineration of all hydrocarbons. The incinerator has a throughput rate of approximately 1,000 lbs/hour of combustible dunnage.

quirements. The exhaust of the afterburner is drawn through the pollution abatement system by an induced draft fan. The quench tower reduces the afterburner exhaust to approximately 180°F and results in adiabatic saturation of the effluent stream. A caustic-brine solution at a pH of 8 is used as a quench media to assure neutralization

POLLUTION ABATEMENT SYSTEMS

Each furnace system has an independent pollution abatement system designed to scrub the products of combustion. The primary products of combustion are shown in Table 9. In addition, impurities in the agents result in trace quantities of heavy metals in the furnace exhaust.

Figure 6 illustrates the basic pollution abatement system; similar systems are utilized for three of the four process furnaces (DFS, LIC, and MPF). The incinerators were designed for compliance with applicable RCRA re-

TABLE 8. DUN DESIGN CRITERIA

	Primary Chamber	Afterburner
Chamber Temperature (°F)	1,600	2,000
Waste Material Residence Time (Min.)	60	—
Flue Gas Residence Time (Sec.)	—	2.0
Waste Feed Rates		
Wood (LB/HR)	1,000	—
Metal (Mine Drums per Hour)	24	—
No. of Burners	4	4
Wood Heat Release (BTU/HR)	8,000,000	—
JP-5 Fuel Heat Release (BTU/HR)	1,000,000	10,000,000

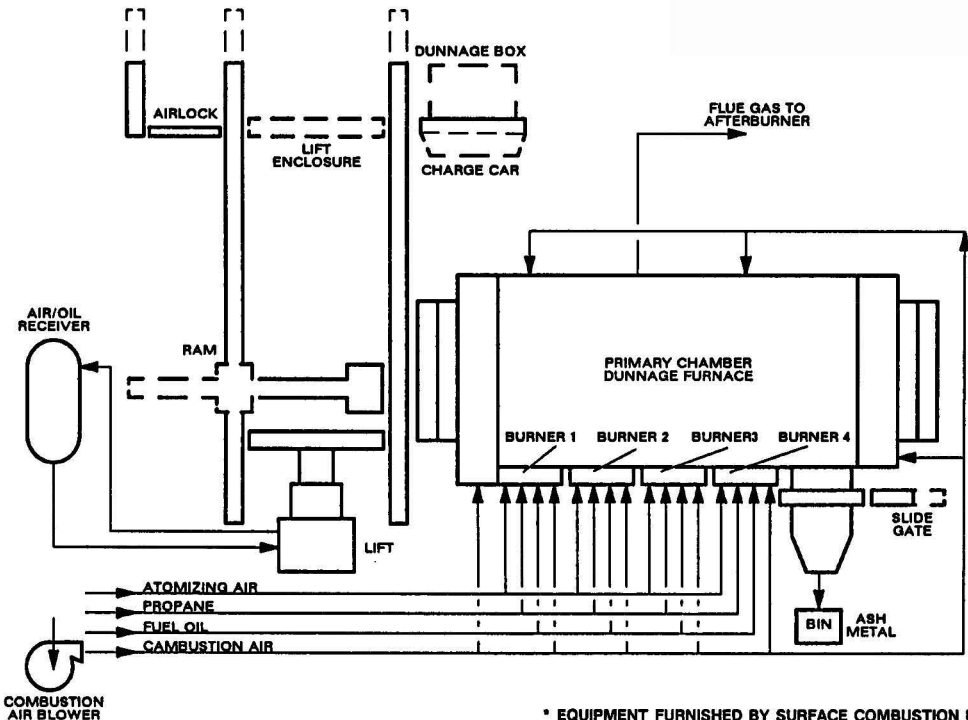


Figure 5. Dunnage furnace system.

of any acid gases. The high energy venturi is a variable throat venturi with an approximate 40-inch WG pressure drop designed to provide 99% efficiency in removal of particulate larger than 0.5 microns. The counterflow caustic packed-bed scrubber uses stainless steel pall rings to scrub the remaining acid gases. Mist eliminators are used primarily for removal of P_2O_5 , and also to entrain particulate not removed by the venturi. The mist eliminators have been designed with a counterflow acid wash to prevent plugging by small particulate metal oxides and are washed at regular intervals.

The DUN pollution abatement system utilizes only a quench tower and baghouse to remove particulates from the furnace flue gas before it is discharged to atmosphere. RCRA performance standards that must be met are:

1. Incinerator destruction and removal efficiency for each principal organic hazardous constituent, 99.99%
2. HCL emissions, 99% removal efficiency or below 4 LBS/HR.
3. Particulate matter discharge, not greater than 180 mg/m³.

Brine Disposal

Liquid effluent from the pollution abatement system is discarded when the specific gravity reaches a 1.08–1.15 range, depending upon the agent being processed. Excess water is evaporated from this effluent by the use of an evaporator and double drum dryers, yielding a waste salt suitable for storage in a RCRA hazardous landfill.

CONTROL SYSTEM

While the four incinerators are the heart of the demilitarization system, the control system is the brain. With the exception of the munition input and residue removal steps, the demilitarization operation is totally automated

and is run by operators in the control room utilizing the central control system (CON).

The CON is capable of controlling operations of sequential (material handling), continuous (pollution abatement system), or hybrid (furnace system) processes. It furnishes operator interface to control operations through shared displays and animated graphics, as well as providing alarm and computer malfunction annunciation and recording. It will also provide a high availability through redundant I/O and data processors, including periodic management reports through the data acquisition computer. The CON temporarily holds all plant information (over 8,000 data points) for the previous 10 minutes, and has the ability to store up to 60 minutes of data permanently.

Control hardware consists of 17 individual programmable logic controllers (PLCs), 8 operator interfaces (Advisor Screens), a local area network (Data Highways), and the process data computer (PDAR). A data concentrator (Network Manager) is used to improve response time. The controllers are Allen-Bradley PLC-3 units programmed using ladder logic. Each controller is a stand-alone unit that can operate without benefit of the data concentrator or operator interference. In practice, however, a loss of communication with the network manager will initiate a controlled shutdown sequence.

The operator interface to the process is the Allen-Bradley Advisor Screen system. Two data highways service the eight advisor consoles. Half are on one and half on the

TABLE 9. AGENT PRODUCTS OF COMBUSTION

Agent	Products of Combustion
GB	CO ₂ , H ₂ O, P ₂ O ₅ , HF, NO _x
VX	NO _x , P ₂ O ₅ , SO ₂ , CO ₂ , H ₂ O
Mustard	CO ₂ , SO ₂ , HCl, H ₂ O, NO _x

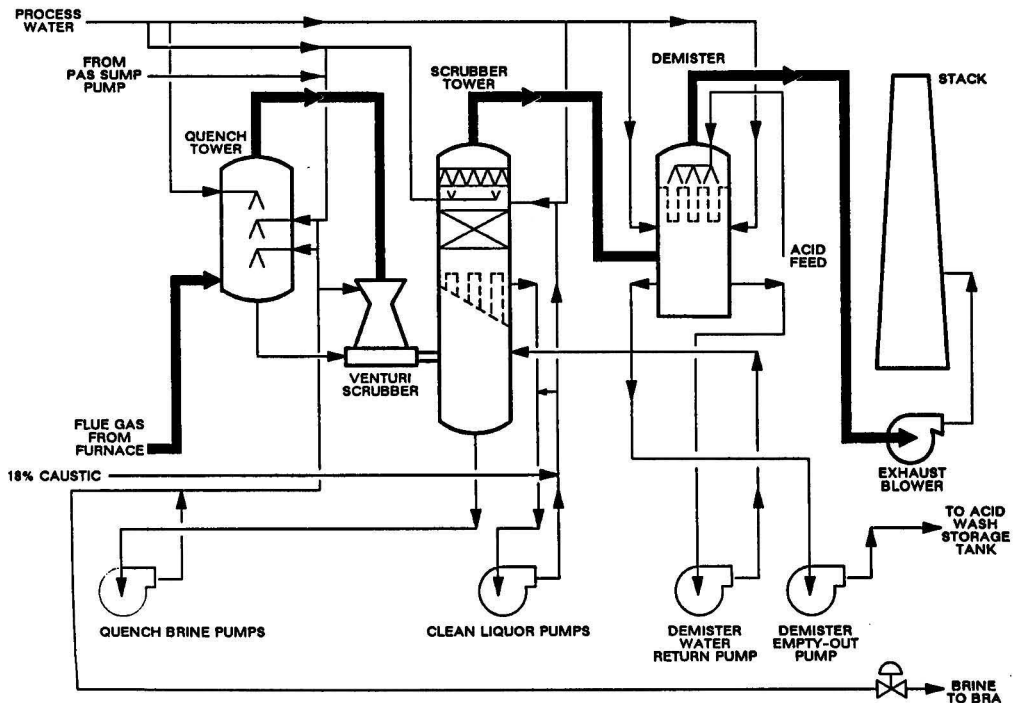


Figure 6. Typical pollution abatement system.

TABLE 10. ALLOWABLE WORK AREA AGENT CONCENTRATIONS*

GB	.0001 mg/m ³
VX	.00001 mg/m ³
H	.003 mg/m ³

* Time Weighted Average

In the noncontaminated areas of the facility, each worker carries a protective gas mask that can be donned in the event of an agent alarm or process upset. The differential pressures within the facility have been designed to prevent migration of agent into noncontaminated work areas. These differential room pressures are constantly monitored by the CON.

MONITORS

All work areas, the control room, and the furnace and filter exhausts are continually monitored for agent during operations. The primary agent monitor used is the Automated Continuous Agent Monitoring System (ACAMS) developed for demilitarization operations. The ACAMS is an online automated gas chromatograph capable of specific identification of the chemical agents at concentrations less than the allowable work area limits established by the DA Surgeon General, and concurred in by the Department of Health and Human Services. These values are shown in Table 10.

Data from the air monitors provide a permanent record of plant emissions, as well as a record of the potential for exposure of personnel to agents. Additionally, routine medical examination of plant personnel is used to monitor indications of agent exposure.

CONCLUSION

Since the termination of ocean disposal in 1970, the Army has safely disposed of over 15,000,000 pounds of CW agents. The results of these operations plus the procedures and equipment developed by the Army at CAMDS and JACADS demonstrate that disposal of even the most hazardous waste can be accomplished safely with minimal risk to the workforce and negligible impact on the environment. The JACADS demilitarization facility is presently scheduled to begin toxic operations in late 1989.

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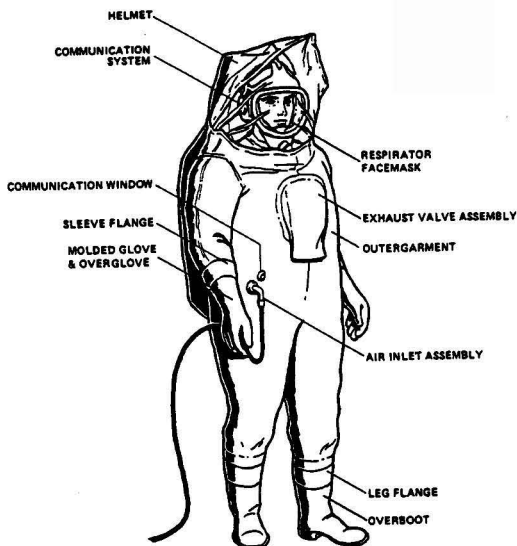


Figure 7. Demilitarization protective ensemble (DPE).

other. This provides redundancy as well as improving response time between the advisors and the network manager. Programs to manipulate process variables are written in an English language type of programming language called GRAFIX.

The process data and reporting computer (PDAR) collects a snapshot of all plant process data every 2.5 seconds and stores these snapshots for 10 minutes. It can retrieve the data as needed in a Sequence of Events Report. The PDAR also produces periodic management reports for ACAMS, process excursions, plant emissions excursions (SOX, NOX), and equipment malfunctions. Data in reports can be accessed via a telephone link with any computer running DECNET. Control room operators are also provided with closed circuit television to facilitate monitoring of the process flow. Additionally, observation corridors surround the process area, allowing for direct viewing of these areas.

LIFE SUPPORT SYSTEM

Although the demilitarization equipment has been designed to preclude the requirement for operators in the process area, personnel entry is required to affect maintenance or repairs. Maintenance personnel entering agent process areas are protected from exposure to chemical agents by the Demilitarization Protective Ensemble (DPE) shown in Figure 7. This air-supplied protective suit was developed specifically for chemical demilitarization operations. In addition to the air supply umbilical, the NIOSH approved suit is provided with a backup self-contained respirator for emergency egress in the event of a loss of supply air.

In use, the worker is heat-sealed into the disposable chlorinated polyethylene suit and a helium leak test is performed to insure a complete seal. Personnel entry into toxic areas requires at least two individuals and visual contact must be maintained between the workers in any one area. DPE workers can communicate with the control room and other personnel via a radio communications system.

Destroying Hazardous Waste On Site— Avoiding Incineration

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Conventional rotary kiln incineration technology is contrasted with the new Thermolytica steam gasification technology from the outlook of the small generator. Technical performance, on-site compatibility, environmental safety, and economics, are discussed from the viewpoint of the small generator together.

INTRODUCTION

A common practice today is for the generator to contract with a waste hauler to pick up solidified drummed waste and deposit it with a landfill operator. Federally mandated liquid restrictions at landfills are forcing the generator to increasingly use adsorbents in the drums. Even this practice is becoming more restrictive and eventually, will not be allowed. Increasingly burdensome restrictions on landfills are just beginning to convince generators to examine other alternatives, particularly on-site waste destruction. This paper describes the alternative of the Thermolytica™ detoxifier, or TLD and contrasts it with conventional incinerators.

The key features in the TLD technology are the use of the atmospheric pressure, steam-hydrocarbon gasification chemistry using non-combustible mixtures in a unique chemical reactor design that provides the right turbulence, temperature, and residence time to get over 99.99% destruction; a process unit operation and piping system that provides the optimal technical requirements for this chemistry, safety features, and energy recovery; and a waste feed evaporator that receives the waste input and provides the right gas chemistry conditions and vapor streams for steam-hydrocarbon gasification destruction. For more details, the reader is referred to previous publications [1-5].

In this paper, the new TLD non-combustion technology is contrasted with that in conventional incineration. The key points are summarized below:

Present Incinerator Technology	Thermolytica Detoxifier
● Explosive Mixtures	● Non-explosive Mixtures
● Oxygen-Hydrocarbon Combustion	● Steam-Hydrocarbon Gasification

- Exothermic Chemistry
- Positive Feed Pressure
- Waste Handling
- No Leak Detection
- Physically Large Units
- Usually Off-site
- Risk Levels Around 5×10^{-5}
- Endothermic Chemistry
- Negative Feed Pressure
- No Waste Handling
- On-line Leak Detection
- Physically Small Units
- Compact, On-site Unit
- Risk Levels Around 1×10^{-7}

BACKGROUND

The TLD consists of a steam gasification convertor, hereafter called SGC, and one or more waste feed evaporators, hereafter called WFE, as is shown in Fig. 1. The SGC is four feet by six feet by seven and one-half feet and uses standard industrial electric power, and the WFE is four feet by five feet by six and one-half feet. The WFE receives waste either by pumping from large tanks or receiving drums of waste directly. The WFE then produces a hot vaporized gas stream of the waste that is blended with inert carrier gases and then fed into the SGC.

The unit operates on a new chemical process that does not use air in any open flame combustion (as incinerators do), but carries out hazardous waste destruction by very high temperature (approaching 1,650°C or 3,000°F) steam gasification chemistry. For typical organic wastes, vent gases are mostly carbon dioxide and water. Destruction levels exceed 99.99% for even the most refractory organics. The TLD has a capacity of one to five drums per

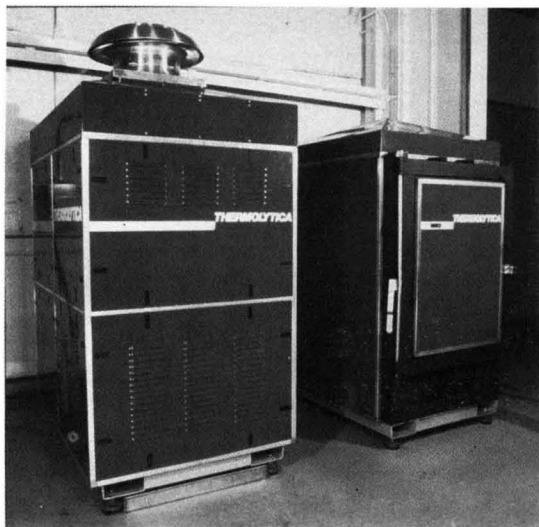


Figure 1. The steam gasification converter and waste feed evaporator uses standard industrial electric power and the WFE is 4' x 5' x 6.5'. The WFE receives waste either by pumping from large tanks or receiving drums of waste directly. The WFE then produces a hot vaporized gas stream of the waste which is blended with inert carrier gases and then fed into the SGC.

day, depending on the waste. The unit is small enough to fit on any industrial and business site. This simplifies permitting, eliminates waste transportation, and greatly reduces risk and liability. The TLD can take drummed solvent and organic-containing waste directly without having to remove the waste from the drum. The drum is heated in a special enclosure (called "waste feed evaporator," WFE) to vaporize the organics and feed the system. Larger volume waste tanks can also be pump-fed to the system.

PROBLEMS WITH CONVENTIONAL INCINERATION

Conventional incinerators are usually of the rotary kiln type, where natural gas or fuel-oil-fired flame combustion is generated at one end of the rotating, brick-lined cylinder. Liquid waste is normally introduced at the location of the flame and is subjected to a variety of effects: mixing, convection, vaporization, radiation, aerosol and solid particulate formation, PIC formation, etc. [6-8]. The residence time for which the waste is actually in the flame region may be much less than one second, in fact, the residence time may be as short as 10 milliseconds. The majority of valuable residence time for the waste is consumed in getting the liquid waste heated and vaporized to the high-temperature vapor state, at which point the actual destruction chemistry can just begin. The destruction processes cannot begin until the waste components are in the vapor state and up to temperature.

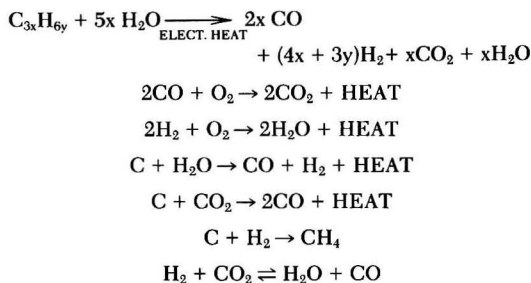
Once the waste has reached the high-temperature vapor state, there is an induction time before the destruction combustion chemistry actually takes place, further consuming valuable residence time. Then, as part of this destruction combustion chemistry, products of incomplete combustion, or PICs, are formed, sometimes on the particulate material that is formed in the original combustion chemistry process. These PICs are formed *after* the combustion chemistry has occurred and therefore takes place, in sequence, later in time after even more valuable residence time is consumed. Finally, these PICs need to

undergo combustion destruction, but usually there is very little remaining high-temperature residence time. PIC destruction kinetics are slow, especially when halogenated aromatic hydrocarbons are involved. This scenario of the incinerator destruction combustion process helps one understand why it is so difficult to get PIC destruction to occur satisfactorily before the combustion gases carry the unconverted waste out of the hot flame region into the much colder (*i.e.*, 1,000°F) stack gas region downstream. In these colder and cooling spent combustion gases any further waste destruction chemistry is quickly quenched and the unfavorable thermodynamic equilibria are frozen by slowed kinetics.

A NEW STEAM GASIFICATION APPROACH

Chemistry

The TLD detoxification chemistry does not involve combustion. The hydrocarbons of the waste are first evaporated in a separate waste feed evaporator process unit, called the WFE. The waste does not leave the WFE until it is completely vaporized. Within the WFE the hydrocarbon vapors are first exposed to superheated steam. In the WFE, steam gasification chemistry starts to occur at temperatures from 700 to 1,100°F. The steam gasification of the hydrocarbon forms CO, CO₂, H₂O, H₂, and a small amount of CH₄. The main chemical reactions are as follows:



Although the steam gasification chemistry has just started in the WFE, it continues to very-near completion as the gas temperature increases along its path through the system into the main reactor. The residence time of one second in the nearly isothermal main reactor is entirely at elevated temperature; not the only brief exposure to high temperatures as in the incinerator flame region.

This TLD chemistry approach avoids using up valuable residence time in getting the waste to vaporize, going through induction delay, through slow combustion kinetics, PIC formation delays, and finally PIC destruction before this gas is cooled following the flame region, as in incinerators. Also, the TLD main chemical reactor is heated electrically, so that the gases are free of the combustion-produced particulates so typical of incinerators that adsorb the PICs and carry them out of the incinerator.

As a result, the TLD achieves high destruction levels over 99.99% and has such low risk levels that locations in an urban and residential setting are acceptable by the public and environmental groups. The TLD has three levels of safety features in the control system design that insure a very high level of safety (United States Patents applied for) that is not found in the industry today. The TLD operates at high temperatures well above 1,800°F up to 3,000°F and does not use air, or flame, or combustion of the hydrocarbon liquid hazardous waste. As a result, it avoids the troublesome NO_x emissions, and the oxygen-radical catalyzed formation of products of incomplete combustion (PIC's) [6].

Waste Feed Evaporator

- Waste can be drum fed or pumped from tanks
- Vaporization heat supplied by hot reactor gases
- Closed-loop process between Evaporator & Converter

Waste Containment

- Dry, solid residue remains in disposable drum
- Minimal handling of wastes
- CO₂ purged to ensure safety
- Double containment to prevent leaks or spills

CO Converter

- Detoxified gases oxidized to CO₂ and H₂O
- Vent gases exceed all air emission standards

Steam Gasification Reactor

- Complete destruction of organic vapors
- Operates under negative pressure
- Electrically heated; no air, fuel or flame

Adsorber Beds

- Activated carbon removes trace organics and metals
- Selexsorb removes any halogens

Process Controls

- Fully automated operation
- Continuous monitoring of all process variables
- Ensures efficient, reliable operation

Heat Exchanger

- Efficient heat recovery for economical operation
- Excess heat is recirculated to the Evaporator

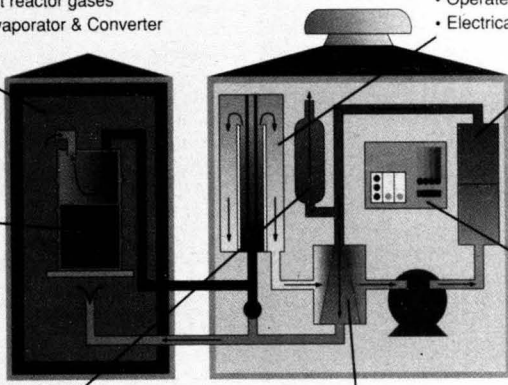


Figure 2. Shows a schematic of the important operational features. Shown at the lower left, the stream "Vapor" is pulled into the SGC under a slight vacuum. The vaporization of the hazardous waste occurs in an Autoclave or Viscous Feed Evaporator, shown in Figure 2. After the SGC removes the wastes, hot gas is generated and fed out to the vaporizers to pick up more hazardous wastes. A small vent stream of clean gas is released to maintain pressure balance. The system is fully automatic, so that the waste handler simply places the waste in the autoclave, selects the waste type, and presses the "on" button.

Process

Figure 2 shows a schematic of the important operational features. Shown at the lower left, the stream "Vapor" is pulled into the SGC under a slight vacuum. The vaporization of the hazardous waste occurs in an Autoclave or Waste Feed Evaporator, shown in Figure 2. After the SGC removes the wastes, hot gas is generated and fed out to the vaporizers to pick up more hazardous wastes. A small vent stream of clean gas is released to maintain pressure balance. The system is fully automatic, so that the waste handler simply places the waste in the autoclave, selects the waste type, and presses the "on" button.

Safety Control Systems

The TLD has a unique control system that achieves the low risk required for an on-site waste destruction application. The operation is highly automated through the application of the latest computer technology—distributed process controllers, fail-safe circuitry logic, redundancy, on-line process modeling, error checking, etc.

Operator errors are minimized in the TLD system by only allowing certain actions to be taken in a menu-driven system. The TLD can be monitored from an off-site support center where alarm conditions can be identified and tracked and where critical operating data can be archived.

In normal operation, the TLD automatically monitors key operating parameters, such as temperature of the core, bed, vessel walls, gas in, gas out, process chemistry, flow rates of TLD feed, adsorption tower capacity, vent composition, pH levels, and hazardous materials in feed tanks, to ensure that these parameters fall within narrow predetermined ranges. If they exceed the alarm limits,

the process controller notifies the operator and the support center is contacted. If the problem is not corrected within 5 minutes, then the TLD automatically shuts down.

There are special safety features to the TLD's processing from multiple tank or drum feeds that are appropriate to on-site operations. To avoid operator error or deliberate abuse, such as placing unexpected hazardous materials into a tank for processing under conditions not "previously approved" for such materials, these tanks have their composition "chemistry checked." The TLD processing conditions must be preapproved before operation as part of the DOHS/EPA permit.

A special waste detoxification approval control system, hereafter called wasteDAC, has been created to provide and manage this safety control. The wasteDAC system provides a dedicated memory or fingerprint of the chemical and operating characteristics of the waste so that it checks the waste in each drum and checks against errors of waste identification in the customer's plant. The wasteDAC system also helps prevent incompatible wastes from being mixed.

ECONOMICS

The basis for comparing economic issues between the TLD and incinerators are as follows. Operating the TLD at high temperature (approaching 1,650°C or 3,000°F) with steam gasification chemistry, the vent gases involve carbon dioxide and water for most organic wastes; thus, no downstream environmental controls are necessary. Destruction levels exceed 99.99% for even the most refractory organics. For these conditions the TLD has a capacity of 1 to 5 drums per day, depending on the waste. The unit is small enough to fit on any industrial and busi-

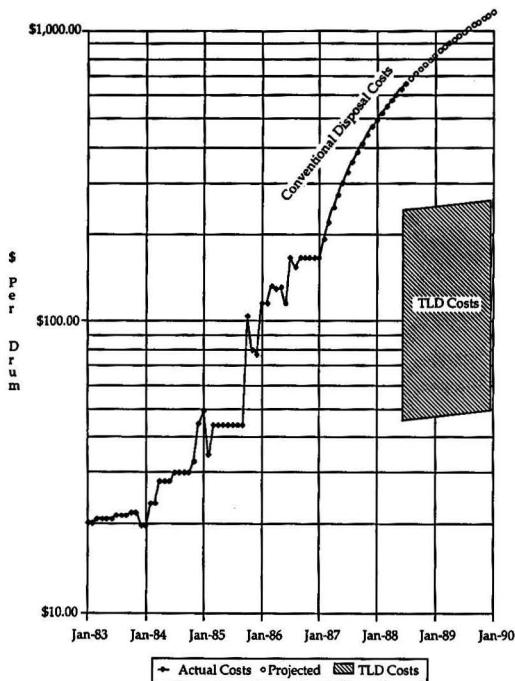


Figure 3. Disposal costs for generators of liquid hazardous wastes.

ness site; this minimizes the cost of installation and permitting, eliminates waste transportation, and greatly reduces risk and liability. The TLD can take drummed solvent and organic containing waste directly without having to remove the waste from the drum. The drum is heated in a special enclosure (called "autoclave") to vaporize the organics into the TLD. Larger volume waste tanks can also be pump-fed to the system.

Rapidly escalating costs of available alternatives to hazardous waste disposal are being felt by the small generator. Typical cost increases experienced by the generators of liquid hazardous wastes are shown in Figure 3. The increases are nearly exponential.

There are a variety of factors that have caused this increase. They are as follows:

1. Landfill regulation and phase-out
2. Liability insurance
3. Legal fees
4. Permitting
5. Solidification
6. Manifesting
7. Repackaging into smaller drums
8. Analytical requirements

The rising cost of landfill disposal is the result of a large increase in landfill ground water monitoring, costs of well boring, landfill lining installation and replacement, increased legal, insurance, and permitting costs, increased analytical and administrative costs, and finally, more care and concern for detail everywhere.

The cost of liability insurance and environmental impairment insurance, if available at all, has sky-rocketed. For example, for a \$2 million dollar insurance coverage, an annual premium in excess of \$250,000 is typical. This has resulted from increased toxic tort litigation and increased settlement costs, which has forced insurance companies to increase premiums to cover unpredictable settlements in the future. The legal defense costs spiral upward in direct proportion to the damage settlements.

The regulatory burden on the small generator has become expensive. For the small generator in politically active urban communities, there are dozens of regulatory agencies, each claiming jurisdiction over the small generator operations. In many cases, there is direct conflict between the agencies—local, county, state, and federal. The whole arena further pulls into the fray the environmental action groups. Each seems to encourage the other to create new and deeper layers of bureaucracy and regulatory hurdles that must be passed.

To comply with the RCRA mandated liquids ban in landfills, the small generator uses increased amounts of adsorbents and other materials to solidify the waste and to immobilize any free liquids. The difficulty is that the addition of large adsorbent quantities to the waste further increases the volume for disposal. Technically, the liquids are still present in the waste, and frequently still can interact with the environment harmfully. Manifesting the waste for the hauler requires increasing care and records detail. Also, landfill disposal is no longer acceptable for a large fraction of the small generator's waste, and other disposal methods, such as incineration, must be used. This requires different sizes and type of containers. Repackaging into small 15 gallon drums for incineration is becoming common. All of this handling is expensive and risky, frequently increasing the cost to dispose of the original drum of waste to over \$400 per drum. Each of these different disposal methods require a variety of different analytical services and documentation before the waste will be accepted by the hauler.

Risk of Small Generator Ongoing Liability

The small generator's concern over ongoing liability stems principally from: 1. on-site spills from storage, handling, and transport of waste, 2. improper manifesting, mislabeling or lost labels, 3. combining incompatible wastes, 4. drum corrosion and leakage, 5. constantly changing regulations, and 6. "toxic torts."

The small generator's liability from on-site spills from storage, handling, and transport of waste result from the fear of soil and groundwater contamination. The cost of decontamination of the soil or groundwater can be extremely large, particularly if groundwater aquifers are migrating off the generator's property.

The manifesting process is also an area of risk for the small generator. It is through this regulatory operation that the written record of the generator and the waste is first made and becomes available for abuse. There is also the whole problem of improper manifesting, mislabeling, or labels that become detached or removed from the waste. Waste without any labels must be reanalyzed again at costs from \$200 to \$600 per drum. The whole cost of manifesting is significant for the small generator, from even the paperwork standpoint. The cost of errors or manifest problems more than doubles the cost in actual practice.

Combining incompatible wastes together can produce flammable or explosive mixtures, toxic gases, corrosive systems, and all combinations of these undesirable effects. Also, the use of drums to contain and hold hazardous waste is a dated and outmoded practice that grew out of garbage can and dump mentality. These potential risks must be factored into a generator's evaluation of storage and handling options. To further complicate the matter the small generator is being subjected to a barrage of new and changing regulations through the news media, technical publications, meetings, etc.

The regulations change in response to public awareness, public whim, and the latest hazardous waste crisis headlining the current media. Regulations are also con-

sidered an opportunity area for politicians to get the needed notoriety and public attention. The situation with landfills is similarly affected. Even highway transportation of hazardous waste, as shown recently, can be blocked by local government and political action.

Finally, different agencies frequently have conflicting regulatory requirements. A good illustration is the difference between a federal RCRA and a California State waste. EPA has defined a RCRA waste to be either a listed waste, consisting of a specific list of compounds, or a waste mixture characteristic of a particular industry type. A California State waste is defined by a specific list of chemical compounds, established by their quantified health and environmental effects. There are many cases where a waste may be either a RCRA or a state waste or both, but the correspondence is not simple. Further complicating this waste identification problem is the matter that both classifications are constantly changing. One day the small generator may be destroying a state waste and meeting regulatory requirements, and the next day the waste may be considered a RCRA waste with entirely different standards and permits required.

THE GROWING NUMBER OF SMALL GENERATORS

Under the 1984 RCRA HSWA Amendments, EPA defines a "small generator" as anyone who generates over 100 kg (220 lbs) per month but less than 1,000 kg (2,200 lbs) per month. This act alone multiplies by ten times the number of businesses that are under RCRA EPA regulation. If a widespread waste pickup service were to be instituted to each of these small generators, the number of truck-hauling vehicle-miles-traveled would be multiplied by ten times, as would be the number of accidents and spills. Obviously, hauling to a centralized treatment facility or even a landfill, if there is capacity remaining, is not the solution.

The large number of small generators across the U.S. are now constrained to the 90-day RCRA limitations for the storage of hazardous waste. This is intended for drums of waste, but is difficult to insure for large tanks of waste with new material constantly being added to the tanks. There is an ever-increasing liability associated with allowing the hazardous waste inventory to build up on the small generator's site. Many small generators have been switching waste storage from drums to tanks in order to reduce their liability.

TERMINATING LIABILITY WITH ON-SITE TREATMENT

The one sure way of terminating the small generator's liability is to never prepare a "manifest" needed for the waste hauler transporting the waste to the landfill or central treatment site. What is needed is no manifest to create the public record that initiates this spiraling liability problem from the start. The troublesome manifest is completely avoided when the waste is destroyed on-site by on-site treatment. Here is where the pessimism ends and the refreshing new direction can begin. Many large corporations have "seen the light" and made the decision to terminate their hazardous waste liability on-site by destruction of hazardous waste by on-site treatment.

There are two kinds of on-site treatment approaches 1. fixed site, permanent installation for on-site treatment and 2. regular visits of a transportable treatment unit to the site. The first topic has been discussed above and in earlier publications [1-5]. The second approach is the transportable treatment unit, hereafter called the TTU, which is the method of choice for the small generator with volumes under about 2 drums per day.

Advantages of a Transportable Treatment Unit

A Panel Van as a TTU is ideal since it is small, economical, and compatible on the highway. This results in a very greatly reduced exposure to accidents. A TTU van can be set up for waste treatment and moved off-site in less than one day. Simple utility connections allow the TTU van to move in and out quickly. The best situation is to have the TTU van be totally self-sufficient, with as many of these utility services supplied on the van. For small volume treatment tasks, the TTU van can have its own electrical power generator, cellular telephone, instrument air compressor, and small supply of water.

Direct communication between the TTU van and a Support Center allows a professional staff of trained and experienced operating people to monitor the performance of the TTU while it is operating on-site. This approach reduces the requirement of having a large and expensive staff. A support center should be equipped with a sophisticated array of computer diagnostic and preventative maintenance analysis tools that will allow a detailed examination of the TTU's performance.

Waste variety and capacity should cover the range of interest for the small generator. There is a full range of wastes from organic solvents to laboratory solid waste that can be processed. Economic payout in two years or less should be possible with the range of wastes of interest to the small generator. Typically, the costs must be from one-half to one-tenth of the costs of waste pickup and disposal at landfill sites.

Risk Minimization

The public demands that any regulatory agency evaluation of a new hazardous waste treatment technology include a thorough consideration of the risks, voluntary and involuntary, to which the public is to be exposed as well as the benefits to the public. There are many similarities between nuclear power generation technology with its uranium ore mining, power generation to spent fuel handling, and hazardous waste treatment technology in the eyes of the public as well as the regulatory community. The public fears about nuclear power are shared with concerns about risks to their health and the environment from hazardous wastes. Hazardous waste and nuclear materials both produce insidious, silent and invisible effects over which the public feels they have no control. Their concern is over both acute effects from spills and accidents and over chronic effects from long-term exposures from contaminated air and groundwater and from the food chain.

The nuclear industry strive to define this risk/benefit balance through a concept called "ALARA." This acronym stands for "As Low As Reasonably Achievable." This concept is implemented by examining the cost tradeoffs between the incremental costs from applying new or additional technology and the savings of human lives due to reduction in death from cancer or other accidents.

The implementation of ALARA is straightforward and can be completely apolitical. First, the technologist proposes some new piece of technology to reduce the risk of hazardous waste-induced cancer deaths. The cost of this new technology is compared against dollar savings over the lives saved from the incremental risk reduction resulting from the application of this new technology.

A numerical example serves to illustrate ALARA. Suppose a new technology costs \$250,000 and reduces the customer's annual per capita risk to the surrounding public from 1×10^{-4} to below 1×10^{-6} . Further, suppose the population exposed originally was 100,000; while after the new technology is installed, only 10,000 people are

exposed. Thus, originally there is calculated 10 cancer deaths, while after the new technology is installed this is greatly reduced to only 0.01 cancer death. This is a thousand-fold reduction in risk. Taking the value of human life (as per the insurance underwriters) at \$200,000, the original 10 cancer deaths per year would justify an expenditure of \$2 million dollars. Spending only \$250,000 to get this risk improvement is obviously an excellent trade-off under the ALARA criterion.

We can also examine under ALARA the advisability of doing more. After the \$250,000 new technology is installed, the 0.01 cancer death result only provides a justification for expending another \$2,000. Perhaps the only improvement that could be made for this small amount might be additional activated carbon beds changed out more often.

The following example illustrates the ALARA concept. Is the goal risk level of 1×10^{-6} low enough? To answer this, the everyday risks to which the populace subjects itself either voluntarily or involuntarily must be considered to place the issue in context. Table 1 provides some typical risks.

Some discussion on Table 1 is in order in comparing hazardous waste treatment technologies. A particularly interesting comparison was made by the EPA [14] in their comparative study of the dioxin emissions from different hazardous waste combustion technologies. The dioxin emissions (PCDD and PCDF) are about 1,000 times worse for municipal waste incinerators, boilers co-firing waste, and copper smelting furnaces than for the rotary kiln incinerator. It would be impossible to site any of these three technologies in the present regulatory climate where air toxics emissions are considered. In fact, in California and several other states, where new air toxics risk analyses are required by the permitting air districts, even the latest technology rotary kiln incinerators have not been sited after rather heroic efforts on the parts of large Fortune 500 companies.

To achieve the particularly low levels of risk that are acceptable to the public (i.e., 1×10^{-6}), the first major change away from incinerator problems is to guarantee that no flammable or explosive hydrocarbon mixtures with air are ever present. Of course, this completely precludes using any kind of combustion of fuel-air mixtures so essential to the operation of an incinerator, boiler, furnace, etc. The TLD detoxifier uses no flame, no air, no combustion, no explosive mixtures. A risk comparison with a rotary kiln incinerator is made in Table 1.

The next area involves hazardous waste feed technology. Incinerators typically pump waste into the furnace section or feed small and combustible fiber drums. These operations are risky and prone to occupational worker exposures. The TLD takes the hazardous waste directly in sealed drums in a proprietary "evaporator"—there is no waste handling or open drums. This waste feed evaporator will also take continuously fed liquid waste pulled into it under negative pressure from an external tank. All waste streams within the TLD are under a negative pressure, thus preventing pressure-driven leaks to the outside. In addition, oxygen is used as a tracer for leaks. If any leaks do develop, the on-line and continuous oxygen detectors instantly detect this, even at very low levels, and take safety action.

On-line monitoring of the carcinogenic products of incomplete combustion (PICs) released from commercial incinerators has been demanded by the public, but both incinerator manufacturers and EPA insist the technology is not yet available. As an interim measure in incinerators, elevated carbon monoxide levels are used to suggest PICs, but they are not measured. Computer and process control interfacing is together with the necessary software for the TLD to utilize a photoionization detector (PID) as

TABLE 1. COMPARISON OF EVERYDAY RISKS TO THE PUBLIC
(Public Mortality in deaths/year per capita)

		Ref.
Coal-based	16.74×10^{-3}	9
Power Generation		
Nuclear-based	0.18×10^{-3}	9
Power Generation		
Coal Mining—	8.0×10^{-3}	10
Black Lung Disease		
Coal Mining—	1.3×10^{-3}	10
Accidents		
Motor Vehicle	2.2×10^{-4}	10
Accidents		
Truck Driving	1.0×10^{-4}	10
Accidents		
Falls	7.7×10^{-5}	10
Home Accidents	1.2×10^{-5}	10
Home Radon	1.0×10^{-3}	11
Exposure (5 pCi/l)		
7 Tablespoons	3.5×10^{-5}	12
Peanut Butter/year		
3 Cigarettes	7.0×10^{-5}	12
per year		
1 Saccharin-based	8.0×10^{-4}	12
Diet Soda/day		
1 Day Visit to	1.0×10^{-6}	12
Denver per year		
1 Chest X-ray	3.5×10^{-4}	11
per year		
Hazardous Waste	1.0×10^{-4}	—
Landfill Failure		
Conventional Rotary	5.0×10^{-5}	—
Incinerator		
Breathing Diesel	1.0×10^{-5}	—
Exhaust		
Benzene from	1.0×10^{-5}	—
Gasoline Evaporation		
TLD detoxifier-	1.3×10^{-7}	13
worst case		

The first two items from Ripon [9], assume the public is equally exposed to a single 1000 MWe power plant. The second six items from Hutt [10] use coal mining data occupational worker risk, rather than public, for comparison purposes. Remaining items from estimates made by the author and the air quality district.

a PIC monitor for the TLD converter feed stream and vent stream. The application of the PID is very different from the conventional chromatograph detector and requires significantly new instrumentation.

The PID, as an integral part of the TLD operation brings new technology forward for continuous monitoring of PICs. The PID can detect organic compounds that are of particular concern to industrial toxicologists. For example, the PID in the TLD is tuned to 10.2 electron volts of ultraviolet energy to selectively discriminate between harmless organics, such as light aliphatics, carbon oxides, etc., and the more toxic aromatic organics, about which the public is particularly concerned. Not only does the PID monitor the PICs that might be in the vent stream at extremely low parts per billion levels, but it will also allow the control system to compute the Destruction and Removal Efficiency (DRE). This allows a near real-time and on-line assessment of the proper operation of the TLD for the EPA-required 99.99% DRE.

THE NEW GENERATION OF PROCESS CONTROL

There are public-demanded assurances that the equipment will be operated correctly and safely and without any releases to the environment. These strong demands derive from the rather poor public image of incinerators based on their actual performance. Incinerator problems,

however, have not been just equipment failures but operator error as well. The kinds of operator error are similar to those experienced in classic chemical plants, refineries, nuclear power, etc.

The classic philosophy for process control used in the last generation of chemical plants and nuclear power plants has involved the "control room operator" at every critical step. Even early attempts at closed-loop computer process control in the 1960's using very large mainframes, such as CDC-6600 and IBM 360 Model 80's, always had the operator "in the loop." The computer hardware was not sufficiently developed or sufficiently reliable to do anything else. The computer simply assisted the operator with fast computation of heat and mass balances, process modeling, economics, operational optimization, etc. In the 1970's when micro-electronics began to make computerized process control a fresh field, little or no new plants were being built to incorporate this new thinking. Only now the chemical and nuclear industry admits that to secure public acceptance, the new generation process control thinking must be a fundamental and integral part of the design from the very beginning [15]. In the hazardous waste field, new facilities are being constructed. There is an opportunity to apply this fresh process control thinking. In fact, anything less would not be accepted by the public.

Today the technical quality of the available labor force is inconsistent. Operator error, in even the most routine functions, sometimes happens. Many companies must essentially retain their new hires from high school level. This is expensive and seriously slows up the development and training of a competent plant operating labor force.

The new approach to computer process control no longer places the plant control operator in the critical loop. In fact, the hardware performance is more reliable than is the human process control workforce. The overall reliability in hazardous waste treatment process control is paramount, particularly in the eyes of the public, having been badly biased by recent chemical (Bhopal) and nuclear plant (Three-Mile Island and Chernobyl) failures.

The TLD makes complete use of this new, highly reliable computer process control. The application of triply-redundant process hardware essentially removes computer failure as a concern. Distributed microprocessor control modules, capable of safely shutting down a given process unit in the TLD, are used throughout the system.

In fact, "ruggedized and hardened" electronic systems are used that have been designed for high reliability and fault-tolerant operation. The operator never touches a valve or a switch in the TLD. The operator only asks the process control system what must be done. The process controllers accept these instructions and take all required actions. Finally, there are specially trained professionals at the support center, looking over the shoulder of the operator and watching for any questionable acts 24 hours per day.

THE ON-LINE SUPPORT CENTER

The above described philosophy operates the support center. The operator is given the reassurance that someone is looking on and guiding every critical decision step. The support center, in fact, can talk to the operator at each site, can closely and more intimately examine critically what the operator is doing, can apply sophisticated computer modeling to analyze the TLD operation, and if absolutely needed, operate the TLD remotely.

The support center will track each operating component within the TLD to maintain a current projected lifetime limit to trigger preventative maintenance replacement. Cyclic failure models for each component are maintained at the support center. The use of these models prevents almost completely any in-service component failures. These models also are integrated into preventative maintenance service scheduling to minimize travel costs, time delays, and manpower as well as to guaranty in-stock service parts, and optimize operational strategy. The support center also has a battery of more powerful computer process models to assist quickly the processing of difficult waste streams and provide an expert systems data base that can be brought into play instantly. In this way, the support center offers real expertise to each TLD user.

Performance

The results presented in Table 2 have been obtained from operating the full-size TLD at a range of temperatures and feed concentrations. Other specific TLD configurations, gas feed and liquid feed to synthetic feed systems have been tested at commercial scale. All detoxification performance data (shown in the column la-

TABLE 2. TLD PERFORMANCE DATA

Component (POHC)	TLD Core °F	SYNFeed %	TLD Exit ppb org.	TLD Exit ppm Co	DRE Level, %
Acetone	2100	9	37	4500	99.9963
Acetone	2100	10	14	5000	99.9976
Acetone	2100	26	—	11400	99.9980
Acetone	2100	40	—	11700	99.9951
Acetone	2100	55	—	12078	99.9949
Carbon Tetrachloride	2100	33	21	—	99.9952*
Chloroform	2100	33	7.8	—	99.9992*
Isopropanol	2100	16.4	3.7	5000	>99.9990
Isopropanol	2100	19	—	11700	>99.9978
Isopropanol	2100	19	6	4500	>99.9994
Isopropanol	2100	19	—	12078	99.9977
Methanol	2100	10	—	11700	99.9972
Methanol	2100	35	—	11500	>99.9996
Methanol	2100	100	—	11100	>99.9996
Methylene Chloride	2100	33	16	—	99.9978*
Methyl Isobutyl Ketone	1800	25	<10	—	>99.99*
Xylene	2100	0.8	—	4500	>99.9815

* These results were obtained from tests conducted on TLD #1001, a prototype unit that was operated at Hercules, CA.

beled "DRE, pohc," (with DRE standing for Destruction and Removal Efficiency of principal organic hazardous constituents, pohcs) were based on the reduction between the quantity in the feed drum or tank and the quantity leaving the TLD. The process configuration tested was a series of runs utilizing a vaporizer feeding the TLD converter. TLD configurations have processed a variety of samples of liquid hazardous mixtures containing a combination of heavy metals as solid suspension, an acidic aqueous phase, mixtures of solvents, paints, photographic emulsions, photoresist, detergents, etc.

The performance evaluation program (PEP) for the TLD is equivalent to the "trial burn" plan required for incinerators. The purpose of the PEP, is to utilize a synthetic feed mixture of regulatory agency recommended surrogates at the 0.5% concentration level added to two different solvent matrices as follows:

Iso-propyl Alcohol: This is a pure, commercial, industrial grade of iso-propyl that is run in drum quantity.

Standard Solvent: This synfeed stream is a mixture of xylene (1%), acetone (70%), isopropyl alcohol (19%), methanol (9%), and butanol (1%). This test simulates a waste stream produced from washing and cleaning operations in the wafer fabrication and other production areas.

Halocarbon in Methanol: This is a drum of commercial, industrial methanol with 0.5% level each of tetrachloroethylene and dichlorobenzene added.

Halocarbon in Toluene: This is a drum of commercial, industrial toluene with 0.5% level of tetrachloroethylene and dichlorobenzene added.

Halocarbon Solvent: This synfeed stream is a mixture of acetone (68%), isopropyl alcohol (19%), methanol (9%), xylene (1%), butanol (1%), Freon 113 (TF) (1%), and Trichloroethane (TCA) (1%). This test simulates a waste stream produced from various solvent collection operations where typical solvents have become contaminated with TF and TCA.

Pump Oil: This synfeed stream is vacuum pump oil with xylene (1%), toluene (1%), isopropyl alcohol (1%), and TCA (1%). This test simulates pump oil collected from wafer fabrication and other production areas. The oil is from vacuum pumps that pull vapor streams off of production operations.

Solid Waste: This synfeed stream is a collection of plastic gloves, lab-wipes, vacuum pump oil filters, and other paper and plastic products all combined into a 5 gallon pail placed into the 55-gallon drum in the autoclave. This test simulates the typical laboratory waste collected from industrial laboratory areas.

ENVIRONMENTAL EMISSIONS

The following discusses the topical subject area required under the RCRA guidelines for a "trial burn" for incinerators, which had to be modified to cover the PEP for the TLD.

Constituents Sampled/Monitored Oxygen and Carbon Dioxide Emissions

As described above, oxygen is monitored in both feed and vent streams. The oxygen levels are important in predicting conditions that might lead to PIC formation possibly even dioxin. Oxygen is also used to monitor the hermetic integrity of the process piping and vessels that might be compromised by leaks. Carbon dioxide is not monitored, since it is produced and controlled by the water-gas shift reaction being controlled by CO and water vapor concentrations.

Total Hydrocarbons Emissions

The major volatile hydrocarbon emissions are methane at about one-third of the CO emissions, or about 8 to 100 ppm, depending on the character of the organic synfeed. The methane level is so low, that further quantification does not appear justified. Total combustibles were occasionally measured with a Teledyne Max-5 combustion analyzer and found to be below about 100 ppm. This would include any hydrogen gas that was not completely converted to water in the CO converter. Heavier volatile hydrocarbons are monitored as described below.

Carbon Monoxide Emissions

The CO in the process vent was controlled by the amount of air being fed to the catalytic CO converter. With only the air into the converter being fed from the turbine labyrinth seal, typically the CO levels in the process vent were around 9,500 ppm, which, upon dilution with air being drawn through the TLD by the exhaust fan yields a calculated 93 ppm at the stack. These stack values are being confirmed by a portable Teledyne Max-5 Combustion Monitor. This is a removal of 97% of the CO. When additional air was added to the CO converter, the TLD stack CO levels were then reduced from 93 to around 23 ppm. This amounts to a CO removal of 99.3%. During test 46, the DOHS Industrial Hygienist brought a portable and sensitive CO monitor to measure the CO around the outside of the TLD at 5 ppm and inside the TLD enclosure at 15 ppm. These are orders of magnitude below safe OSHA workplace limit values.

For the purposes of comparison, the San Francisco Bay Area AQMD mass emission level under Rule 8 for hydrocarbon processors would be 550 lbs/day and Rule 2 for miscellaneous operations would be 15 lbs/day to trigger a major source review and CO permit requirement. For comparison, the typical pre-1968 automobile (i.e., VW) has highway cruising emissions around 250 lbs/day, whereas a new larger American vehicle meeting EPA standards has a cruise emissions limit of 238 lbs/day and an idle limit of 49.6 lbs/day. Thus, by comparison the typical TLD emissions of from 4 to 20 lbs/day seems to be completely acceptable.

In Table 2 the CO emissions from the TLD process vent inside the TLD enclosure have been presented as mass emission rates in lbs/day, and the CO being released to the environment via the roof fan after dilution with the air being circulated through the inside of the TLD enclosure is shown in the last column labeled "stack." These CO levels are very low and considered very acceptable for a roof-top emission. Typically, the TLD will use a BAAQMD-recommended "up-blast" roof-top fan (i.e., such as manufactured by Chelsea) that achieves very high levels of mixing and dilution for roof-top safety. CO levels inside the duct above the TLD enclosure were measured with the Teledyne Max-5 monitor and found to reach a maximum of about 300 ppm. After mixing within the duct and fan housing, CO concentrations of around 23 to 100 ppm are experienced.

Particulate Matter (PM) Emissions

Particulate matter concentrations are being determined by means of a heated absolute (2 micron) filter, manufactured by Balston. This unit has a pre-dried and quantitatively weighed cylindrical cartridge that is removed after an extensive time period (i.e., 4-8 weeks). From the integrated volumetric flowrates through the filter, the mass

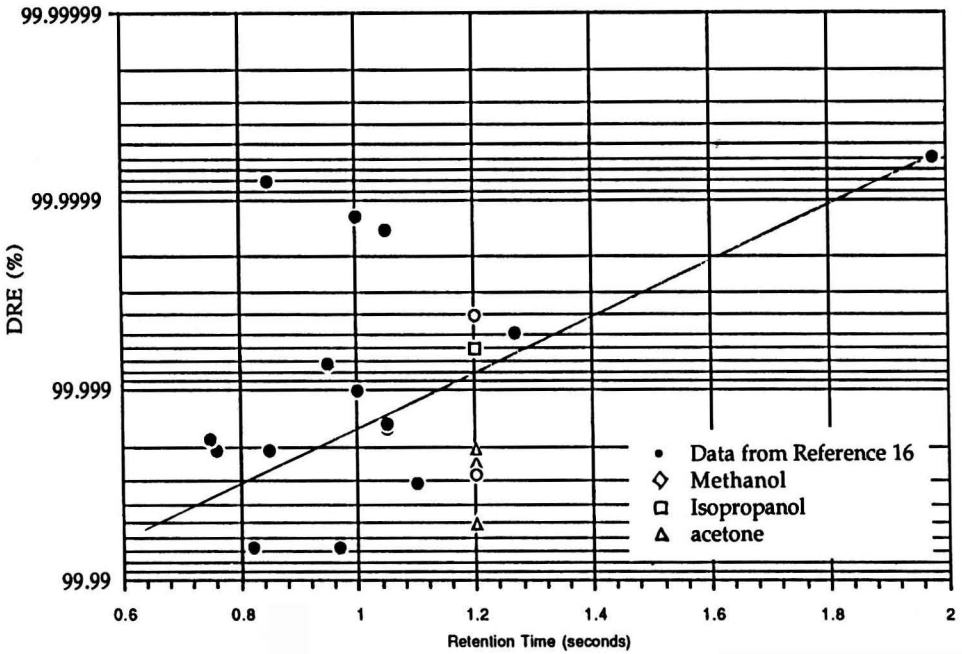


Figure 4. DRE dependence on residence time.

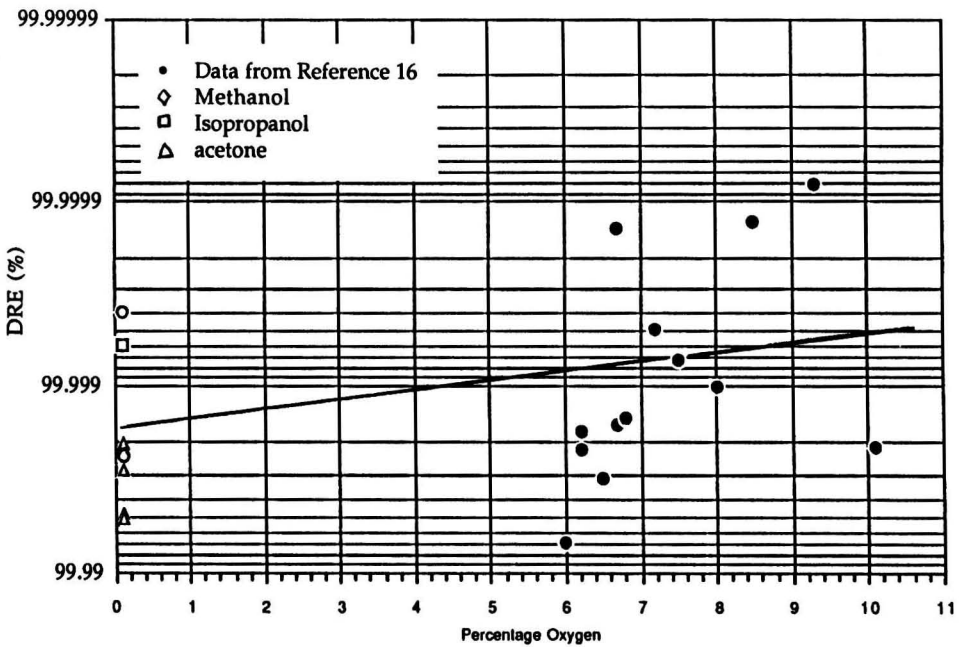


Figure 5. DRE dependence on oxygen concentration.

concentration of particulate emission will be computed and reported.

Halogen Chlorides

These halogen chlorides are being measured continuously, when appropriate, by a total halogen chloride cell in the analytical system. There is also a cell that is specific to fluorides, so that if there are freon or TF solvents containing fluorine-containing organics that can be detected real-time.

Total Organic Halides

When appropriate, organic halides will be measured by Tenax sorbent tube traps provided that there are halogens present in the feed in amounts greater than 2.5%.

Monitoring POHCs and PICs with Sorbent Traps

The emissions of the heavier (non-methane) volatile hydrocarbons are so low that NIOSH methods with optimized high sensitivity, developed for industrial hygiene for human inhalation protection, are being used to monitor TLD operation. The technique involves using the smallest size (i.e., 140 mg) SKC dual-bed charcoal sorbent tube traps, through which is drawn an accurately monitored "slip-stream" quantity of vent gas. From the ratio of flow rates of full vent gas to the small "slip-stream" captured by the sorbent trap, the quantity of heavier volatile hydrocarbon can be calculated. This is compared to the heavier volatile hydrocarbon being fed into the TLD in the synfeed (synthetic waste), to arrive at destruction and removal efficiency, DRE, see Table 2.

A comparison of the above DRE results with PCB DRE's published in a review article [16] has been made in Figures 4 and 5. First, the TLD data fall right in the range of published data for 1.0 second residence time, slightly better DRE than oxygen-starved incinerators. TLD acetone data do not show the concentration dependence that incinerators do.

In addition to the above techniques and results, work has been done with XAD2 Resin-containing sorbent tube traps from PIC determination. Samples of tests have been taken for Dioxin and Furan using the XAD2 resin sorbent sample traps. Results from one test have shown the Dioxin (specifically 2, 3, 7, 8 TCDD) was not detected below the level of detection at 16 picograms. Another test showed that 2, 3, 7, 8 TCDD measurements were below the level of detection at 3.7 picograms. These results were used to compute the TLD risk levels discussed earlier.

Samples of the original commercial solvents have been analyzed using advanced GC/MS techniques. The purpose of these tests were to look for any of the more general dioxin, furan, benzopyrene, anthracene, chlorophenol isomer classes that might show up as possible, incompletely destroyed POHCs that would otherwise be erroneously determined as PICs formed in the TLD. It has been found by others working with incinerators that commercial feed chemicals are frequently contaminated with such complex organics. The GC/MS results show no detectable contaminants that could be confused with PICs.

CONCLUSIONS

New chemical process equipment that destroys hazardous waste in a small, automated package for on-site use has been developed that uses steam gasification technology. This unit is called the TLD. It is aimed at the small

generator, particularly for the electronics, petrochemical, petroleum, and general manufacturing industries. The TLD's operating characteristics are:

- Uses steam gasification chemistry to avoid combustion & oxygen.
- Achieves destruction levels of 99.99% or more, consistent with literature.
- Has better micromixing, temperature, and residence time than incinerators.
- Is small enough to fit into a building's mechanical area.
- Destroys organics in the solid, liquid, or vapor state.
- Processes continuous waste feed streams.
- Processes drummed wastes without removal from drums.
- Operates high-temperature waste feed system for drum loading.
- Utilizes advanced microprocessor controls for automated operation.
- Achieves low risk levels by unique chemistry and environmental controls.

Performance data has been presented with examples of the unit's performance on a wide range of hazardous waste materials. The economics of operation are extremely competitive with costs for landfill disposal, deepwell injection, regional incinerators, and rotary kilns. This TLD solution to on-site hazardous waste management is a new generation that has a promising future.

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Public Impact on Technical Research: The Dissimilar Fates of Two Waste Gasification Projects

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Gasification is an innovative process that offers considerable potential for highly efficient thermal destruction of hazardous wastes. To explore this potential, plans were made to use gasification to destroy polychlorinated biphenyls (PCBs) in a demonstration project at the University of North Dakota Energy Research Center's pilot-plant lignite gasifier. The Center received the necessary state and federal environmental permits in July 1986. However, shortly after the permits were granted, public opposition to the PCB program developed. The state operating permit was revoked and the project was terminated. In contrast to the North Dakota experience, research conducted by the Thermolytica Corporation in California has resulted in commercialization of a gasification detoxifier for hazardous waste destruction. The nature and dissimilar fates of the North Dakota and California projects are reviewed.

INTRODUCTION

Protection of human health and the environment is of paramount concern in the field of hazardous waste management. In the case of hazardous organic compounds, this protection has traditionally been sought through isolation of the hazardous materials. Waste isolation has involved such practices as disposal in landfills, surface impoundments, and injection wells. However, it is now becoming apparent that thermal destruction of hazardous organic compounds is a preferable and achievable alternative to traditional isolation techniques. Thermal destruction involves exposing the hazardous materials to high temperatures in an oxidizing environment [1].

The toxicity and hazards of organic molecules usually are determined by their structures. To the extent that a thermal process can convert waste molecules to carbon dioxide, water, and inorganic substances, the potential hazards to public health and the environment are eliminated or reduced, and the volume of waste to be managed

is decreased. A beneficial side effect is that it may be possible to recover energy or other useful by-products from thermal destruction systems.

BACKGROUND

Performance Standards

The U.S. Environmental Protection Agency (EPA) has developed performance standards for thermal-destruction systems under the Resource Conservation and Recovery Act (RCRA) of 1976 [2]. An incinerator for hazardous waste must achieve a destruction and removal efficiency (DRE) of at least 99.99% for each principal organic hazardous constituent (POHC).

The pollution-control systems of hazardous-waste incinerators usually include a combustion gas quench and scrubber to cool, neutralize, and control particulate matter in the hot gas. With poorly controlled thermal-destruction conditions, some of the hazardous waste may decompose only partially to form products of incomplete combustion (PICs). When thermal-destruction facilities have high DREs for the identified POHCs, the air emis-

This research was not funded through Argonne National Laboratory. Dr. Wentz was employed at the University of North Dakota Energy Research Center at the time the gasification research discussed here was in progress.

sion concentration of PICs is low and not of environmental concern.

The EPA also has developed performance standards for the incineration of liquid PCBs under the Toxic Substances Control Act of 1976 [3, 4]. An incinerator for liquid PCBs must meet the following criteria:

- Maintenance of the introduced liquids for a 2-s dwell time at $1,200^{\circ} \pm 100^{\circ}\text{C}$ and 3% excess oxygen in the stack gas; or
- Maintenance of the introduced liquids for a 1.5-s dwell time at $1,600^{\circ} \pm 100^{\circ}\text{C}$ and 2% excess oxygen in the stack gas.

The EPA has interpreted these conditions to require a DRE of at least 99.9999% for liquid PCBs. An incinerator for nonliquid PCBs, PCB articles, PCB equipment, or PCB containers must also attain a DRE of at least 99.9999% [5].

Gasification Process

High-temperature gasification can provide highly efficient destruction of hazardous waste. Oxygen, steam, and hazardous substances are injected into the gasifier, and combustion of the hazardous substance occurs at the point of introduction of the oxygen. The hazardous hydrocarbon is converted to carbon dioxide and water through oxidation. This oxidizing zone is like an incinerator, except the minimum temperature in this zone of the gasifier is $3,000\text{--}3,200^{\circ}\text{F}$, compared with a maximum temperature of less than $2,600^{\circ}\text{F}$ in a conventional incinerator.

Following the oxidizing zone is a reducing zone where the oxygen is consumed completely. The steam in the gasifier contacts the carbon source to create the reducing atmosphere, generating hydrogen and carbon monoxide. The combination of high-temperature oxidation followed by high-temperature reduction should ensure thermal destruction of the hazardous waste.

The rate of thermal destruction of any hazardous substance is directly proportional to the destruction temperature. Since pure oxygen is used, the destruction temperature should reach $3,000^{\circ}\text{F}$ within 1 s. The traditional 2-s residence time required by EPA for conventional PCB incinerators should be orders of magnitude longer than the time required for gasification to achieve similar DREs. The DREs achieved through gasification are significantly higher than those achieved in conventional incinerators and offer the opportunity to more thoroughly destroy hazardous wastes. These extremely high DREs should result in a more cost-effective process and provide greater protection to human health and the environment.

An additional merit of gasification could be the production of large volumes of hydrogen, carbon monoxide, and methane. Production and recovery of these valuable gasification by-products represents a desirable environmental goal, compared with the production of carbon dioxide and water from conventional incineration processes.

PCB Research

The chemistry of the gasification of chlorinated hydrocarbons is similar to the gasification of coal. Chlorinated hydrocarbons such as trichlorobenzene and PCBs are gasified to produce carbon monoxide, hydrogen, and methane, as well as hydrogen chloride. Hydrogen chloride must be recovered or removed through a neutralization process.

When PCBs and other chlorinated hydrocarbons are incinerated, there is a potential to produce undesirable chlorinated dibenzo-p-dioxins and chlorinated dibenzofurans (CDF) [6]. Numerous possible isomers exist for both of these chemical substances [7]. The most toxic

chlorinated dibenzo-p-dioxin to guinea pigs is 2, 3, 7, 8-tetrachloro dibenzo-p-dioxin (TCDD). The formation of TCDD and CDF can occur when chlorinated hydrocarbons are subjected to temperatures of $500\text{--}1,250^{\circ}\text{C}$. However, only insignificant quantities, if any, of either CDF or TCDD could survive the normal operating temperatures of the gasifier.

NORTH DAKOTA PROJECT

Early Stages

Recognizing the potential of the gasification process, Union Carbide Corporation contracted with the University of North Dakota's Energy Research Center in Grand Forks to demonstrate the use of this technology to destroy PCBs in the Center's pilot-plant gasifier [8]. Once Union Carbide and the Energy Research Center agreed on the details of the experimental program, the Center applied for the necessary state and federal permits. The project was discussed with EPA Region VIII personnel, and their recommendations were followed in preparing the permit application. The EPA application was filed April 28, 1986, and the permit was granted July 2, 1986 [9].

North Dakota State Department of Health personnel were also informed of the proposed research, and their recommendations were followed in the preparation of the permit application submitted to that agency. On July 11, 1986, the state issued a one-time approval for the PCB program at the Energy Research Center [10].

Shortly after the State Health Department and EPA permits were granted, a group of local citizens began a campaign in opposition to the PCB-destruction research program, and the local newspaper became involved in the issue. Several times a week, the newspaper featured stories on PCBs and the potential risk of the gasification program. (Later, in January 1987, the paper changed its position and became supportive of the project.)

In July 1986, the Energy Research Center began issuing informational press releases and holding public meetings to address the concerns expressed by local citizens and the news media. The PCB project came under intense public scrutiny and remained in the news limelight for the duration of the program.

Pilot Plant Modifications

The pilot plant gasification unit at the Energy Research Center was modified, as shown in Figure 1, for the PCB thermal-destruction demonstration. A hydrocarbon liquid injection system was installed to feed PCB and surrogate liquid chemicals to the hottest zone of the gasifier. The steam and oxygen were to be injected in the same manner as during previous coal operations. Petroleum coke replaced coal in the gasifier to enhance the analytical reliability. Additional sampling points were added for the sensitive measurements that would demonstrate the extremely high thermal-destruction efficiencies. The scrubber system was modified slightly to accommodate a caustic solution to remove hydrogen chloride. Several safeguards were added throughout the gasification system to ensure no unreasonable risk to human health or the environment. Any condition that conceivably could lead to incomplete PCB thermal destruction would cause automatic shutoff of the PCB flow.

The hottest zone of the gasifier would be operating at $3,000^{\circ}\text{F}$ or higher, with a residence time of greater than 1 s, followed by a second zone at $2,100^{\circ}\text{F}$ for at least 1 s. Thermal-destruction efficiencies of 99.999999% were expected for all chlorinated hydrocarbons. Verification required a high degree of precision in the analytical tech-

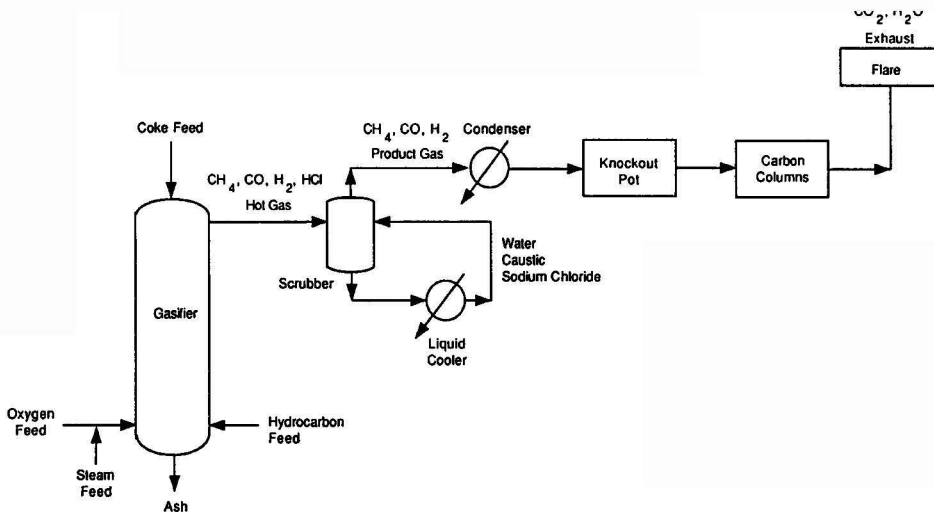


Figure 1. Gasification process for liquid chlorinated hydrocarbons.

niques. Standard EPA-developed controls would be used to monitor this research program, and additional, internally developed analytical techniques would be employed to ensure efficient and safe gasifier performance.

Gas samples would be taken continuously at the 10-foot level of the gasifier, and results would be available within 20–30 minutes. These samples would determine the levels of PCB and other chlorinated hydrocarbon destruction efficiencies to at least 99.999999%. This sampling and on-site testing would quickly disclose any disruption in the thermal-destruction process for PCBs and other chlorinated hydrocarbons. Analysis of additional samples of the off-gas taken by Battelle Columbus Division (Columbus, Ohio) would require a turnaround of between 10 days and 2 weeks. Battelle would measure PCB destruction efficiencies to at least 99.999999% and possibly 99.9999999%, as well as determine the presence of any trace amounts of TCDD and CDF.

Pilot Plant Testing

The unit was tested to establish the general operability of the modifications made to the gasifier, the scrubber, and other equipment. Once the gasifier performed satisfactorily using only coke, steam, and oxygen as feedstocks, injection of liquid hydrocarbons began. A test matrix was designed consisting of a chlorinated hydrocarbon surrogate (trichlorobenzene) that would simulate PCBs.

Use of surrogates in a stepwise test program is a standard research procedure that allows research to proceed in a controlled manner permitting maximum data collection while minimizing the risk of operational and environmental problems. Before the trichlorobenzene was tested, however, a nonchlorinated hydrocarbon surrogate was needed to check the general operability of the liquid hydrocarbon injection system and the analytical procedures. Toluene was selected as a suitable nonchlorinated hydrocarbon surrogate. Later virgin mineral oil was added to initiate startup operation on liquids.

By November 1986, the opposing citizens and their attorneys were threatening to file a lawsuit to terminate the project. In the face of this public pressure, the State Department of Health suspended their previously granted research permit, and the president of the University of

North Dakota halted the project pending a public hearing.

In December 1986, the state and the university administration agreed to allow a brief gasifier run with diesel fuel to test equipment modifications, particularly the new liquid injection system. Also, the test would afford the opportunity to refine analytical sampling techniques and chemical analysis procedures.

The initial startup was promising. During this initial testing, DREs in excess of 99.9999% were achieved for several alkane hydrocarbons in the fuel oil surrogate. The sensitivity of the analytical results with diesel fuel was limited by the similar origin of the petroleum coke, which contributed background hydrocarbons to the off-gas that were identical to the feed components of the diesel fuel being tested. As a result, it was believed (but could not be verified) that the DREs were well in excess of 99.9999%.

Project Termination

The public hearing on the project was held in February 1987 and lasted three days. It was carried live by the local radio station. During the hearing, the scientific merit of the project was not debated by those speaking in opposition. Instead, the testimony opposing the permit was based on emotional issues, stressing the alleged risk of operating this project at an in-town campus location [11, 12]. During the hearing, an expert witness concluded that this project was many orders of magnitude less risky than common, everyday activities of the general population [13].

On April 13, 1987, the State Department of Health revoked its permit for the project, stating that the residential location of the Energy Research Center should not be used for the PCB project or for any future research involving hazardous materials. Later the president of the University banned all hazardous waste research on the campus.

THERMOLYTICA DETOXIFIER PROJECT

At about the same time the gasification project was being pursued at the University of North Dakota, the

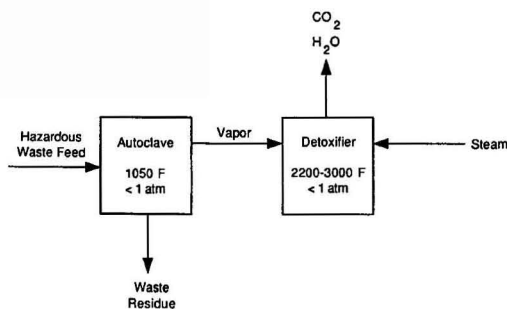


Figure 2. The thermolytica process for hazardous waste detoxification.

Thermolytica Corporation was also studying gasification technology for destruction of hazardous waste. This research, performed in California and independent of the effort in North Dakota, has resulted in the commercialization of a gasification detoxifier, described in detail in another paper in this issue.

The Thermolytica process unit (TLD), shown in Figure 2, consists of an autoclave and detoxifier that are operated in series to ensure high DREs for hazardous waste destruction. A drum containing the hazardous waste is placed in the autoclave and heated to as high as 1,050°F to volatilize the organic waste. The organic vapors then flow to the detoxifier, where they come in contact with injected steam and are destroyed by the gasification reactions.

Typical detoxifier operating conditions are about 2,100°F and a slight negative pressure. At 2,100°F the TLD has consistently demonstrated DREs in excess of 99.99%, which is the RCRA regulatory requirement. DREs greater than 99.999% have also been measured at the 2,100°F temperature level, thereby demonstrating the feasibility of the engineering principles in the North Dakota program, which was to operate at 3,000°F or greater.

It should be noted that tests have now been performed on the TLD that substantiate the theory that no significant quantities of TCDD are produced in a high temperature gasification process for the destruction of chlorinated hydrocarbons [14]. A mixture of toluene and xylene, containing 0.5% perchloroethylene was gasified by the TLD with 31% molar excess steam. Within the 0.2 part per trillion sensitivity limits of the EPA-recommended analytical process used, no detectable amounts of 2,3,7,8-TCDD were found in the TLD off-gas samples. Hydrocarbons that contain chlorine such as PCBs may produce TCDD in uncontrolled fires, and previously no data existed to refute the contention that high-temperature gasification processes might generate TCDD. Much of the opposition to the North Dakota program was focused upon the uncertainty of the formation and survival of significant amounts of TCDD in the 3,000°F gasification process.

ROLE OF PUBLIC OPINION

Several factors contributed to the successful development of the TLD in California. A major factor was that the project had the support of the area citizens, particularly the local Sierra Club. This support allowed the scientists and engineers to concentrate their efforts on the technical aspects of the research and development project. In contrast, those involved in the North Dakota project found it necessary to divide their time between developing the project and defending it in the face of public and media opposition.

The attitudes of state agencies also were a factor in the different fates of the two projects. The State of California regulatory agencies that interacted on environmental matters were strongly supportive of the gasification concept for hazardous waste destruction. In fact, the California Department of Health Services, Advanced Technology Section, awarded Thermolytica a grant to assist in the development of the market test units [15]. Both local citizens and California regulators recognized the need for research to improve upon existing processes for hazardous waste management. This degree of support was lacking for the North Dakota project.

To those involved in the project, the potential environmental and economic benefits of the PCB destruction demonstration program at North Dakota appeared to greatly outweigh the potential risks. The research involved small quantities of substances that would have been confined and treated to minimize any potential environmental impact from accidental spills or discharge during the operation. However, the ultimate permitting decision that ended the project seemingly was based not on the technical merits of the effort, but on subjective perception and emotion.

In contrast, within an atmosphere of general public and state agency support, the Thermolytica project was allowed to proceed on the basis of its technical merits. The result was the development of a highly promising commercial process for the destruction of hazardous waste.

CONCLUSION

These two cases demonstrate that meaningful progress can be made on the crucial issues of hazardous waste disposal when the all too prevalent "not-in-my-backyard" attitude is replaced by public willingness to evaluate a project in terms of its technical merits and potential benefits, balanced against objective (not emotional) consideration of potential risks. Well-designed research is necessary to arrive at meaningful solutions to waste-disposal problems. If promising research studies (such as the North Dakota project) are smothered in a blanket of subjectivity, the environment will continue to be abused. The public and regulatory agencies must become willing to accept constructive roles in efforts to solve these problems.

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Innovative Thermal Destruction Technologies

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Five innovative technologies for thermally destroying hazardous wastes were selected and are described. They are oxygen-enriched incineration, Westinghouse/O'Connor combustor, circulating bed combustion, infrared system, and plasma arc. Two important criteria used in selecting these technologies are that they are at least at the stage of pilot-scale demonstration and appear to be promising in terms of destruction effectiveness.

INTRODUCTION

The disposal of solid wastes is an environmental issue of the 1980s and will continue as long as waste is continuously produced. EPA's research data and industry's operating experience indicate that incineration, when compared to the other alternative technologies, has the highest overall degree of destruction and control for the broadest range of various waste streams [1].

Incineration has been used for waste disposal for many decades. Major conventional incineration technologies used for various waste types are summarized in Table 1.

One of EPA's functions in their RCRA and Superfund programs is to assist industry in developing innovative technologies for waste destruction. Their main activities in this area are described below.

During 1980-1984, EPA's Hazardous Waste Engineering Research Laboratory in Cincinnati, Ohio sponsored a research program under RCRA to evaluate the performance of innovative thermal technologies for hazardous waste destruction. The program selected and tested the following six innovative technologies [2]:

- Fluidized bed
- Molten salt
- Advanced electrical reactor
- Plasma arc
- Wet air oxidation
- Supercritical water

This paper describes selected innovative technologies supported either by EPA's RCRA and SARA programs or developed by industry since 1980. Two of the important criteria used in selecting these technologies are that they are (or had been) at least at the stage of pilot-scale demonstration and appear to be promising in terms of destruction effectiveness. The technologies selected are listed in Table 2.

TECHNOLOGY DESCRIPTIONS

Oxygen-Enriched Incineration

Successful hazardous waste incineration requires an intensive, complete destruction/oxidation of waste molecules with oxygen. Current incinerators require about 150% excess air to provide enough oxygen for oxidation, and require that the so-called 3-T factors (temperature, turbulence, and residence time) be adequate to ensure efficient destruction. Because 79% of air is nitrogen, the majority of any excess air used will not contribute to the effectiveness of incineration and will only result in extra energy required to raise the nitrogen to combustion temperature, and additional product gas handling and cleaning requirements. As a matter of fact, two of the 3-T's (turbulence and residence time) are essentially the physical parameters used to promote the contact of hazardous waste particles with oxygen. Therefore, it seems logical that increased oxygen concentration should improve incineration or destruction efficiency.

In 1987, under the sponsorship of EPA's Office of Research and Development, the Union Carbide Corporation (UCC) tested its oxygen-enrichment burner, the Linde Oxygen Combustion System (OCS), on EPA's Mobile Incineration System (MIS). The burn took place using the dioxin-contaminated solids and liquid waste located at the Denney Farm in McDowell, Missouri. EPA's MIS was built in 1981 [3]. It originally consisted of four heavy duty, over-the-road semi-trailers. They were:

- Trailer 1: Rotary kiln (4.9 MMBtu/hr, i.e., million Btu/hr)
- Trailer 2: Secondary combustion chamber (3.9 MMBtu/hr)
- Trailer 3: Scrubber and air pollution controls (APC)
- Trailer 4: Combustion and stack gas monitoring equipment

TABLE 1. WASTE TYPES AND THEIR CONVENTIONAL INCINERATION TECHNOLOGIES

Waste Type	Conventional Incineration Technologies
Hazardous Waste	● Rotary kilns
Biomedical Waste	● Liquid injection incinerators
Municipal Waste	● Excess-air modular incinerators
Industrial Sludges	● Starved-air (two-stage) modular incinerators
Municipal Sludges	● Mass-burning incinerators
	● Refuse-derived fuel (RDF)-burning incinerators
	● Multiple hearths
	● Fluidized beds
	● Multiple hearths
	● Fluidized beds

The conventional air burner system was replaced by the Linde OCS. The Linde OCS consists of the patented "A" Burner, an oxygen flow control piping skid and a control console [4-6]. The control console utilizes a programmable controller to optimally integrate all system components into a flexible combustion package while providing for easy operator interfacing and safety interlocking. The A Burner allows the use of up to 100% oxygen in place of air for incineration without creating high flame temperatures, high NO_x, poor mixing and non-uniform heat distribution. However, for incinerators under even a slight vacuum, close to 100% oxygen enrichment would be very difficult to achieve due to the inevitable air infiltration.

Operation of the modified MIS from early June to mid-September 1987, reportedly confirmed that the system had achieved the following major research goals [4]: throughput increase, specific fuel savings over 60%, and kiln puff reduction. Each of these achievements is described below.

Throughput increase: The maximum contaminated solid throughput of the Mobile Incineration System during its operation with air burners was designed to be 2,000 lb/hr. However, this maximum rate was not sustainable. For example, the average throughput rate of four test runs in the spring of 1985 had been only 1,478 lb/hr. With the Linde Oxygen Combustion System, the MIS achieved a sustainable solid throughput rate of 4,000 lb/hr, as confirmed by a certified verification test. The comparison of the two sustainable conditions is shown in Table 3.

Fuel savings: Without oxygen enrichment, supplemental fuel was added to provide the heat required to operate the rotary kiln at 1,500-1,600°F and the secondary com-

bustion chamber at about 2,100°F because the waste materials did not have a sufficient heating value to sustain self-combustion. Specific fuel savings of over 60% was achieved during operation of the EPA/MIS with the Linde system. This result can also be expressed as 50 MMBtu saved per ton of oxygen used, as shown in Table 3.

The economics of using oxygen to save fuel, of course, depend on the relative cost of fuel and oxygen. With No. 2 fuel oil costing \$0.70 per gallon (or \$5.50 per million Btu) and a fuel savings of about 50 million Btu for every ton of oxygen used, the breakeven oxygen cost is \$275 per ton of oxygen. The cost of oxygen depends on the method of oxygen generation, the size of the plant, and the location. For example, it ranges from about \$50 per ton of oxygen produced by a large on-site facility to about \$120 per ton for delivered liquid.

Kiln puff reductions: When high-Btu wastes are fed into rotary kiln incinerators in an intermittent mode, the transient combustion behavior of these materials creates unsteady releases of combustible gases that may momentarily deplete the oxygen supply to the incinerator. These temporary oxygen deficient conditions could cause the release of products of incomplete combustion (PICs) and often are called kiln "puffs" [7, 8].

In the field operation of the EPA/MIS, large quantities of plastic materials were burned periodically. These materials were ramfed in the rotary kiln every 1-2 minutes. To respond to the transient oxygen demand for burning these materials, an oxygen feed-forward/feedback control logic was designed into the Linde system. Automatic water spray was used to modulate kiln temperature when required.

TABLE 2. INNOVATIVE TECHNOLOGIES

Process	Key Feature
Oxygen-Enriched Incineration	High-temperature oxidation (1,500-2,000°F). High-purity O ₂ is used as a replacement for combustion air (gas flows and N ₂ -content are low).
Westinghouse/O'Connor Combustor	High-temperature oxidation (1,500-2,000°F). It reportedly can be used for both hazardous waste and municipal waste incineration.
Circulating-Bed Combustor (CBC)	Low-temperature oxidation (1,000-1,500°F). Incineration coupled with simultaneous removal of products by bed materials, which are generally lime or limestone powders.
Infrared System	High-temperature pyrolysis or oxidation (1,500-2,000°F). It can be operated under starved-air or excess air conditions.
Plasma Arc	High-temperature pyrolysis (18,000°F). Plasma is an ionized gas flow that breaks the bond of chemical compounds in a microsecond.

TABLE 3. EPA MOBILE INCINERATION SYSTEM: OXYGEN DEMONSTRATION SUMMARY

	Air Case ⁺	Oxygen Case	Percent Change
Contaminated Soil (lb/hr)	1478	4000	+171%
Firing Rate (MMBtu/hr)			
Kiln	4.9	3.9	
SCC (Secondary Combustion Chamber)	3.9	5.4	
Total	8.8	9.3	+6%
Specific Fuel Use (MMBtu/Ton Soil)	11.9	4.7	-61%
Pure Oxygen Input (lb/hr)			
Kiln*		574	
SCC		0	
Total		574	
Specific Oxygen Consumption (Ton O ₂ /Ton Soil)		0.14	
Fuel Savings (MMBtu/Ton O ₂)		50	
Kiln Superficial Velocity** (Ft/Sec)	8.1	3.3	-59%
SCC Residence Time** (sec)	2.6	2.6	0
Quenched Gas Flow (DSCFM)	3250	2500	-23%

* Average of four runs. Maximum throughput was 2000 lb/hr.

** 58% of total oxygen entering the kiln (equivalent to 40% O₂ enrichment).

** Calculated data.

Before the implementation of this O₂ control feature, the MIS had difficulty in burning these plastic materials smoothly, partly due to its relatively small capacity. Even though the normal excess oxygen level was high, occasional feeding-practice upsets caused puffs to occur as evidenced by the drop in the O₂ concentration and the CO spikes.

After the implementation of the oxygen control feature, the transient upset conditions associated with the release of the combustible gases were virtually eliminated in the operation of the MIS.

Current status: Although Union Carbide Company (UCC) completed its burn evaluation with the MIS, EPA is continuing to use UCC's burner to test-burn other wastes. Test results relative to destruction and removal efficiency (DRE) may be available later.

In addition to UCC's oxygen-enrichment tests, the American Combustion Company (ACC) also tested its Pyretron oxygen-enrichment burner at EPA's Combustion Research Facility (CRF) in Jefferson, Arkansas. Testing results are being evaluated at this writing.

Technology advantages for oxygen enrichment are increased waste throughput and the gas residence time, the fuel consumption is lowered primarily due to the reduced sensible heat loss to the flue, the DRE should be improved, and pollution control of the reduced flue gas is less costly and more effective. The major technology disadvantage is the cost of the oxygen supply.

Westinghouse/O'Connor Combustor

The heart of the system is the Westinghouse/O'Connor combustor, a water-cooled rotary barrel constructed of alternating longitudinal water tubes and flat perforated steel plates welded together to form the perimeter. The combustor is installed on a slight incline and is slowly rotated by a chain and roller drive. The perforations between the water tubes provide controlled distribution of combustion air, while the water cooled walls remove heat and protect the barrel from overheating.

Waste is fed directly from the receiving area into the upper end of the tilted combustor. As the waste tumbles down the length of the rotating barrel, it dries and then progressively burns. Ash dropping out of the lower end is about one-tenth of the original waste volume; remaining unburned material is more completely combusted in an afterburner grate.

The city of Panama City, Florida constructed two Westinghouse/O'Connor units at its Bay County Resource Management Facility to incinerate 510 tons per day of municipal solid waste (MSW) in 1987 [9]. Heat generated by the combustion of waste produces steam to drive a turbine generator.

All MSW received at the plant enters through an automatic gate system and is unloaded on the tipping floor. Large items are separated from the MSW; the large combustible items are processed through a shear shredder. The large noncombustible items are removed and stored temporarily for landfill disposal. After sorting, the MSW is then fed into the combustor to begin its incineration. The slightly inclined combustor barrel rotates slowly, causing the waste to tumble and advance as combustion proceeds. A forced-draft fan draws combustion make-up air from the tipping area to reduce odor and dust levels in the tipping hall and to prevent them from escaping the building. The air is preheated before entering the multiple zone wind-box located beneath each combustor barrel.

Figure 1 shows the cross-section of the rotary combustor and the flow of underfire and overfire air into the combustor. The combustor barrel has a diameter of 10 feet and is constructed by alternating steel tubes with carbon steel perforated webs and welding them together. The steel webs have a width of 1-1/2 inches with 3/4-inch diameter holes used to bring in combustion air. The tubes direct cooling water through the outside wall of the combustor barrel which, upon heating, is delivered to the boiler through the rotary joint. Hot gases, produced during the combustion process, flow from the combustor barrel through the boiler's radiant, superheater, and convection sections. The combustion gases exiting the convection section pass through a heat exchanger that preheats the incoming combustion air.

The flue gases from the air heater enter the electrostatic precipitator (ESP) to remove particulate matter before exiting the stack. The flue gas is drawn from the ESP by an induced-draft fan before being discharged to the atmosphere through a separate flue in the common stack.

Three types of ash by-products are produced by the process: fly ash, siftings, and bottom ash. Fly ash is collected in hoppers under the convection, superheater, air heater, and ESP sections of each combustor/boiler train and is conveyed pneumatically to the bottom ash conveyor. Siftings are collected underneath the combustor by the siftings conveyor and are transferred by an ash drag system to the bottom ash conveyor. Bottom ash falls from

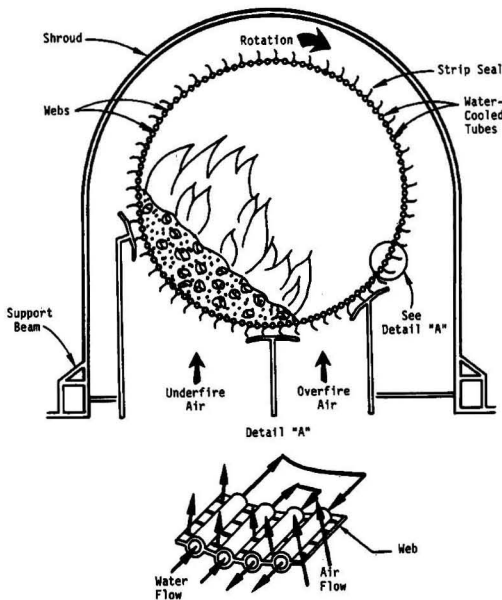


Figure 1. Cross-section of the Westinghouse/O'Connor water-cooled rotary combustor.

the rotary combustor onto a fixed afterburner grate located beneath the combustor outlet. The fly ash, siftings, and bottom ash mixture are water-quenched, dewatered, and removed by one of two redundant bottom ash drag conveyors into trucks, then disposed of in a landfill.

Test results: Particulate emission was tested on the Panama City units from April 22 through June 5, 1987 [9]. The results indicate that both Units 1 and 2 are in compliance with the particulate and visual emissions levels required by the State of Florida Department of Environment's PSD Regulations. The PSD (Prevention of Significant Deterioration) Regulations require particulate matter emissions to be less than 0.03 gr/dscf corrected to 12% CO₂ and limits plume opacity to no more than 10%. The particulate matter concentration levels at the design capacity of 255 tons of MSW per day per unit averaged 0.0193 gr/dscf at 12% CO₂ for Unit 1 and 0.0243 gr/dscf at 12% CO₂ for Unit 2. The EPA Method 5 particulate measurements conducted for determining compliance are given in Table 4. The EPA Method 9 opacity measurements were consistently at or less than 10% for both units during the test runs.

Gaseous emissions tests were also conducted during April through June, 1987 to determine the stack gas concentration of SO₂, NO_x, and HCl. The testing was conducted to verify the emission factors used to project the annual emission rates in the PSD permit application. EPA Method 8 was used to determine SO₂ emissions. The average SO₂ concentration from nine tests performed on five days was 111 ppmv corrected to 12% CO₂ [dv = dry volume]. A CEM (Continuous Emission Monitor) was used to measure NO_x emissions over a nine-day test program. EPA Method 7 was also used to verify the NO_x levels measured by the CEM during an eight-hour period by simultaneous sampling. The average of the NO_x emissions data from the CEM and EPA Method 7 were 180 and 157 ppmv corrected to 12% CO₂, respectively, for the eight-hour test. NO_x emissions measured by the CEM during the 9-day test period were in the range of 150 to 200 ppmv with a maximum of 300 ppmv during

boiler excursions. NIOSH Method 112B was used to determine HCl concentrations. Twenty samples were taken on seven different days with an average HCl concentration of 467 ppmv corrected to 12% CO₂.

Current status: Currently, there are 11 modular combustors in operation at 6 different facilities. Three facilities with a total of 7 combustors are under construction and Westinghouse has contracted to construct 4 more plants with a total of 14 combustors. This represents an aggregate processing capacity of more than 9000 tons of solid waste per day. It appears that the technology has good potential for the future [9].

The technology can handle a variety of wastes, including municipal wastes, hazardous wastes, and possibly even hospital wastes. It can burn liquids, semi-solids, solids, sewage sludges, and residual oils or refinery bottoms.

The technology can be quite flexible in that the individual modular units can be as large as 500 tons-per-day of MSW and, therefore, 4 units would allow for over 2,000 tons-per-day capacity. The technology has a high energy recovery efficiency because the water tubes are used as an integral part of the reactor wall. Siftings from the combustion chambers may contain residuals that are not completely incinerated, which could be a disadvantage.

Circulating Bed Combustor (CBC)

Conventional technologies for the thermal destruction of wastes are often faced with operation at high temperatures with relatively low throughputs and must use afterburners and scrubbers. Ogden Environmental Services, Inc. (OES) has developed a circulating bed combustor (CBC), which uses lower temperatures, compared to conventional rotary kiln or liquid injection incinerators, to obtain the same destruction efficiency as high-temperature processes and relatively higher throughputs at a lower thermal rating, reportedly eliminating the need for afterburners or scrubbers.

The CBC uses high-velocity air to entrain circulating solids in a highly turbulent combustion loop. The combustion chamber is typically 30 ft high and has a 12-in.-thick ceramic liner. Solid feed is introduced into the combustor loop at the loop seal where it immediately contacts the hot recirculating solids stream exiting the hot cyclone. Liquid feeds are typically injected directly into the combustion zone of the CBC. Upon entering the CBC, hazardous materials are rapidly heated and continue to be exposed to high temperatures (1,450° to 1,600°F) throughout their stay in the CBC. Residence times in the combustor range from 2 seconds for gases to 30 minutes for larger feed materials (<1.0 in.). The high combustion-air velocity for circulating solids creates a uniform temperature

TABLE 4. EMISSION COMPLIANCE TEST RESULTS FROM THE BAY COUNTY RESOURCE MANAGEMENT CENTER

Bay County Compliance Test Results—Unit 1					
Flue Gas Flow kdscfm	Flue Gas Flow kacfm	Stack Temp deg F	Steam Flow klb/hr	Percent of Rated Capacity	Particulate Matter gr/dscf @ 12% CO ₂
25.8	52.4	425.0	71.1	104.5	0.0140
27.9	55.1	429.0	66.5	97.8	0.0240
25.8	52.8	427.0	65.0	95.6	0.0200
Bay County Compliance Test Results—Unit 2					
27.7	52.6	429.0	69.7	102.5	0.0250
28.4	58.1	449.0	62.7	92.2	0.0190
29.2	59.0	451.0	62.3	91.6	0.0290

TABLE 5. CHEMICAL REACTIONS THAT OCCUR IN CBC COMBUSTION CHAMBER

Reactants	Intermediates	Final Products
CxHy + O ₂ (Hydrocarbons)		CO ₂ + H ₂ O
(CxHy)Sz + O ₂ (Sulfur Compounds)	SO ₂	
CaCO ₃ (Limestone)	CaO + _____	CaSO ₄ (s) (Gypsum) + CO ₂
(CxHy)Clz (Chlorine Compounds)	2 HCl	CaCl ₂ (s) + H ₂ O (salt)

(+/- 50°F) around the combustion loop (combustion chamber, hot cyclone, return leg), reportedly resulting in extremely efficient combustion and eliminating the need for an afterburner. During operation, ash is periodically removed from the CBC by means of a water-cooled ash removal system. The hot gas leaving the cyclone is cooled in a flue gas cooler and particulates escaping the cyclone are collected in fabric filter baghouses.

Table 5 shows the generic chemical reactions that take place in the CBC and enable the conversion of harmful acid gases to salts. The rapid combustion and quick neutralization of acid gases within the combustion chamber effectively eliminates the need for high alloy combustor components or post-burner treatment units, such as wet or dry scrubbers, for acid gas capture.

Cooling removes the thermal energy that is released during combustion reactions. Recovery of energy is accomplished in both the combustor zone and the flue gas cooler. In the combustion chamber, the heat transfer is enhanced due to solid particle contact with the cooling tubes. Sensible heat is further removed from the flue gas with conventional heat exchangers located between the cyclone and baghouse filters. Because acid-gas scrubbing takes place within the combustion chamber, the flue-gas coolers are not subjected to the high acid gas concentrations prevalent with conventional waste combustors.

A two million Btu/hr pilot plant was built in San Diego, California. Development and testing programs at this facility have demonstrated the flexibility and effectiveness of the CBC in destroying a wide variety of hazardous wastes [11]. Table 6 lists key data from several waste test burns. The test results indicate that 99.99% DRE is readily attainable for many sludge-like and chemical wastes.

In 1986, EPA's SITE program also selected OES's CBC for Superfund waste destruction testing. According to OES, its first unit (with a 36-inch diameter reactor), that is especially designed for Superfund waste cleanup, will be

deployed to a Superfund site. However, no Superfund site has yet been selected.

Advantages/disadvantages: The advantages of the CBC include the following: wastes can be combusted at lower temperatures than that of conventional incinerators, temperatures in the vessel are low enough to prevent formation of significant amounts of NO_x, and the bed material acts as a scrubber to capture acid gas from the process, reportedly creating a non-toxic solid residue.

Potential disadvantages include the following: disposal of the supposedly inert residual bed material may represent a problem, relatively large amounts of fine particulate matter entrained in the exhaust gases may require elaborate pollution control devices, and waste feed particle size must be controlled to maintain a uniform feed rate.

Infrared Systems

In general, an infrared system has the following major components: primary combustion chamber (PCC), secondary combustion center (SCC), air pollution control equipment (APCE), and a process management and monitor control center. The electric-powered PCC utilizes a high-temperature-alloy wire-mesh belt for waste feed conveyance and is capable of achieving temperatures up to 1,850°F by exposure to infrared radiant heat provided by horizontal rows of electric-powered silicon carbide rods located above the conveyor belt. The gas-fired SCC is capable of reaching temperatures of 2,300°F. It provides residence time, turbulence, and supplemental energy, if required, to destroy gaseous volatiles emanating from the waste. The APCE equipment includes an emissions control system where particulates are removed generally in a venturi section, acid vapor is neutralized in a packed tower scrubber, and an induced draft blower draws the cleaned gases from the scrubber into a free-standing exhaust stack. The Center contains all process and mechanical controls and monitors, including control

TABLE 6. CIRCULATING BED TEST RESULTS ON CHEMICAL FEEDS

Waste	Form	DRE (%)	HCl Capture, %	Ca/Cl ₂ Ratio
Carbon				
Tetrachloride	Liquid	99.9992	99.3	2.2
Freon	Liquid	99.9995	99.7	2.4
Malathion	Liquid	>99.9999	—	—
Dichlorobenzene	Sludge	99.999	99	1.7
Aromatic Nitrile	Tacky solid	>99.9999	—	—
Trichloroethane	Liquid	99.9999	99	1.7
PCB	Liquid	>99.9999	—	—

Note: Results were obtained in tests at the Ogden Environmental Inc., pilot plant.

panels, emissions monitors, motor control units, and office space.

Beginning in the 1950s, Peak Oil Company operated a used oil processing facility at a site on Reeves Road in Brandon, Florida. Various liquid and sludge waste streams from the re-refining operation, which included toxic organics and heavy metals, were dumped into an existing natural lagoon located on the property. The lagoon has some 7,000 tons (and approximately the same number of cubic yards) of material in it and is about one-quarter to one-half of an acre in size [12].

EPA's Region IV office in Atlanta initiated actions for a cleanup program. The Regional Office contracted with the firm of Haztech, Incorporated, an emergency response contractor, to proceed with the clean-up program. EPA's Hazardous Waste Engineering Research Laboratory (HWERL) in Cincinnati, through its Superfund Innovative Technology Evaluation (SITE) program, also participated in the cleanup for this particular lagoon. The HWERL effort primarily involved on-site monitoring and the performance evaluation of the Infrared System.

Initial efforts required that the lagoon be drained of water; the remaining sludge was mixed with sand, soil, and lime to form a waste/soil solid matrix that could be handled by earth-moving equipment. (The lime, in addition to providing binder to the moisture-laden matrix, also counteracted and neutralized the acidic properties of the waste.) This approach greatly facilitated the use of the Infrared System (with a high-temperature afterburner). The SITE demonstration of this innovative incineration system was carried out between July 31, 1987 and August 5, 1987.

The waste/soil matrix was excavated from the lagoon area and screened with a power screen. This device effectively broke up the lumpy waste, blended and aerated the feed, and prepared it for further processing. The screening system allowed the one inch and smaller clumps to be separated from the rock, roots, and other extraneous material found in the lagoon. From the power screen, the waste feed soil was weighed and conveyed to the infrared system.

The infrared system was brought to the site in four individual units consisting of: a 67-foot long electrically heated infrared primary chamber capable of gas temperatures up to 1,850°F; a 72-foot long gas-fired secondary combustion chamber (afterburner) capable of reaching temperatures of 2,300°F; an emissions control system with a 60-foot tall stack; and a process management and monitoring control center.

Wastes were metered, spread to the proper width, leveled to optimum process thickness, and were fed into the PCC at a rate of 3.6 to 4.0 tons per hour in this nominal 100 ton-per-day unit. The waste was exposed to infrared radiant heat provided by horizontal rows of electric-powered silicon carbide rods located above the conveyor belt. Typically, the waste was retained on the primary chamber conveyor belt for 18 to 19 minutes. The processed feed material dropped off the end of the belt into a discharge module and was quenched with water sprays prior to being discharged by the screw conveyor system to an outside receiving container.

Exhaust gases from the primary combustion chamber were introduced into the secondary combustion chamber, which provided over 3.0 seconds of residence time, turbulence, and supplemental energy to destroy any gaseous organics from the primary furnace. The gases leaving the secondary combustion chamber were quenched, particulates were removed in a venturi section, and acid vapor was neutralized in a packed tower scrubber using a sodium hydroxide solution. An induced-draft fan drew the cleaned gases from the scrubber into the exhaust stack which was equipped with sample ports.

TABLE 7. WASTE FEED SOLID MATRIX PROPERTIES—(UNIT IS MICROGRAMS PER GRAM FEED, EXCEPT PERCENT SPECIFIED)

PCB (total)	3.48 to	5.85
Heptachlorobiphenyl	0.94 to	2.20
Hexachlorobiphenyl	1.10 to	1.70
Pentachlorobiphenyl	0.20 to	0.49
Tetrachlorobiphenyl	0.40 to	0.83
Trichlorobiphenyl	0.57 to	0.82
Dichlorobiphenyl	0.12 to	0.19
Ethyl benzene	0.08 to	0.14
Methylene chloride	0.08 to	0.12
Toluene	0.13 to	0.44
Xylenes	0.26 to	0.78
Lead	0.44 to	0.59 percent
Antimony	2.1 to	3.6
Arsenic	2.0 to	2.9
Cadmium	3.9 to	4.6
Chromium	20 to	24
Copper	44 to	55
Strontium	50 to	62
Vanadium	7 to	11
Zinc	950 to	1,100
Moisture	14.2 to	16.6 percent
Carbon	7.0 to	7.8 percent
Sulfur	1.8 to	2.5 percent
Chlorine	less than 0.1 percent	
Ash	70 to	75 percent
Btu value (HHV)	1,640 to	2,065 Btu/lb

During a series of three replicate test runs, samples of the solid waste feed, liquid streams, furnace ash, and stack gas emissions were obtained under rigorous, EPA-approved sampling protocols and quality assurance criteria. The most intricate sampling procedures involved the stack gas emissions collection. Sampling methods include a Method 5 train for HCl and particulates, and a Source Assessment Sampling System (SASS) for PCBs, dioxins, furans and semi-volatile priority pollutants. A modified Method 5 train for soluble chromium, a Volatile Organic Sampling Train (VOST) for volatile priority pollutants, and various continuous emission monitors (for O₂, CO₂, CO, THC, and NO_x) were employed. Ambient air monitoring stations were also deployed both upwind and downwind of the unit to monitor any air contamination from the operation of the unit beyond the defined site perimeter [12].

Table 7 shows the typical range of organic and metallic contaminants in the waste feed excavated from the lagoon after the material was blended into a matrix with sand, soil and lime in order to facilitate its handling. The primary organic of concern was the PCB, while the primary metal of concern was lead. Other characteristics, such as heating value and moisture, are also shown.

Results: Table 8 shows that the unit successfully achieved a DRE in excess of 99.99% for the PCB contaminants, thus satisfying the required RCRA standard. TSCA regulations, which require 99.9999% DRE, were not applicable since the contaminated material at the site contained less than 50 ppm of PCBs. Operational temperatures of approximately 1,900°F in the secondary combustion chamber and more than 3 seconds of residence time, instead of the TSCA-mandated 2,200°F and 2 seconds level, accounted for the unit's satisfactory operation in this situation. Residual PCBs in the ash were below the 1 ppm target level mandated by Region IV, thereby achieving one of the most important test objectives.

As shown in Table 8, the Infrared System at the Peak Oil site demonstrated problems with particulate emissions and failed to meet the regulatory limit of 0.08 grains/dscf at 7% O₂ (by volume) on two of the 3 days they were measured. Emission control system modifications and maintenance before the second test run appear to have

TABLE 8. STACK EMISSIONS DATA

Date of Run	DRE for PCB (percent)	Particulates Grains/DSCF @ 7% O ₂	HCl in g/hr	SO ₂ in g/hr
8/1/87	99.99967	0.1590	<0.8	27.24
8/2/87	99.9988	0.0939	8.6	1070.0
8/3/87	99.99972			
8/4/87	99.99905	0.0768	2.9	22.0
8/4/87 (Duplicate)		0.0761	2.7	20.6

been responsible for lowering particulate emissions and eventually meeting RCRA standards in the last two runs.

Interpretation of the data indicates that the inability of the unit's emissions control system to meet particulate emissions requirements was probably due to the lead content in the waste feed and the subsequently high lead oxide loading in the feed to the emissions control equipment.

The emissions of HCl and SO₂ are also shown in Table 8. The HCl emissions were relatively low since the chlorine concentration in the waste feed was below the 0.1 weight percent detection limit. An actual HCl removal efficiency could therefore not be determined. The more difficult to remove SO₂ constituent was reduced by an average of 99.1 weight percent. With sulfur at approximately 2% in the waste feed or a sulfur input rate of about 150 pounds per hour, SO₂ emissions were under 2.5 pounds per hour at a maximum measured rate of 1070 g/hr.

One of the objectives of this test program was to determine the fate of heavy metal contaminants in the waste feed and whether any metals remaining in the ash were significantly reduced in concentration or would be stabilized in the ash residue and other solid effluents rendering the ash potentially suitable for delisting as a hazardous waste. The solid waste feed, furnace ash, and scrubber effluent solids were subjected to both the current Toxicity Characteristic Leaching Procedure (TCLP) and the EP Toxicity leaching tests.

The results on the waste feed for both TCLP and EP testing showed that the waste feed exceeded regulatory limits only for lead. The TCLP regulatory limit for lead of 5.0 mg/l was exceeded in one sample of waste feed at 8.8 mg/l, while other samples showed values of 2.5 to 3.5 mg/l. However, the EP regulatory limit (also 5.0 mg/l) was exceeded for lead in the waste feed by larger amounts, namely values of 24.0 to 29.0 mg/l and one sample investigation (though not within acceptable spike recovery limits) showed 57.0 mg/l. All other metals tested for their TCLP and EP values in the waste feed (eight metals total) were found to be below regulatory levels.

For the ash residue, the results of TCLP and EP testing are summarized in Table 9. Here, TCLP results were lower than regulatory limits in every case. However, the EP results again showed a regulatory limit exceedance for lead, which would probably prevent delisting of the ash residue even though the other metals appeared well below their regulatory limits.

Similarly, for the scrubber water effluent solids, Table 9 shows that again the EP testing values for lead would prevent the material's delisting, while other metals were found to pass the regulatory levels. Thus, the hoped-for result that lead and other heavy metals would somehow be inactivated by some process of conversion into non-leachable forms was not met (if EP test results are used and not the TCLP ones) [12].

TCLP testing for organic materials other than PCB was done on the waste feed, the ash residue, and the scrubber solid samples. The results, which involved testing for some 36 organic hazardous compounds, will be reported in EPA's upcoming final report. However, other than those compounds reported in Table 7 for the waste feed material, all 36 compounds were generally found to be either non-detectable or far below any TCLP regulatory levels.

The largest mass release of metals measured in the stack emissions was that of lead. The specific amounts varied from a release of 2,000 grams per hour of lead for the first test run (on 8/1/87) down to a range of 780–1,000 grams per hour in subsequent runs where changes were made to the operation of the pollution control system. It is interesting to note that the calculated net input feed rate of lead from the waste ranged between 17,000 to 19,000 grams per hour for the test runs made. Thus, the amount of lead exiting the stack represented only about 11.2% of the feed rate of lead for the first run and between 4.2% to 5.5% for subsequent runs. Also, it should be noted that lead (or lead compounds) represented 54% to 60% of the mass of particles from the stack.

In total, 30 different metals were sampled for and analyzed in the stack particulate material. Other than lead,

TABLE 9. LEACHING TEST RESULTS

Metal	Regulatory Level mg/l	Ash EP Toxicity avg. mg/l	Ash TCLP Test avg. mg/l	Scrubber Effluent Solids EP Test avg. mg/l	Scrubber Effluent Solids TCLP Test avg. mg/l
Arsenic	5.0	0.020	0.007	ND	<.22
Barium	100	1.35	0.25	<.56	<.80
Cadmium	1.0	0.98	0.008	0.5–1.9	<.22
Chromium	5.0	0.57	0.037	<.65	<.08
Lead	5.0	31	0.011	3.1–40.0	.12–.38
Mercury	0.2	0.0015	ND	ND	ND
Selenium	1.0	ND	0.031	ND	ND
Silver	5.0	0.031	0.059	<.04	<.06

ND = not detectable

TABLE 10. METALS ANALYSIS

Parameter	Solid Waste Feed micrograms per gram	Ash micrograms per gram	Average Stack Emission Rate grams/hr
Antimony	2.15	3.3	.13
Arsenic	2.55	2.6	.065
Cadmium	4.15	4.1	3.4
Chromium	22	27	.54
Copper	49	64	.37
Lead	4800	6400	1150
Mercury	ND	ND	ND
Sodium	5550	5600	33
Strontium	57	76	.017
Vanadium	9	13	<.036
Zinc	1030	1060	16

ND = not determined

the next highest amounts of metals emitted as particulate were measured to be zinc (16–17 grams per hour), sodium (31–34 grams per hour), and chromium (0.51–0.53 grams per hour). Stack sampling and analysis for chromium VI concentrations yielded results of less than 160 micrograms per cubic meter.

A partial listing of the data for metals is presented in Table 10. Presented there are 11 metals in terms of their levels in the waste feed, in the ash residue, and their levels emitted via the stack gas particulate material.

Since PCB was in the waste, it was desirable to investigate whether there may have been any significant levels of dioxins and/or furans in the lagoon and thus, in the waste matrix processed by the infrared system. Sampling and analysis for these compounds was conducted for the waste matrix, the ash, the scrubber waters, scrubber solids, and the stack gas [12].

All of the above analyses resulted in less-than-detectable levels of these compounds as summarized below for TCDD, TCDF, PCDD, and PCDF (tetra- and poly-chlorinated dibenzo dioxins and furans):

Sample	TCDD	PCDD	TCDF	PCDF	Detection Limit
Waste feed matrix	ND*	ND	ND	ND	1.1 ppb
Ash after treatment	ND	ND	ND	ND	1.4 ppb
Scrubber water	ND	ND	ND	ND	0.022 nanograms per liter
Stack gas	ND	ND	0.47**	ND	0.34 micrograms cubic meter

*ND = Non-detectable

**Reported for one out of 4 tests

The Infrared System is, so far, probably the most used technology of all the innovative thermal technologies for both RCRA-waste destruction and Superfund waste remediation.

The technology has the ability to more accurately control residence time and temperature in the primary combustion chamber (PCC) compared to other technologies. However, the waste feed should be pretreated so as not to exceed recommended size limitations. If the waste is a liquid, it should be mixed with sand, or other solid material, in order to destroy it effectively in the PCC.

Plasma Arc

The plasma arc technology has been used in the United States space program. The evaluation of heat shields that protect space vehicles on re-entry required an intense heat source with plasma characteristics. Plasmas have been referred to as the fourth state of matter since they do

not always behave as a solid, liquid, or gas. A plasma may be defined as a conductive gas flow consisting of charged and neutral particles, having an overall charge of approximately zero, and all exhibiting collective behavior. The plasma, when applied to waste disposal, can best be understood by thinking of it as an energy conversion and energy transfer device. The electrical energy input is transformed into a plasma with a temperature equivalent of up to 18,000°F at the centerline of the reactor. As the activated components of the plasma decay, their energy is transferred to waste materials exposed to the plasma. The wastes are then broken into atoms, ionized, pyrolyzed, and finally destroyed as they interact with the decaying plasma species. The heart of this technology is that the breakdown of the wastes into atoms occurs virtually instantaneously and no large molecular intermediary compounds are produced during the kinetic recombination [2].

Test results: The New York State Department of Environmental Conservation (NYSDEC) Division of Solid and Hazardous Waste and the U.S. Environmental Protection Agency (USEPA) Hazardous Waste Engineering Research Laboratory established a cooperative agreement in 1982 for the construction and testing of a mobile plasma arc system for the high-efficiency destruction of hazardous wastes [13].

The Plasma Pyrolysis System consists of a liquid waste feed system, plasma torch, reactor, caustic scrubber, on-line analytical equipment, and flare. The system is rated at 4 kg/min or approximately 55 gallons per hour of waste feed. Product gas production rates are about 5–6 m³/min prior to flaring. For the purposes of this program, a flare containment chamber and 10-meter stack were constructed to facilitate testing. After flaring, the stack gas flow rate is approximately 30–40 standard m³/min.

A gas chromatograph is installed in the system's mobile trailer to provide information on bulk gas composition. Pre-flare gas samples are analyzed for hydrogen, carbon monoxide, carbon dioxide, water, nitrogen, methane, ethylene, ethane, acetylene, propane, propylene, and 1-butene. A Hewlett-Packard Model 5792A gas chromatograph is also coupled to a Hewlett-Packard Model 5970A mass selective detector and used to analyze pre-flare gas samples for waste feed residuals.

One-hour carbon tetrachloride (CCl₄) tests were conducted in Canada to demonstrate the destruction of a simple chlorinated compound and to demonstrate effective HCl removal by the scrubber. The CCl₄ was introduced into the system in a blend of MEK (methyl ethyl ketone), ethanol, and water at a rate of 1 kg CCl₄ per minute. The stack testing was conducted by GCA Corporation. Results of the three tests are presented in Table 11.

The results indicate that the system is capable of achieving destruction and removal efficiencies much greater than the 99.99% required under RCRA for this listed waste.

Three one-hour tests using PCBs were also conducted to determine the DRE for PCBs and to acquire operating data for this environmental containment. Upon reaching a product gas temperature of 2,000°F at the reactor exit while using MEK/MeOH (methanol) as the feed material, the feed was then switched to a blend of PCBs, MEK, and

TABLE 11. CARBON TETRACHLORIDE TEST RESULTS

	Run 1	Run 2	Run 3
Date	2/18/85	2/26/85	2/26/85
Sample Time, min.	60	60	60
Feed Rate, L/min			
CCl ₄	0.63	0.63	0.63
MEK mixture	2	1.6	2
Total Mass Fed, CCl ₄ , kg	60.0	60.6	60.6
Chlorine Loading, mass %	35	40	35
Reactor Operating Temperature (C)	974	1,008	1,025
Plasma Torch Power, kW	280	298	300
Average Stack Gas Flow Rate, dscfm	1,346.3	1,048.2	1,052.7
dscmm	38.13	29.69	29.81
Average temperature (C)	893.3	807.1	667.3
No. conc., ppm (v/v)	106	92	81
Emission Rate, kg/hr	0.46	0.31	0.28
CO conc., ppm (v/v)	48	57	81
Emission Rate, kg/hr	0.13	0.12	0.17
O ₂ percent	12.7	14.4	15.1
CO ₂ percent	6.0	5.7	4.9
HCl, mg/dscm	(1)	137.7	247.2
Emission Rate, kg/hr	(1)	0.25	0.44
CCl ₄ conc., ppb	<2 ⁽²⁾	<2 ⁽²⁾	<2 ⁽²⁾
Emission Rate, mg/hr	<29.3	<22.8	<22.9
Scrubber Effluent Flowrate, L/min	30.0	30.0	30.0
CCl ₄ conc., ppb	1.3	5.5	3.3
Discharge Rate, mg/hr	2.3	9.9	5.9
Destruction Removal Efficiency ⁽³⁾			
CCl ₄ , percent DRE	99.99995	99.99996	99.99996

(1) Invalid data.

(2) The detection limit of 2 ppb CCl₄ in the stack gas was used to calculate the CCl₄ mass emission rate for each run.

(3) The DRE is based on stack emissions and excludes scrubber effluent.

MeOH. The scrubber water was retained before discharge to sewer to ensure that the concentration of BAP, PCBs, dioxins, and furans did not exceed criteria established by Canadian regulatory authorities. Operating data are presented in Table 12.

The stack gases were monitored for particulates, PCBs, dioxins, furans, NO_x, HCl, flow rate, and temperature. For these runs the stack monitoring was conducted by IMET, Inc. (Markham, Ontario). The sampling and analysis program included the necessary quality assurance/quality control protocols. The procedures and equipment were standard. A summary of the results is presented in Table 13 [13].

The research on another plasma arc system is sponsored by the Electric Power Research Institute (EPRI) and Arc Technologies Company (ATC) which is a joint venture of Chemical Waste Management Inc. and Electro-Pyrolysis, Inc. The purpose is to destroy whole, unopened PCB capacitors at the rate of 3,000–5,000 pounds per hour. The sponsors have obtained RCRA permits for the construction of the system in Model City, New York and are in the process of constructing the unit [14].

Basically, the process involves four steps, as follows:

Step 1: A whole, unopened PCB capacitor is fed into a molten metal (iron) bath.

Step 2: The capacitor shells melt and the internal organic components (PCBs) are subjected to intense radiation from the plasma arc and heat from the molten metal. As a result, the PCB fluids evaporate and decompose.

Step 3: The PCB and/or decomposition products are further directed through the plasma arc in the vicinity of the high current (DC) arc for complete destruction.

Step 4: The products are channeled to a scrubber system where any inorganic materials in capacitors are converted to inert solid residues. Metals may be recovered if desired from both the metal bath and scrubber ash.

Since the Canadian tests, Westinghouse has built a mobile plasma unit (Pyroplasma) of 3 gallons/minute (1 ton/hr) capacity. Also, for the same high-temperature application, Westinghouse constructed a "Westinghouse Electric Pyrolyzer" for contaminated soil detoxification.

The Westinghouse Electric Pyrolyzer uses electric energy to heat the waste feed to about 3,000°F. At this temperature, the organic contaminants are destroyed by decomposition to carbon monoxide and water, and the inorganics melt to form a glass-like fluid which is removed. Both the Pyro-plasma and the Pyrolyzer units have been selected for EPA's SITE program tests. However, no Superfund site has yet been identified for testing.

Advantages include a plasma system that has very intense radiative power and therefore is capable of transferring its heat much faster than a conventional flame, it virtually does not need oxygen, and because of its compactness, a plasma arc system has potential for use in a mobile trailer for easy movement of the system from site to site.

Disadvantages may include the temperatures are so high (about 18,000°F at the arc's centerline), the durability of the arc and the refractory materials could be a po-

TABLE 12. OPERATING DATA FOR PCB RUN #1

Elapsed operating time: 70 min. at operating temperature	
Feed rate	
Total feed	3.09 L/min (liters/min)
	2.83 kg/min
PCB feed	0.40 kg/min
Feed Composition (mass)	14.1% PCB
	11.0% TCB*
	74.9% MEK/MeOH
Reactor Operating Temperature	1,136°C
Plasma Torch Power	327 kW

*Trichlorobenzene

TABLE 13. PCB 1-HOUR TEST RESULTS

	Run 1	Run 2	Run 3
Date	12/5/85	12/17/85	1/16/86
Sample Time, min.	50	60	60
Stack Gas Parameters			
Flow rate, dscmm	37.9	45.0	38.1
Temperature (C)	836	678	962
NO _x , ppm	117	N/A	139
HCl, mg/dscm	N/A	43	68
O ₂ , percent	14	14.5	16.5
CO ₂ , percent	5.5	5.0	3.0
CO, percent	0.01	0.01	0.01
Total PCB*	<0.013	0.46	3.0
µg-dscm**	<0.013	0.32	<0.011
Total Dioxins, µg/dscm	0.076***	<0.43	<0.13
Total Furans, µg/dscm	0.26	1.66	<0.30
Total BaP, µg/dscm	0.18	0.45	2.8
Scrubber Effluent Parameters			
Effluent Flowrate, L/min	41	36	33
Total PCB, ppb (1)	1.56	2.15	9.4
(2)	0.06	4.7	<0.01
Total Dioxins, ppt	5.8	<259	<1.05
Total Furans, ppt	1.5	399	<1.05
Total BaP, mg/L	0.04	0.92	2.0
Destruction Removal Efficiency			
PCB, percent DRE			
(1)	99.99999	99.99994	99.9999
(2)	99.99999	99.99997	99.99999

*These values are based upon monodechlorobiphenyl.

**These values are based upon tridecachlorobiphenyl.

***No tetra or penta dioxins were detected at 0.05 ng on a GC column, except for Run #1 where 0.06 ng tetra dioxin was reported.

tential problem, and the operation of the system requires highly-trained professionals.

CONCLUSION

The authors felt that the five technologies are the most worthy of compilation for illustrating the development of innovative thermal destruction/incineration technologies. Evaluation of these technologies indicates that in most cases, they can meet either RCRA or TSCA destruction requirements, depending upon which compound or chemical (waste) is to be destroyed. Because of the needs, especially under the SITE program, it is believed that more advanced thermal technologies will be developed in the future.

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Physical Properties and Chemical Species Distributions Within Municipal Waste Combuster Ashes

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Incineration of municipal solid waste has been viewed as a preferred alternative to landfilling in recent years. Fly ash and bottom ash are of particular concern because of the high concentration of heavy metals on and within the ash matrix. This paper presents chemical, physical, and structural properties of the ashes from several municipal waste combustors. Properties of both the bulk ash and ash fractions separated by particle size are included. Results have shown significant variability based upon both ash type and particle fraction.

INTRODUCTION

Landfilling of municipal solid waste has become a less attractive management option because of diminishing available landfill capacity. Municipal waste combustion is a viable management option, achieving up to 80 and 90 percent reduction in waste mass and volume, respectively. However, all MWC process effluents, including stack emissions, solid residues, and wastewater, must be considered and managed in an environmentally acceptable manner. Solid residuals from MWC facilities are of particular concern because heavy metals such as lead, cadmium, and chromium and other inorganic species originally present in municipal waste are concentrated in these ashes.

Incineration residuals are classified into several primary categories: bottom ash recovered from the primary combustor; fly ash recovered through removal of particulates entrained in the combustion gas stream; scrubber residue resulting from acid gas removal from the combustion gas stream; and combined ash that is a blend of bottom ash, fly ash, and other residuals. Fly ash typically is recovered using either electrostatic precipitators or baghouses. Scrubber residue is recovered either as a slurry (wet) or as a dry particulate stream. Each residual type exhibits different physical and chemical characteristics that are dependent on facility design, operating conditions, and feed (waste) characteristics.

A thorough understanding of the physical, chemical, and structural properties of ash is required to estimate potential environmental threats from these materials and to

develop appropriate management strategies. This paper examines the bulk properties of several MWC ashes and the distribution of these properties within particle-size fractions of the ash. Properties examined extend beyond distribution of heavy metals because physical and chemical properties of major ash constituents most likely will play a determining role in the fate and management of the regulated heavy metals.

MATERIALS AND METHODS

Incinerator Sampled

Ash utilized in this study was sampled from four incinerators at three locations in Canada, New Jersey, and Massachusetts. Two incinerators sampled were part of a system of incinerators burning municipal solid waste (MSW) in Canada. A three-tiered vibrating grate primary combustion chamber provided a mean residence time of approximately three hours. Incinerator #1 provided all of the combustion air as underfire air to the vibrating grate. Incinerator #3, a modified version of incinerator #1, provided 40% of the combustion air in the primary chamber as secondary air above the burning surface. In addition, a full waterwall was extended to control slagging. An acid gas scrubber was not employed in the Canadian incineration system and fly ash was collected by means of a series of two electrostatic precipitators.

The Massachusetts incinerator system employed a three-tiered stationary primary combustion chamber that

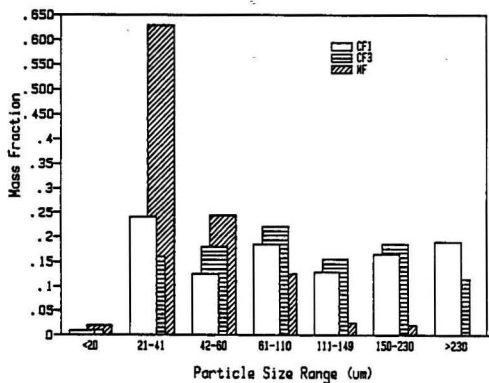


Figure 1. Particle size distribution.

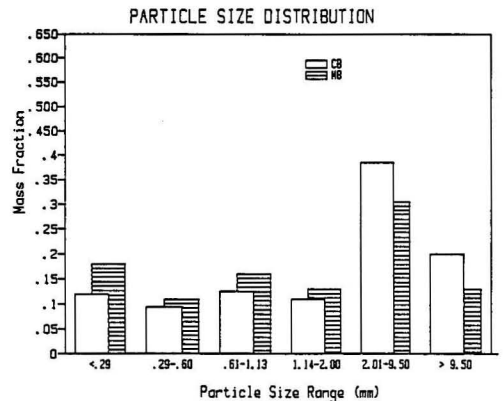


Figure 2. Particle size distribution (CB versus MB).

shifted the waste from tier to tier by means of a hydraulic ram. A calcium carbonate quench treated the flue gases before existing the stack. Fly ash was collected by means of a rotating electrostatic gravel bed coupled to a baghouse.

The New Jersey incinerator employed a rotating conical primary combustion chamber followed by an afterburner. A quench and a wet sodium hydroxide scrub contacted the flue gases before passage through a baghouse and final exit out the stack. Additional design and operating information for all systems sampled is available elsewhere [1].

Grab samples of both bottom or combined ash and fly ash were collected from each of the incinerators studied. The Canadian incinerators combined in a communal ashpit both fly ash effluent from the electrostatic precipitators and bottom ash from the fallout of the primary combustion chamber. Samples from this ashpit are designated CB. Flyash samples taken from the electrostatic precipitators of Canadian incinerator #1 and #3 are designated CF1 and CF3, respectively. Grab samples of the Massachusetts fly ash were taken from the filter baghouse and are designated MF. Bottom ash samples were taken from the conveyor exiting the quench after brief cessation of the fly ash stream and are designated MB. The New Jersey incinerator did not combine fly and bottom ashes. Bottom ash samples were taken from the ashpit and designated JB. Fly ash was sampled from the filter baghouse and designated JF.

Ash Fractionation

A particle size separator was designed to separate bulk fly ash into seven particle size ranges <20 μm , 20–41 μm , 42–60 μm , 61–110 μm , 111–149 μm , 150–230 μm , and >230 μm . The separator consisted of four interlocking stacked 14 cm O.D. polyethylene cylinders. Woven polymer mesh screens (20 μm , 40 μm , 60 μm , 110 μm , 150 μm , and 230 μm) were fitted between cylinders. Ash samples were placed in the top cylinder and the resulting sieve assembly was shaken on a roto-tap shaker to achieve fractionation. Copper rods were inserted through the sides of the containers to prevent ash agglomeration induced by static charge during separation. The rods were positioned just above the mesh screens and the outer protruding rod was grounded during the sieving process. The bulk bottom ash was sieved using commercial 8-inch O.D. screens into <0.295 mm, 0.295–0.599 mm, 0.600–1.167 mm, 1.168–1.99 mm, 2.00–9.4 mm, and >9.5 mm particle size ranges.

Analytical Methods

Total metal content was assayed using sequential nitric (HNO_3) and perchloric (HClO_4) acid digestion [2]. Elemental concentrations were determined by atomic absorption spectroscopy (AAS). An air-acetylene flame was used exclusively for metal determination with the exception of the elements aluminum and barium, which required an acetylene-nitrous oxide flame. Total volatile solids (TVS) was assayed by drying samples at 105°C to a constant mass (minimum 24 hours) followed by ash at 550°C for one hour. TVS was calculated as the change in mass between the dried and ashed sample.

Aqueous extractions of both bottom and fly ash for determination of principal soluble ionic species used deionized water and a liquid to solid ratio of 20:1 by mass. Anion analysis (chloride, sulfate, etc.) was carried out using ion vacancy high pressure liquid chromatography (HPLC) techniques and employing an Interaction ION-110 anion chromatography column and 2.5 mM sodium salicylate eluant [3]. All total metal digestions, metal assays, and anion assays were carried out at least in triplicate.

The following assays were carried out by the David Sarnoff Research Center in Princeton, NJ. Micrographs of the ash were obtained using an Amray 1400 scanning electron microscope (SEM) instrument with EDAX 9100 EDX apparatus. Surface area was determined on a Micromeritics 2100E apparatus. The samples were dried

TABLE 1. BULK DENSITY AND PARTICLE DENSITY AND SURFACE AREA OF SELECTED ASH FRACTIONS

Bulk Ash	Bulk (Apparent) Density (g/cm^3)			
	CF3	MF		
CF1	0.37			
CF3	0.57			
CB	1.04			
MF	0.73			
MB	0.82			
Ash Fraction	Particle Density (g/cm^3)		Surface Area (m^2/g)	
	CF3	MF	CF3	MF
150-230 μm	2.50	2.57	7.75	36.93
110-149 μm	2.77	3.76	5.95	15.66
61-110 μm	2.57	2.66	4.66	13.56
42-60 μm	2.66	2.93	4.79	9.31
21-41 μm	2.39	2.81	3.95	7.78
<20 μm	2.10	4.04	2.83	7.77

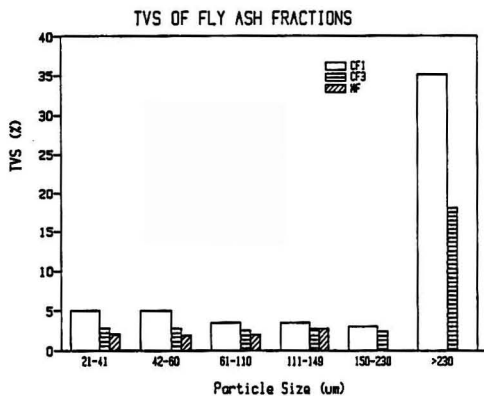


Figure 3. TVS of fly ash fractions.



Figure 5. Micrograph of Canadian fly ash.

overnight under vacuum at 100–110°C. Four to seven adsorption points in the BET range were obtained. The correlation coefficients for the data exceeded 0.9999 for all calculations. Density determinations were performed on a Micromeritics helium Autopycnometer.

RESULTS AND DISCUSSION

Physical Properties and Morphology

The particle size distributions for fly ash samples are presented in Figure 1. Both Canadian incinerators had

similar fly ash size distributions. The largest fraction, >230 µm, consisted mainly of char flakes. The finer particles appeared to consist mainly of black and white particles, imparting a salt and pepper appearance. Incinerator #1 produced more ash in the 21–41 µm and in the >230 µm particle ranges than incinerator #3; otherwise, both ashes had very similar size distributions. It was obvious from the two bulk ashes that incinerator #3 had less char particles. Since this incinerator had secondary air induction, particles most likely were more thoroughly com-

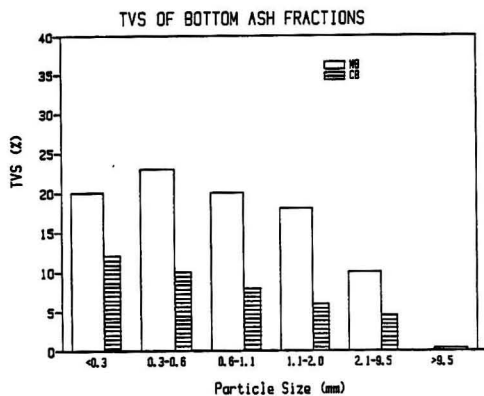


Figure 4. TVS of bottom ash fractions.

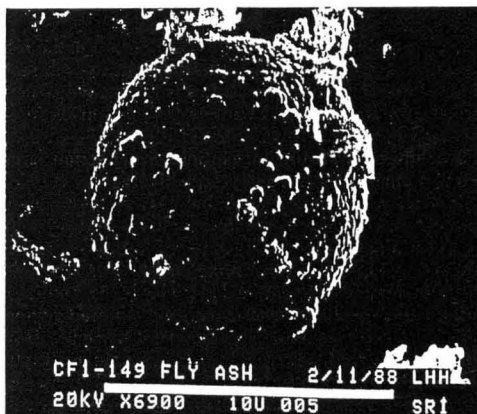


Figure 6. Canadian fly ash #1, 150-230 µm fractions.

TABLE 2. TOTAL METAL ASSAY (µg/g)

Metal	Fly Ash				Bottom Ash		
	CF1	CF3	MF	JF	CB	MB	JB
Al	42000	48800	79600	—	41400	44300	45000
Ba	2910	1870	1940	2353	1260	730	1920
Ca	77000	76100	60000	9800	65000	41000	24700
Cd	190	200	230	597	45	10	22
Cr	390	420	420	35	350	400	90
Cu	620	520	780	1900	1540	620	3600
Fe	9480	10000	13400	—	63000	44000	22000
K	14900	15500	10134	39200	3700	2900	1900
Mg	14100	15100	15900	—	11700	11800	8620
Mn	1330	1270	910	—	960	660	470
Na	21300	21400	16100	37350	6640	5360	12400
Ni	70	80	200	50	90	70	120
Pb	5530	5580	8380	4271	4540	1670	18900

busted. The Massachusetts incinerator ash was uniformly gray in appearance and had a much greater ash fraction in the lower particle ranges than the Canadian fly ashes.

Particle size distributions for the bottom ashes are presented in Figure 2. Comparing the bottom ashes, Canadian ash had 55% of the total bulk existing in the two largest particle ranges. Broken glass, metal fragments, pebbles, and slag were the major components in this fraction. After the two largest ranges, the particles were evenly distributed throughout the remaining particle ranges.

Table 1 presents the bulk density for each ash and selected particle densities and surface area analysis for selected particle size fractions. The complete CF3 particle range, excepting the >230 μm fraction, the complete CF1 and the complete MF incinerator particle range were analyzed.

Density measurement on bulk fly ash indicated that the Massachusetts fly ash was denser than both of the Canadian fly ashes. CF3 fly ash was denser than the one produced from CF1, indicating that the added combustion air was enhancing complete incineration.

Particle density for CF3 generally remained constant around 2.5 g/cm^3 while the surface area declined with decreasing particle size. MF ash particles were denser and had substantially higher available surface area. This phenomena could be attributed to either incinerator efficiency or to process equipment collection efficiency. It may be a combination of both, for example, the Massachusetts incinerator may have a higher combustion efficiency and also collects the smaller particle size more efficiently. Alternatively, since the Massachusetts incinerator uses a rotating charged-pea gravel bed, the ash particles could be reduced to smaller fragments due to the grinding action of the gravel pieces.

Total volatile solids was assayed to determine the relative amount of uncombusted materials within each particle size fraction (Figures 3 and 4). Fly ashes from all combustors exhibited similar TVS between 2% and 4% for all particle size fractions smaller than 230 μm . The CF1 and CF3 exhibited TVS for the particle size fraction larger than 230 μm of 17% and 34%, respectively.

SEM micrographs for several fly ash fractions above were obtained; two typical micrographs are presented in Figures 5 and 6. A wide diversity of highly crystalline structures were observed. Unlike coal fly ash, which exists predominantly as spherical particles [4, 5], municipal fly ash contains planar, cylindrical, and sintered agglomerations of particles as well as spherical particles. However, the spherical particles do not predominate. Taylor, et al. [6] also observed the same types of MSW fly ash particles but called them, perhaps more descriptively, "shredded sponge," "rolled paper," and "paint chips."

The most dominant feature in the micrographs was the occurrence of crystals residing on the fly ash particles. This can be explained by the "vortilization-condensation" theory proposed by Cahill and Newland [7] to explain fly ash formation. Aluminum and silicon, with boiling points above the typical combustion temperatures, would form nucleation particles whereupon volatilized elements would condense. Furuya, et al. [4] identified CaSO_4 crystals residing on fly ash particles. With the ash samples studied here, the crystalline outcroppings are most likely CaSO_4 , NaCl , or KCl .

Bulk Chemical Properties

Total metal content was determined for the bottom and fly bulk ashes using sequential nitric/perchloric acid digestion to dissolve the ash matrix (Table 2). Statistical analysis was used to identify, with a 95% confidence level, any significant differences in the partitioning behavior of the metals. Using a least significant difference

TABLE 3. LEAST-SIGNIFICANT-DIFFERENCE MEANS TEST

Metal	Means Test					
	MF	CF3	JB	MB	CF1	CB
Al	MF	CF3	JB	MB	CF1	CB
Ba	CF1	MF	JB	CF3	CB	MB
Ca	CF1	CF3	CB	MF	MB	JB
Cd	MF	CF3	CF1	CB	MB	JB
Cr	CF3	MF	MB	CF1	CB	JB
Cu	JB	CB	MF	CF1	MB	CF3
Fe	CB	MB	JB	MF	CF3	CF1
K	CF3	CF1	MF	CB	MB	JB
Mg	MF	CF3	CF1	MB	CB	JB
Mn	CF3	CF1	CB	MF	MB	JB
Na	CF3	CF1	MF	JB	CB	MB
Ni	MF	JB	CB	CF3	MB	CF1
Pb	JB	MF	CF3	CF1	CB	MB

(LSD) t-test, generated by analysis of variance (ANOVA) on each mean metal concentration, gave the necessary correlations. Since the acid digestion experimental design contained equal cell sizes, the pairwise t-tests performed are equivalent to Fisher's least-significant-difference test for all main-effect means [8]. The results are indicated in Table 3. The ashes are listed in decreasing order with the ash having the largest mean concentration being listed first. Ashes that are statistically similar are grouped together by a continuous underline; ashes that are significantly different have a separate underline.

Significant differences existed between the ashes. Potassium, sodium, and cadmium favored deposition on fly ash by a factor of three. Massachusetts fly ash showed a significant amount of nickel, at least twice that of its bottom ash. The Canadian bottom ash had at least six times more iron than the fly ashes from the same facility. Calcium, magnesium, and manganese also favored deposition to the fly ash, but not as strongly as the previous metals.

Aluminum, barium, chromium, copper, and lead were equally distributed between the bottom and fly ashes. However, the New Jersey bottom ash had more than twice the amount of lead than all of the other ashes and more than twice the amount of sodium than the other bottom ashes. Also, lead was four times more prevalent in the Massachusetts fly ash than in its bottom ash. Since the

TABLE 4. PRINCIPAL AQUEOUS EXTRACTABLE IONIC SPECIES

Species	Mass Balance (mg/g ash)					
	CF1	CF3	MF	CB	MB	JB
SO_4	70.5	97.4	61.3	10.6	11.1	3.2
Cl	47.3	51.8	11.8	11.3	1.9	2.5
Ca	34.8	34.2	19.2	8.0	5.8	3.0
K	31.9	34.3	6.6	0.6	0.4	0.7
Na	22.2	24.0	13.2	1.3	2.1	1.8
Total	206.7	241.7	112.1	31.7	21.3	11.9
TDS	234.0	248.0	137.0	42.3	24.9	11.4
% Error	11.7	2.5	18.2	25.0	14.6	2.3
Species	Charge Balance (meq/g ash)					
	CF1	CF3	MF	CB	MB	JB
SO_4	-0.73	-1.01	-0.64	-0.11	-0.12	-0.03
Cl	-1.33	-1.46	-0.33	-0.32	-0.05	-0.07
Ca	0.87	0.85	0.48	0.20	0.14	0.07
K	0.82	0.88	0.17	0.02	0.01	0.02
Na	0.97	1.04	0.57	0.06	0.09	0.08
Total	0.58	0.30	0.25	-0.16	0.08	0.07
% Error	58.20	29.80	25.10	15.70	7.80	6.90

TABLE 5. "CORE" METAL CONCENTRATION (mg/g Average Values)

Species	CF1	CF3	MF
Al	43.0	48.0	8.0
Ba	2.5	3.0	0.8
Fe	10.0	10.0	12.0
K	22.0	24.0	10.0
Mn	1.2	1.3	0.8
Ni	0.1	0.1	1.4

concentrations greatly varied in bottom ash samples, lead did not show a strong statistical difference between the ashes even though there were striking differences.

Generally, the fly ash metal concentrations fell within a close range; the Canadian fly ashes were very similar in metal composition except that CF3 appeared to have a slightly greater concentration in all metals than CF1; this disparity, however, was statistically insignificant. On the other extreme, New Jersey bottom ash frequently had the lowest concentration in metals with one notable exception, lead. The predominant metal species found were aluminum, calcium, iron, potassium, magnesium, and sodium.

Aqueous batch extractions were carried out to identify principal cationic and anionic species that readily partitioned from ash into solution. Three serial extractions were carried out at a 20:1 liquid-to-solid (deionized water: ash) ratio. Mass and charge balances were used to verify measurements. TDS was assumed to equal the sum of mass of the ionic species in solution and total charge neutrality was assumed. Results are presented in Table 4.

The results indicated that potassium and sodium exist mainly as chlorides. All three ionic species remained constant throughout extraction ratios studied. The Canadian incinerators each contained approximately 5% chloride salts by weight while the Massachusetts incinerator contained less than 1% chloride salts. A significant mass fraction of each of the fly ashes examined was water soluble, with 23.4%, 24.8% and 13.7% soluble in deionized water for CF1, and CF3, and MF ashes, respectively.

It appears calcium existed primarily as sulfates since levels in solution of both species increased with increasing dilution factor. However, calcium alone accounted for only 20% of the sulfate extracted from ash; therefore, potassium and sodium must also exist as sulfates. The minimum amount of sulfates extracted from the Canadian fly ash was approximately 7-10%. The Massachusetts fly ash, though, attained a maximum extractable amount of ap-

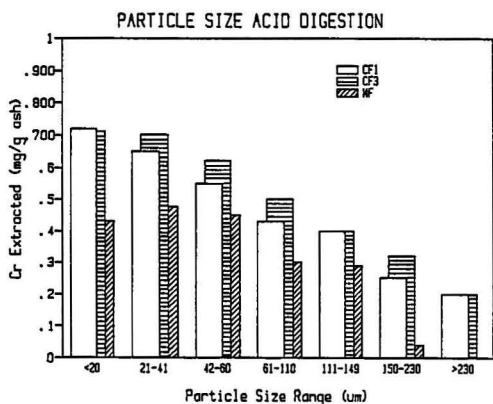


Figure 8. Particle size acid digestion.

proximately 6% sulfate by weight. Nitrate was also detected although the amount present (<2 mg/g ash) was negligible in comparison to chloride and sulfate. The trends displayed in the fly ash solutions also were apparent in the bottom ash solutions.

Generally, for fly ash, individual species analysis accounted for over 85% of the TDS. TDS values were usually higher than the sum of the major species indicating that either another species was present in solution or the salts were not completely free of water. Similar trends for the bottom ash were displayed; however, the error was generally greater. The Canadian bottom ash showed the greatest error, usually around 40%.

The charge balances for fly ash solutions showed approximately 20% error while the bottom ash solutions displayed lower errors. The charge balances were usually positive indicating that an anionic species, most likely carbonate, was not accounted for.

Metals Distributions within Particle Size Fractions

Knowledge of metals distributions within ash particle size fractions is important for clarifying formation mechanisms and management approaches. Kaufherr and Lichtman [9] found aluminum, potassium, magnesium, and iron to be common throughout various sized particles. Hansen and Fisher [12] found these same metals with titanium, sodium, hafnium, and thorium were associated with the aluminosilicate matrix in coal fly ash.

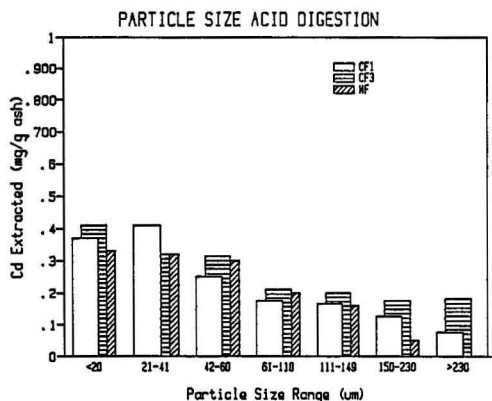


Figure 7. Particle size acid digestion.

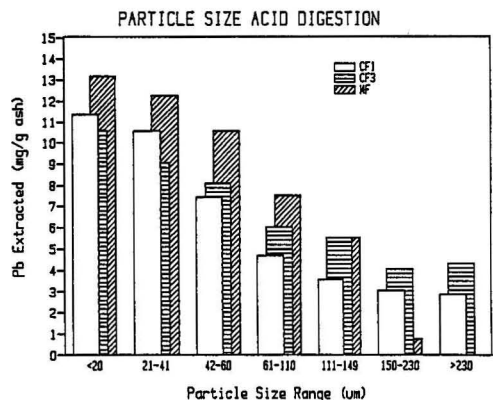


Figure 9. Particle size acid digestion.

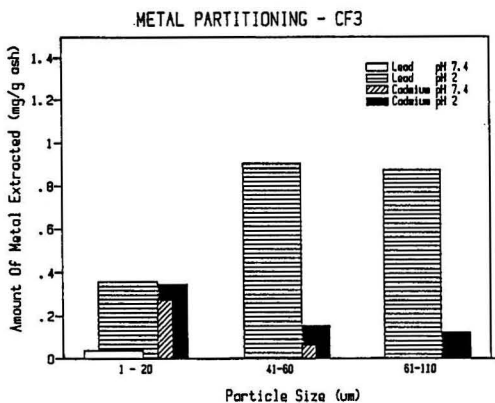


Figure 10. Metal partitioning—CF3.

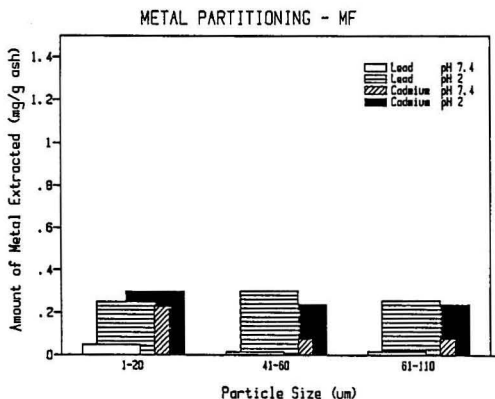


Figure 11. Metal partitioning—MF.

Cahill and Newland [7] theorized that metals with a higher boiling point than that typically found in a combustion chamber would serve as the nucleation particles. Thus, aluminum, silicon, and manganese would form the core of the fly ash particle. Metals with a lower boiling point would volatilize in the combustion chamber and condense onto the fly ash particle. Lead and cadmium would be expected to be surface deposited metals since they would readily volatilize.

Total metal content for each fly ash particle size range was assayed. The Canadian fly ashes were very similar in their elemental composition with CF3 containing slightly higher metal concentrations. In all cases except for nickel, each ash displayed analogous characteristics. If the metal concentration increased with decreasing particle size, it did so for all three ashes. Most metals displayed this trend, although aluminum, manganese, barium, iron, nickel, and potassium generally remained constant throughout the particle range (Table 5). This would indicate that these elements comprise the core of the ash matrix. Nickel concentration decreased from approximately 1.4 mg/g ash for particles smaller than 110 µm to 0.2 mg/g ash for particle larger than 110 µm. The other elements concentrated on the smaller ash particles.

The surface area of each particle range was used for comparison because an increased amount of surface area is available for condensation as the particle size decreased. The metal concentrations for MF, CF1, and CF3

ash were normalized using the surface area of each particle range. The "core" metals, aluminum, barium, iron, manganese, nickel, and potassium, remained relatively constant although concentrations increased slightly as the particle size decreased. Cadmium, chromium, and lead as well as the remaining metals indicated a sharp preference towards the smaller particle sizes (Figures 7, 8, and 9). In most cases the increases were predominantly linear.

It was of particular interest to ascertain fly ash leaching behavior for cadmium and lead at pH 7.4 and 2 because these pHs are physiologically relevant. Inhalation of particles may result in lung deposition where the pH of the environment is equivalent to that of blood and remains stable at 7.4. Gastric pH, important because of possible ash ingestion, is acidic and usually remains at about 2.0. Ingestion occurs when particles deposited in the nasal, pharyngeal, and bronchial regions of the respiratory system are transported by ciliary action to the stomach [11]. Inhalation of fly ash could represent potentially more of a risk than ingestion because absorption is directly into the bloodstream rather than passage through the liver or intestine. About 25% of inhaled airborne particles settle in the lung tissue and, thus, accumulate with increased exposure [12]. Particles less than 1 micron in diameter deposit predominantly in the alveolar regions of the lung where absorption efficiency of most trace elements is between 50-80% [13]. Figures 10 and 11 present the aqueous phase of cadmium and lead off the surface of three fractions of the MF and CF3 ashes. An equilibrium pH of 7.4 and 2.0 was maintained with hydrochloric acid because the buffering capacities of the ash fractions tended to raise solution pH above neutrality. A 20:1 liquid-to-solid ratio was employed and extractions equilibrated for 24 hours. Lead did not seem to be mobile at a pH 7.4 in the larger particle size ranges. However, the fraction of particulate between 1-20 µm showed a significant amount of mobile lead. At a pH of 2, substantial amounts of lead were seen to leach from the surface and there appeared to be no correlation between particle size and amount of lead leached. In contrast, cadmium leached significantly at both pHs and this leaching was linear with decreasing particle size.

The amount of lead extracted from the MF fraction 1-20 µm at a pH of 7.4 is approximately 0.5% of the total lead present. In contrast, at a pH of 2 and a particle fraction size of 41-60 µm (greatest leaching) the amount of lead leached is approximately 3% of the total lead. The CF3 data is similar with the 1-20 µm fraction at pH 7.4 leaching 0.5% of the total lead and at a pH of 2, (greatest leaching), 11.3% of the total lead.

The cadmium leached, regardless of particle size or pH, is a substantial fraction of the total cadmium available. At the most severe conditions and smallest particle size for the MF, approximately 93% of the total cadmium was removed.

CONCLUSIONS

Proper management of municipal waste combustor ashes requires a detailed understanding of the physical and chemical properties of these materials, not limited to the presence of regulated heavy metals. Configuration and operational parameters of the incinerator influence both the structure of the ash matrix and the partitioning of the heavy metals in the fly and bottom ashes. Physical properties, including particle size distributions, surface area, morphology, and densities, have been determined for several ashes and ash fractions separated, based on particle size. Chemical characteristics also have been determined for the same ashes. Principal aqueous extracta-

ble ions present in ashes include sulfate, chloride, calcium, sodium, and potassium. Up to 24% (by mass) of the fly ashes examined were soluble in deionized water. Cadmium, chromium, and lead were present in highest concentrations on the smallest particle size fractions of fly ash. Extraction of lead and cadmium was examined at pHs of 7.4 and 2, representing physiological pH of the respiratory tract and stomach. Less than 12% and 0.5% of the total lead was extractable at pH 2 and 7.4, respectively. Conversely, a large percentage of the total cadmium (up to 93%) was extractable at these pHs.

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Exposure and Risk Assessment for a Proposed Hazardous Waste Incinerator

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In supporting a firm's application for a Part B permit to operate a hazardous waste incinerator in Rhode Island, an exposure/risk assessment was conducted estimating: the maximum concentrations associated with the emissions of hazardous constituents from the incinerator; and the risks due to the exposure to these concentrations. This included determining the probability of the Most Exposed Individual (MEI) developing a cancer case and the number of cancer cases that may develop within a 50-km radius of the proposed incinerator.

INTRODUCTION

Exposure and risk assessments were conducted for a proposed hazardous waste incinerator in order to determine:

- The ambient air exposure levels created by these emissions;
- the incremental health risks to the most exposed individual (MEI) posed by air emissions from the incinerator. (The MEI is defined as the individual who is exposed to the highest concentrations of hazardous constituents emitted by the incinerator.); and
- the incremental health risks to the total population within a 50 km radius of the incinerator as a result of exposure to the emissions from the incinerator.

These assessments were prepared in the interest of providing the Rhode Island Department of Environmental Management (DEM) and the public with a full disclosure of the predicted air quality impacts of the proposed incinerator.

This paper discusses how these assessments were conducted, (including the selection of waste incineration scenarios, operating levels, and dispersion modeling), and what results were attained.

EXPOSURE ASSESSMENT

Description of the Two Waste Incineration Scenarios

Emissions and exposures for two theoretical waste incineration scenarios were investigated. These scenarios are described below.

Scenario A, in which the toxic constituents listed in Table 1 of proposed Regulation 22 of the Rhode Island Air Toxics Guidelines are assumed to be fed to the incinerator at the highest rates likely to be employed during full-scale operation of the incinerator. (Proposed Regulation 22 sets the compliance requirements for individuals to obtain permits to construct, install, or modify any stationary source.) Included in this scenario was the inorganic metal lead since lead emission levels are being proposed by EPA for hazardous waste incinerators. Consequently, this scenario is designed to show that the incinerator always will comply with the ambient air levels (the acceptable ambient air exposure levels) set forth in proposed Regulation 22. The estimated feed rates for these constituents are listed in Table 1.

Scenario B, in which only pesticide wastes are fed to the incinerator at the highest feed rates likely ever to be employed in full-scale operation of the incinerator. This scenario is designed to show that the incinerator can burn

TABLE 1. ASSUMED FEED RATES OF REGULATION 22 ORGANIC CONSTITUENTS [1], [2]
SCENARIO A

Constituent	Percentage of Total	Constituent Feed Rate (lbs/hr)
Acrylonitrile	8	212
Aniline	<0.05	1
O-Anisidine	<0.05	1
Benzene	8	212
Benzidine	<0.05	1
Benzotrachloride	<0.05	1
Benzyl Chloride	<0.05	1
Carbon Tetrachloride	8	212
Chloroform	3	80
3,3'-Dichlorobenzidine	<0.05	1
Diocetyl Phthalate	<0.05	1
Diphenyl	<0.05	1
Diphenylamine	<0.05	1
Epichlorohydrin	<0.05	1
Ethylene Dichloride	8	212
Ethylene Oxide	2	53
Hydrazine	<0.05	1
Methyl Cellosolve	<0.05	1
Methylene Bisphenyl Isocyanate	<0.05	1
4,4'-Methylene bis	<0.05	1
Methylene Chloride	8	212
5-Nitro o-anisidine	<0.05	1
2-Nitropropane	<0.05	1
Perchloroethylene	8	212
Styrene	<0.05	1
Toluene	>15	402
Toluene-2,4-diisocyanate	<0.05	1
o-Toluidine	<0.05	1
1,1,2 Trichloroethane	8	212
Trichloroethylene	8	212
Triethylamine	<0.05	1
Xylenes	>15	403
	100	2,654

Constituent	Feed Rate (lbs/hr)
Antimony	4.19
Arsenic	0.13
Cadmium	0.07
Chromium	2.20
Lead	4.19
Manganese	4.19
Nickel	0.18

very large amounts (very high feed rates) of highly toxic pesticide wastes without creating unacceptable ambient air exposures of the toxic pesticide ingredients. In the exposure assessment it was assumed that the feed rate of any of the pesticides would not exceed 10 lb/hr during any normal waste feed scenario employed during full-scale operation of the incinerator.

It is extremely unlikely that the Scenario A waste feed regime ever will be encountered in full-scale operation of the incinerator. This scenario assumes the highest likely feed rates of organic wastes to the incinerator and further assumes that the organic content of these waste feeds is composed exclusively of those organic constituents listed in proposed Regulation 22. The organic constituents of hazardous wastes typically burned in incinerators are dominated by comparatively easy to burn and generally less toxic non-chlorinated solvents. Thus, it is very unlikely that the assumed aggregate feed rates of Regulation 22 organic constituents ever will be encountered in actual operations.

Scenario A also assumes the highest likely feed rates of the inorganic constituents listed in proposed Regulations 22 (and for lead). It is unlikely that these high feed rates of inorganic constituents will coexist with the high feed rates of organic constituents discussed above. For this reason and the reason cited above, Scenario A is clearly a conservative worst-case scenario.

It also is extremely unlikely that Scenario B ever will be encountered in full-scale operation of the incinerator because it will be unusual for the facility to receive wastes that are exclusively concentrated pesticide wastes. Typically, pesticide waste receipts will be wastes that are contaminated with pesticides at low concentrations (e.g., used pesticide containers). Occasionally, concentrated pesticide wastes will be received, but these receipts typically will compose a small portion of daily waste receipts and will be blended with other waste receipts for incineration. If large amounts of pesticide wastes are received (e.g., from the planned disposal of large stocks of a cancelled pesticide), the facility will store these receipts and gradually blend them with other wastes before they are incinerated. Thus, Scenario B is a conservative worst-case scenario.

Description of the Two Operating Levels

For each scenario, the emissions and exposures for two operating levels were assessed:

1. The highest level at which destruction and/or removal efficiencies (DREs) for organic constituents and the removal efficiencies (REs) for HCl and HF will be 99.9999% and 99.998%, respectively [4].

2. The lowest level at which DREs for organic constituents and REs for HCl and HF will be 99.99% and 99%, respectively.

Metal emissions and exposures for a worst-case operating level were assessed. This worst-case operating level assumes that the removal efficiencies (REs) for metals are 99.9% [5].

The highest level is that at which the incinerator is designed to operate. This level will be demonstrated in the trial burn of the incinerator, and, during full-scale operation, it will be the normal level of operation. The lowest level is the level that the incinerator is required by regulations to achieve (except when burning F020, F021, F022, F023, F026, and/or F027 wastes) and is the level that all permitted hazardous waste incinerators have demonstrated as achievable. This is the lowest level at which the incinerator can operate because automatic waste feed cut-off controls will stop waste feeds when this level fails to be achieved. During full-scale operation of the incinerator, it is expected that this level of operation will be experienced infrequently and for only comparatively short periods of time (e.g., a few minutes) during such occurrences.

The emission rates for the Regulation 22 constituents are listed in Table 2. Since the feed rates for the pesticides under Scenario B are the same (10 lb/hr), the emission rates for these pesticides will be the same under the worst-case and normal operating conditions (1.26 E-04 g/sec and 1.26 E-06 g/sec, respectively).

Description of the Dispersion Modeling

For the exposure assessment, the emission rates of each of the subject toxic constituents were calculated for each operating level within each scenario. Then the maximum annual average exposure concentrations for each of the toxic constituents for each operating level within each

TABLE 2. REGULATION 22 ORGANIC CONSTITUENTS EMISSIONS FROM INCINERATOR UNDER AVERAGE AND WORST-CASE OPERATING CONDITIONS [6] SCENARIO A

Regulation 22 Organic Constituent	Stack Emission Rate (g/sec)	
	Average	Worst-Case
Acrylonitrile	2.67E-05	2.67E-03
Aniline	1.26E-07	1.26E-05
O-Anisidine	1.26E-07	1.26E-05
Benzene	2.67E-05	2.67E-03
Benzidine	1.26E-07	1.26E-05
Benzotrichloride	1.26E-07	1.26E-05
Benzyl Chloride	1.26E-07	1.26E-05
Carbon Tetrachloride	2.67E-05	2.67E-03
Chloroform	1.01E-05	1.01E-03
3,3'-Dichlorobenzidine	1.26E-07	1.26E-05
Dioctyl Phthalate	1.26E-07	1.26E-05
Diphenyl	1.26E-07	1.26E-05
Diphenylamine	1.26E-07	1.26E-05
Epichlorohydrin	1.26E-07	1.26E-05
Ethylene Dichloride	2.67E-05	2.67E-03
Ethylene Oxide	6.68E-06	6.68E-04
Hydrazine	1.26E-07	1.26E-05
Methyl Cellosolve	1.26E-07	1.26E-05
Methylene Bisphenyl Isocyanate	1.26E-07	1.26E-05
4,4'-Methylene bis	1.26E-07	1.26E-05
Methylene Chloride	2.67E-05	2.67E-03
5-Nitro o-anisidine	1.26E-07	1.26E-05
2-Nitropropane	1.26E-07	1.26E-05
Perchloroethylene	2.67E-05	2.67E-03
Styrene	1.26E-07	1.26E-05
Toluene	5.06E-05	5.06E-03
Toluene-2,4-diisocyanate	1.26E-07	1.26E-05
o-Toluidine	1.26E-07	1.26E-05
1,1,2-Trichloroethane	2.67E-05	2.67E-03
Trichloroethylene	2.67E-05	2.67E-03
Triethylamine	1.26E-07	1.26E-05
Xylenes	5.08E-05	5.08E-03

Constituent	Stack Emission Rate (g/sec)
Antimony	5.28E-04
Arsenic	1.64E-05
Cadmium	8.82E-06
Chromium	1.39E-05
Lead	5.28E-04
Manganese	5.28E-04
Nickel	2.52E-06

TABLE 3. PREDICTED MAXIMUM ANNUAL AVERAGE EXPOSURE CONCENTRATIONS ($\mu\text{g}/\text{m}^3$) OF LEAD AND REGULATION 22 CONSTITUENTS FROM INCINERATOR EMISSIONS UNDER AVERAGE AND WORST CASE OPERATING CONDITIONS [8] SCENARIO A

Chemical	Operating Conditions	
	Average	Worst-Case
ORGANICS		
Acrylonitrile	2.59E-05	2.59E-03
Aniline	1.22E-07	1.22E-05
O-Anisidine	1.22E-07	1.22E-05
Benzene	2.59E-05	2.59E-03
Benzidine	1.22E-07	1.22E-05
Benzotrichloride	1.22E-07	1.22E-05
Benzyl Chloride	1.22E-07	1.22E-05
Carbon Tetrachloride	2.59E-05	2.59E-03
Chloroform	9.77E-06	9.77E-04
3,3'-Dichlorobenzidine	1.22E-07	1.22E-05
Dioctyl Phthalate	1.22E-07	1.22E-05
Diphenyl	1.22E-07	1.22E-05
Diphenylamine	1.22E-07	1.22E-05
Epichlorohydrin	1.22E-07	1.22E-05
Ethylene Dichloride	2.59E-05	2.59E-03
Ethylene Oxide	6.47E-06	6.47E-04
Hydrazine	1.22E-07	1.22E-05
Methyl Cellosolve	1.22E-07	1.22E-05
Methylene Bisphenyl Isocyanate	1.22E-07	1.22E-05
4,4'-Methylene bis	1.22E-07	1.22E-05
Methylene Chloride	2.59E-05	2.59E-03
5-Nitro o-anisidine	1.22E-07	1.22E-05
2-Nitropropane	1.22E-07	1.22E-05
Perchloroethylene	2.59E-05	2.59E-03
Styrene	1.22E-07	1.22E-05
Toluene	4.91E-05	4.91E-03
Toluene-2,4-diisocyanate	1.22E-07	1.22E-05
o-Toluidine	1.22E-07	1.22E-05
1,1,2-Trichloroethane	2.59E-05	2.59E-03
Trichloroethylene	2.59E-05	2.59E-03
Triethylamine	1.22E-07	1.22E-05
Xylenes	4.92E-05	4.92E-03
INORGANICS		
HCl	1.83E-03	9.16E-01
HF	1.78E-06	8.91E-04

Chemical	Worst-Case Conditions
INORGANICS	
Antimony	5.11E-04
Arsenic	1.59E-05
Cadmium	8.54E-06
Chromium	1.34E-05
Lead	5.11E-04
Manganese	5.11E-04
Nickel	2.44E-06

scenario were calculated using the calculated emission rates and EPA's Industrial Source Complex Long Term (ISCLT) dispersion model [7]. The ISCLT is a steady-state Gaussian plume model that can be used to assess pollutant concentrations from a wide variety of industrial air emission sources. The maximum exposure concentration levels for Scenario A are presented in Table 3. Since the emission rates for the pesticides under Scenario B are the same, the maximum exposure concentration levels for the pesticides are the same ($1.22 \text{ E-}06 \mu\text{g}/\text{m}^3$ and $1.22 \text{ E-}04 \mu\text{g}/\text{m}^3$ under average and worst-case operating conditions, respectively).

RISK ASSESSMENT

Maximum Exposed Individual (MEI) Risks and Hazard Indices

MEI risk values were obtained by taking the ratio of the maximum exposure concentration for each constituent

from the exposure assessment to its accepted ambient level (AAL) as calculated by DEM in the Rhode Island guidelines. For pesticides, their AALs were based on the EPA's Integrated Risk Information System (IRIS) Chemical Files [9]. For the risk assessment, individual pollutants were separated into two categories of toxicity depending on whether they induce carcinogenic or noncarcinogenic effects. The MEI risk estimates the risk for carcinogenic constituents; it represents the upper-bound lifetime increased probability of cancer due to the combined chronic exposures of a single individual to multiple carcinogens. The carcinogenic risk was calculated by multiplying the ratio of the constituent's exposure concentration level to its AAL by $1 \text{ E-}06$. Multiplying by $1 \text{ E-}06$ was performed because the AALs were

TABLE 4. MEI RISK^a FROM REGULATION 22 CARCINOGENS SCENARIO A

Chemical	Operating Conditions	
	Average	Worst-Case
ORGANICS		
Acrylonitrile	4 E-10	4 E-08
o-Anisidine	6 E-12	6 E-10
Benzene	3 E-10	3 E-08
Benzidine	6 E-09	6 E-07
Benzotrichloride	2 E-10	2 E-08
Benzyl Chloride	1 E-11	1 E-09
Carbon Tetrachloride	9 E-10	9 E-08
Chloroform	2 E-10	2 E-08
3,3'-Dichlorobenzidine	6 E-11	6 E-09
Diocetyl Phthalate	2 E-13	2 E-11
Epichlorohydrin	2 E-13	2 E-11
Ethylene Dichloride	6 E-10	6 E-08
Ethylene Oxide	6 E-10	6 E-08
Hydrazine	4 E-10	4 E-08
5-Nitro-o-anisidine	2 E-12	2 E-10
Methylene Chloride	1 E-10	1 E-08
Perchloroethylene	5 E-10	5 E-08
Toluene-2,4-diisocyanate	4 E-12	4 E-10
o-Toluidine	3 E-12	3 E-10
1,1,2-Trichloroethane	4 E-12	4 E-10
Trichloroethylene	9 E-11	9 E-09
INORGANICS ^b		
Arsenic	8 E-08	8 E-08
Cadmium	1 E-08	1 E-08
Chromium	2 E-07	2 E-07
Nickel	1 E-09	1 E-09
MEI Risk ^c	3 E-07	1 E-06

^a A 1 E-06 cancer risk represents a 1 in 1,000,000 chance of developing cancer.
^b For the inorganics, the exposure assessment calculated concentrations only under worst-case operating conditions. Therefore, the risks listed under average operating conditions are the same as the risks listed under worst-case operating conditions.
^c These values were rounded to one significant number.

calculated based on a 1 E-06 excess lifetime cancer risk level. A risk level of 1 E-06 indicates that there is a one in 1,000,000 chance that cancer will develop in a person who is chronically exposed (i.e., exposed for a period of 70 years) to a maximum concentration of a carcinogenic compound equal to the AAL. For noncarcinogens, a MEI hazard index was estimated. The MEI hazard index is a parameter used by risk analysts to evaluate whether a potential health risk is posed by exposure to multiple noncarcinogens. A hazard index less than one generally indicates the lack of potential health risk from noncarcinogens. The greater the difference between the MEI and one, the greater the confidence one has that there is no health risk.

TABLE 5. MEI RISK^a FROM CARCINOGENIC PESTICIDES SCENARIO B

Chemical	Operating Conditions	
	Average	Worst-Case
Aldrin	4 E-10	4 E-08
Chlordane	6 E-10	6 E-08
DDT	1 E-10	1 E-08
Dieldrin	1 E-09	1 E-07
Ethylene Dibromide	1 E-09	1 E-07
Heptachlor Epoxide	1 E-09	1 E-07
Lindane	4 E-10	4 E-08
Toxaphene	4 E-10	4 E-08
MEI Risk ^b	5 E-09	5 E-07

^a A 1 E-06 cancer risk represents a 1 in 1,000,000 chance of developing cancer.
^b These values were rounded to one significant number.

TABLE 6. MEI HAZARD INDEX^a FOR LEAD AND REGULATION 22 NONCARCINOGENS SCENARIO A

Chemical	Operating Conditions	
	Average	Worst-Case
ORGANICS		
Aniline	2 E-07	2 E-05
Diphenyl	3 E-07	3 E-05
Diphenylamine	6 E-10	6 E-08
Methyl Cellosolve	6 E-09	6 E-07
Methylene Biphenyl Isocyanate	2 E-06	2 E-04
4,4'-Methylene bis	5 E-07	5 E-05
2-Nitropropane	7 E-07	7 E-05
Styrene	6 E-09	6 E-07
Toluene	1 E-07	1 E-05
Triethylamine	6 E-09	6 E-07
Xylenes	3 E-07	3 E-05
INORGANICS ^b		
Antimony	1 E-05	1 E-05
HCl	9 E-06	5 E-03
HF	6 E-07	3 E-04
Lead	3 E-04	3 E-04
Manganese	3 E-03	3 E-03
MEI Hazard Index ^c	3 E-03	9 E-03

^a Note that these values are not related to risk estimates, but rather indicate the distance between the hazard index and one—i.e., 1 E-05 represents a hazard index five orders of magnitude less than one.
^b For antimony, lead and manganese, the exposure assessment calculated concentrations only under worst case operating conditions. Therefore, the ratios listed under average operating conditions are the same as the ratios listed under worst-case operating conditions.
^c These values were rounded to one significant number.

Carcinogens

The estimated MEI risks due to the Scenario A and Scenario B carcinogens are presented in Tables 4 and 5, respectively. The estimated total MEI risk resulting from the combined lifetime exposures to Scenario A carcinogens under the worst-case incinerator operating conditions is 1 E-06 (one is a million), which is the lower end of the range of acceptable risk levels established by DEM. The estimated total MEI risk resulting from the combined lifetime exposures to Scenario B carcinogens under the worst case incinerator conditions is 5 E-07, which is far below the lower end of the range of acceptable risk levels given by DEM.

Because the assumptions used in the exposure assessment report clearly result in an overstatement of the

TABLE 7. MEI HAZARD INDEX^a FOR NONCARCINOGENIC PESTICIDES SCENARIO B

Pesticide	Operating Conditions	
	Average	Worst-Case
Carbaryl	3 E-09	3 E-07
Dalapon	4 E-09	4 E-07
Dinoseb	9 E-08	9 E-06
Disulfoton	3 E-07	3 E-05
Endosulfan	2 E-05	2 E-03
Malathion	2 E-08	2 E-06
Sodium Diethyldithiocarbamate	1 E-08	1 E-06
Strychnine	1 E-06	1 E-04
Warfarin	1 E-06	1 E-04
Zineb	7 E-09	7 E-07
MEI Hazard Index ^b	2 E-05	2 E-03

^a Note that these values are not related to risk estimates, but rather indicate the distance between the hazard index and one—i.e., 1 E-05 represents a hazard index five orders of magnitude less than one.
^b These values were rounded to one significant number.

TABLE 8. TOTAL POPULATION RISK FOR REGULATION 22
CARCINOGENS
SCENARIO A

Chemical	Operating Conditions	
	Average	Worst-Case
ORGANICS		
Acrylonitrile	9 E-06	9 E-04
o-Anisidine	1 E-07	1 E-05
Benzene	7 E-06	7 E-04
Benzidine	1 E-04	1 E-02
Benzotrichloride	5 E-06	5 E-04
Benzyl Chloride	2 E-07	2 E-05
Carbon Tetrachloride	2 E-05	2 E-03
Chloroform	5 E-06	5 E-04
3,3'-Dichlorobenzidine	1 E-06	1 E-04
Diethyl Phthalate	5 E-09	5 E-07
Epichlorohydrin	5 E-09	5 E-07
Ethylene Dichloride	1 E-05	1 E-03
Ethylene Oxide	1 E-05	1 E-03
Hydrazine	9 E-06	9 E-04
5-Nitro-o-anisidine	5 E-08	5 E-06
Methylene Chloride	2 E-06	2 E-04
Perchloroethylene	1 E-05	1 E-03
Toluene-2,4-diisocyanate	9 E-08	9 E-06
o-Toluidine	7 E-08	7 E-06
1,1,2-Trichloroethane	9 E-08	9 E-06
Trichloroethylene	2 E-06	2 E-04
INORGANICS^a		
Arsenic	2 E-03	2 E-03
Cadmium	2 E-04	2 E-04
Chromium	2 E-03	4 E-03
Nickel	2 E-05	2 E-05
Total Population Risk^b	6 E-03	3 E-02^c

^a For the inorganics, the exposure assessment calculated concentrations only under worst-case operating conditions. Therefore, the risks listed under average operating conditions are the same as the risks listed under worst-case operating conditions.

^b These values were rounded to one significant number.

^c A 3 E-02 total population risk represents 0.03 additional cases of cancer for the 1,600,000 exposed population.

constituent emissions from the incinerator and the resulting maximum annual average exposure concentrations of these constituents, these MEI risks are also overstated and therefore, are very conservative estimates of adverse health effects. Therefore, the actual MEI risks are likely to be lower than the values here estimated.

Noncarcinogens

The estimated MEI hazard indexes for the Scenario A and B noncarcinogens are presented in Tables 6 and 7, respectively. The MEI hazard index resulting from the

TABLE 9. TOTAL POPULATION RISK FOR CARCINOGENIC PESTICIDES
SCENARIO B

Pesticides	Operating Conditions	
	Average	Worst-Case
Aldrin	9 E-06	9 E-04
Chlordane	1 E-05	1 E-03
DDT	2 E-06	2 E-04
Dieldrin	3 E-05	3 E-03
Ethylene Dibromide	3 E-05	3 E-03
Heptachlor Epoxide	3 E-05	3 E-03
Lindane	9 E-06	9 E-04
Toxaphene	9 E-06	9 E-04
Total Population Risk^a	1 E-04	1 E-02^b

^a These values were rounded to one significant number.

^b A 1 E-02 total population risk represents 0.01 additional cases of cancer for the 1,600,000 exposed population.

combined lifetime exposures to Scenario A noncarcinogens under the worst case incinerator operating conditions is 9 E-03. This low value indicates that there is little likelihood of a hazard associated with exposure to the emissions of Scenario A noncarcinogens from the incinerator. The MEI hazard index resulting from the combined lifetime exposures to Scenario B noncarcinogens under the worst-case incinerator operating conditions is 3 E-03, which also indicates that there is little likelihood of a hazard associated with exposure to the emissions of Scenario B noncarcinogens from the incinerator. Because conservative assumptions were used in the exposure assessment report, these indices also are overstated and the actual indices are likely to be lower.

Population Risks

The population risk estimates the additional number of cancers that the population in the area around the incinerator may experience as a result of a 70 year exposure to the Scenario A and B carcinogens emitted by the incinerator. These estimates provide an additional measure of the health risks posed by the incinerator.

Using the results of the exposure assessment along with population data from the U.S. Census Bureau, it was estimated that only 6 E-03 to 3 E-02 additional cancers might develop in the population of 1,600,000 living within 50 km of the incinerator. These cancers will develop over a period of 70 years as a result of Scenario A carcinogen emissions. For Scenario B emissions, it is estimated that only 1 E-04 to 1 E-02 additional cancers might develop in this population over a 70-year period. These results are presented in Tables 8 and 9, respectively.

CONCLUSIONS

In all cases, the proposed hazardous waste incinerator will produce acceptable ambient air exposure levels even when operating at the lowest DREs and REs, and when feeding the toxic constituents at the conservatively high feed rates assumed in the two scenarios. Consequently, it is concluded that the proposed hazardous waste incinerator will not adversely affect human health and the environment.

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Continuous Recovery of Heavy Metals from MSW Incinerator Ashes

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The leachable concentrations of heavy metals from ash residues from the incineration of municipal solid waste (MSW) often exceeds the Extraction Procedure Toxicity Test (EP Tox) limits, requiring these materials to be considered as a potential hazardous waste. The kinetics of Pb, Cd, and Cr extraction were determined through a series of batch extraction studies. The specific incinerator design and the equilibrium conditions strongly influenced the ash matrix and subsequently the extraction kinetics. Recovery of the metals from the extractant solution was accomplished utilizing electrochemical plating techniques.

INTRODUCTION

The problem of municipal solid waste (MSW) disposal must be addressed within the near future, as the demand for disposal is increasing, and available landfill space is at a premium. One of the present solutions is the minimization of waste utilizing resource recovery facilities. The reduction in volume from the disposal of residual ashes (as compared to the disposal of the MSW) averages about a 75% reduction [1]. Heavy metal concentrations extracted from MSW ashes, however, were found to exceed the EP Tox text limits, which is the procedure established by the United States Environmental Protection Agency (USEPA) in testing for leachable inorganic species from solid wastes [2]. The leachability of heavy metals from MSW ash residues must be considered, prior to disposal or utilization of these materials.

Extraction studies employing ash obtained from several resource recovery facilities provided insight to the leaching characteristics of the ashes and the dependency on the extract solution composition [3, 4]. The purpose of this paper was to define the kinetics of the leaching process, and to allow the design of a continuous extraction process.

Incinerator Designs

Two incinerators were sampled for ash residues, one located in Canada and one in Massachusetts. The Canadian incinerator contains a three tiered vibrating grate primary combustion chamber and a secondary combustion chamber. Solids are fed to the combustion chamber using a hopper and have about a three hour residence period. Sixty percent of the combustion air is provided as underfire air, the remainder of the air is circulated above the burner beds. A full waterwall is provided in the incinerator. A shell and tube heat exchanger cools down the exit gases and fly ash. Separation of the gases and the fly ash occurs in an electrostatic precipitator.

The Massachusetts incinerator utilizes a baffled, three tiered combustion chamber in which the solids are periodically moved tier to tier via a hydraulic ram. The solid residue is quenched in the ash pit and then removed, while the gases and the fly ash pass through a secondary combustion chamber. The ash is separated from the combustion gases utilizing a charged gravel bed and a bag house. Detailed descriptions of both incinerators are available [4].

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KINETICS STUDIES

Batch extraction studies investigated the ability of the extractant solution to separate and remove the metals from the ash matrix. The ashes investigated were either bottom ashes, fly ashes, or a mixture of the two. The extract solution utilized was 1.0 N NaCl, acidified with HCl to achieve equilibrium pH of 3.0. This extract solution was found to be highly efficient in earlier experimentation [4]. The waste extractant was measured for various concentrations of extracted heavy metals (Pb, Cd, Cr), pH, and conductivity. The concentrations of the metals and the pH were determined up to a steady state time period, and their interdependence investigated.

Methods and Materials

The batch extraction studies investigated the ash/extractant conditions at eight different time periods, each carried out in triplicate. Five types of ashes were investigated; Canadian fly ash (CF3), Canadian bottom ash (CB), Massachusetts fly ash (MF), Massachusetts bottom ash (MB), and Massachusetts mixed bottom and fly ash (MM). Twenty-four HDPE bottles containing 10.0 grams of ash (dry weight) and 200.0 ml of 1.0 N NaCl solution, acidified with HCl to achieve an equilibrium pH of 3.0, were placed on a rotary shaker. At the time intervals of 10, 20, 30, 45, 90, 180, 300, and 720 minutes, three bottles were removed and the solid and liquid portions immediately separated through vacuum filtration.

All liquid fractions were analyzed for pH, conductivity, Pb, Cd, and Cr. Metals concentration was determined utilizing atomic absorption spectroscopy.

KINETIC STUDIES

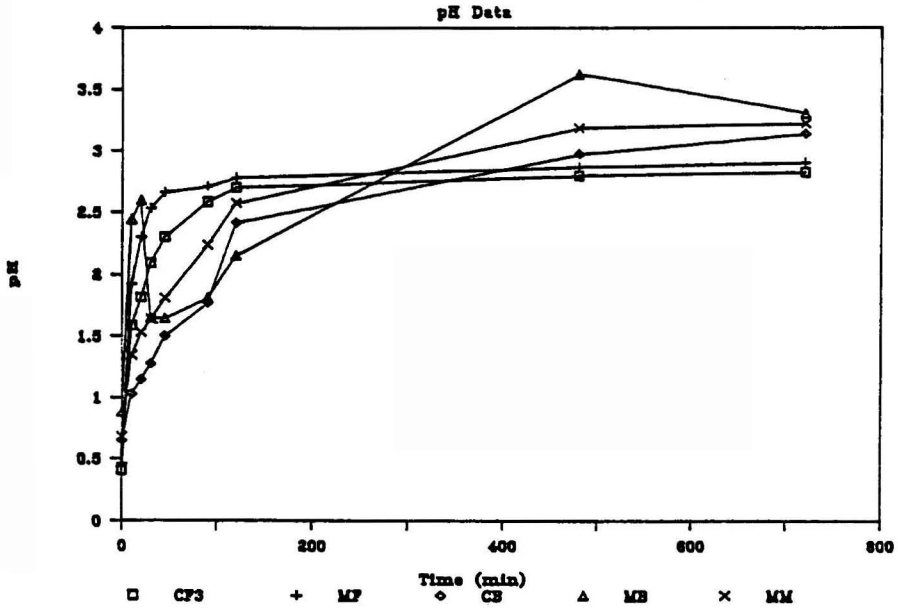


Figure 1. pH data.

Experimental Results

The change in the various measured variables with time was observed for each of the residual ashes utilized in the experiments. The pH was measured at various time intervals (Figure 1). Values all increased from the initial extractant pH to steady-state equilibrium pH values of

3.0 ± 0.4 . The differences observed in the unsteady state time period resulted from the varied structures of the ashes and their related buffering capacities. The conductance of the extracts sharply decreased from their initial values, between 111.2 and 195.7 mmhos, and leveled off at steady state values between 90 to 110 mmhos (Figure 2). The trend in the change in conductance for all the ashes is that of a sharp decrease until an asymptotic value

KINETIC STUDIES

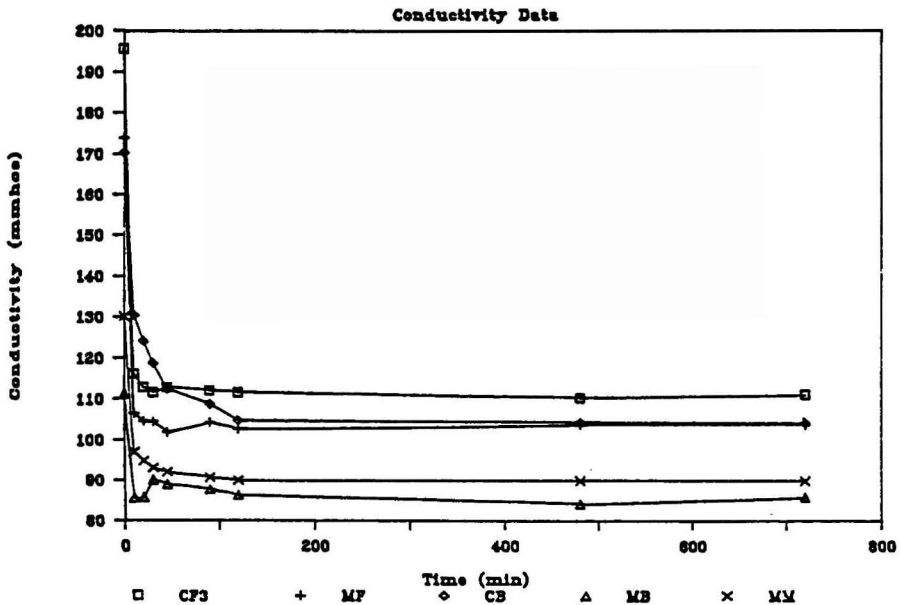


Figure 2. Conductivity data.

KINETIC STUDIES

Extractable Lead Concentration

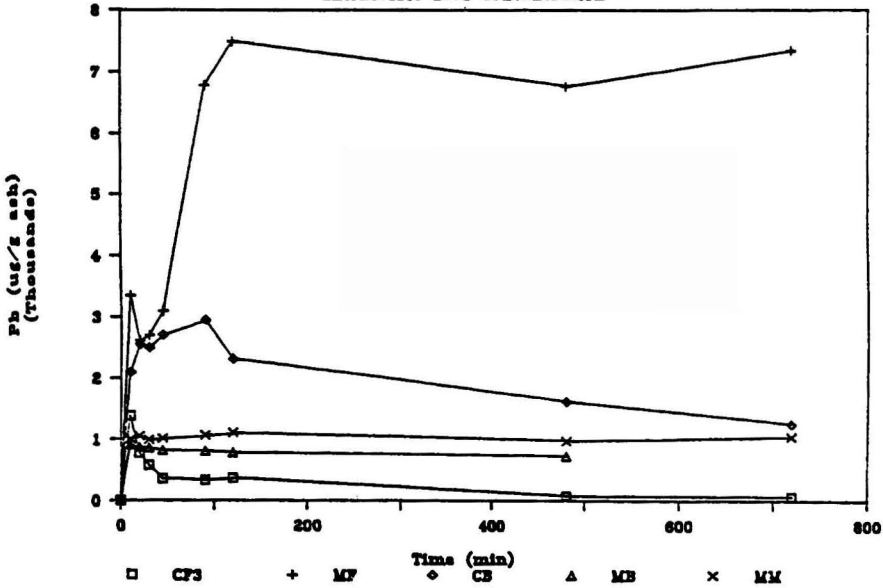


Figure 3. Extractable lead concentration.

is obtained, and then the conductance is maintained throughout the rest of the time period.

A definite variance was observed between the ashes for the lead concentration curves (Figure 3). The CF3 extract peaks at 10 minutes at a value of 1380 $\mu\text{g Pb/g ash}$, and then subsequently decreases. The CF3 lead extraction process was observed to be dependent on the pH of the system, upon comparison of the lead and pH curves for the ash. The rate of removal of lead occurred at a much

faster rate than the rate of the neutralization process for the ash. A similar trend was observed for the CB extract, although at a slower rate, which can be attributable to the larger particle size of the bottom ash.

Extractable lead values up to 7500 $\mu\text{g Pb/g ash}$ are achieved for the MF extract at a time period of two hours. The fly ash obtained from the Massachusetts facility exhibits a possible diffusion controls kinetics for the lead extraction procedure.

KINETIC STUDIES

Extractable Cadmium Concentration

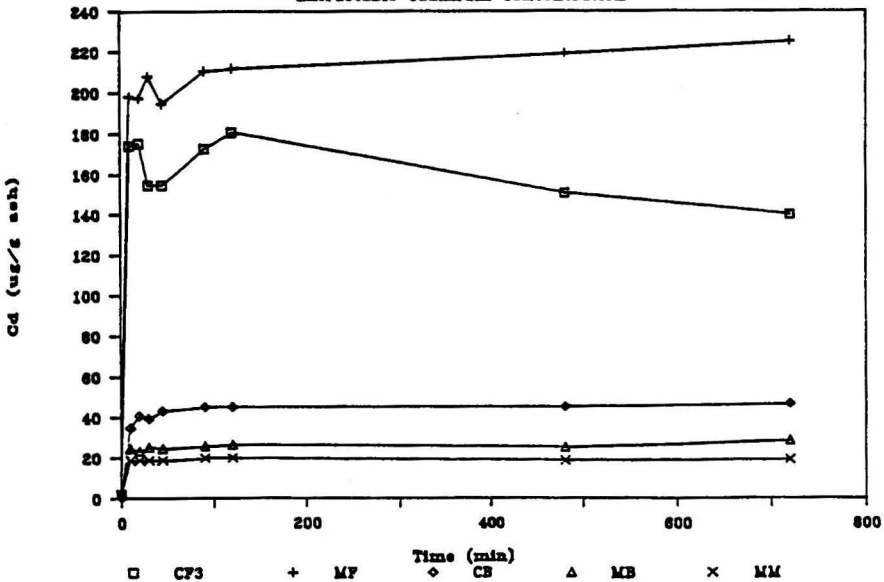


Figure 4. Extractable cadmium concentration.

KINETIC STUDIES

Extractable Chromium Concentration

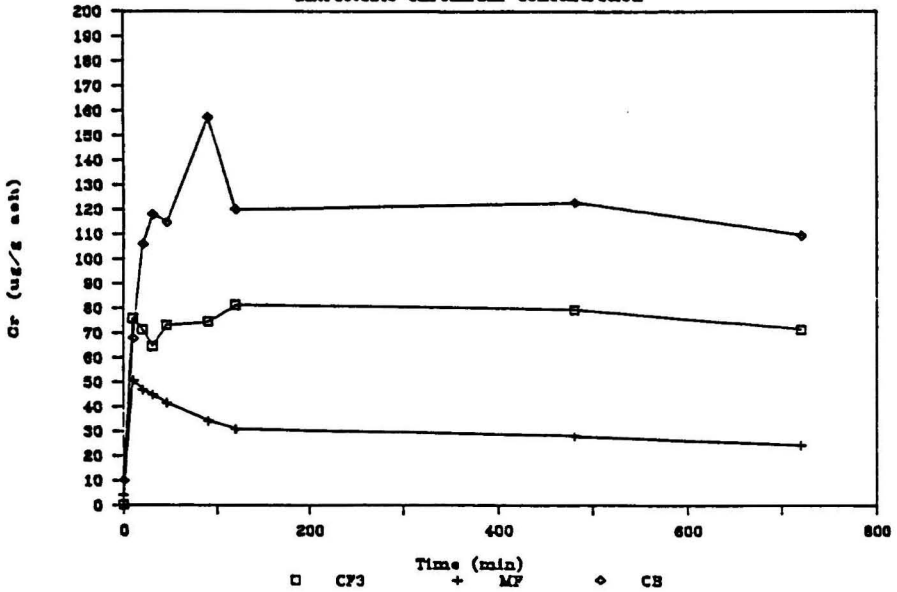


Figure 5. Extractable chromium concentration.

The extractable levels of cadmium for all of the residual ashes stabilized rapidly, and the removal mechanism did not exhibit a pH dependency (Figure 4). The MF extract contained the highest amount of cadmium; the concentration of cadmium in the extract increased slightly from 198.0 to 225.3 $\mu\text{g Cd/g ash}$. Once again, a quick stabilization was observed for the chromium concentrations for all the ashes analyzed (Figure 5).

ELECTROCHEMICAL RECOVERY

Electrochemical methods offer the advantage of the recovery of a relatively pure metal in a usable form; precipitation methods generate a flocculent that requires disposal. Electrodeposition of metals does not require the addition of any extraneous compounds to an already complex solution. Cyclic voltammetry was carried out on standards of known metal concentration and compared to

CYCLIC VOLTAMMETRY

LEAD STANDARD

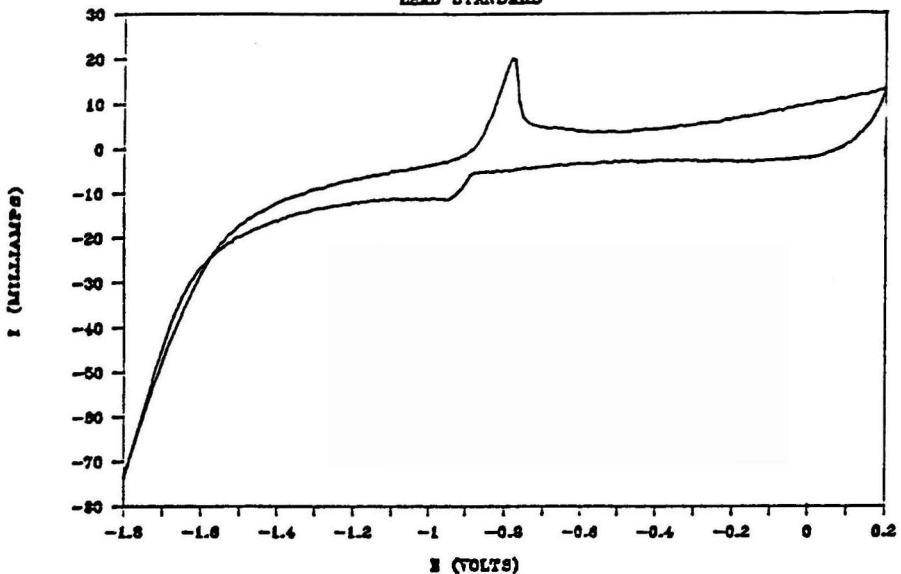


Figure 6. Lead standard.

CYCLIC VOLTAMMETRY

ASH EXTRACTANT SOLUTION

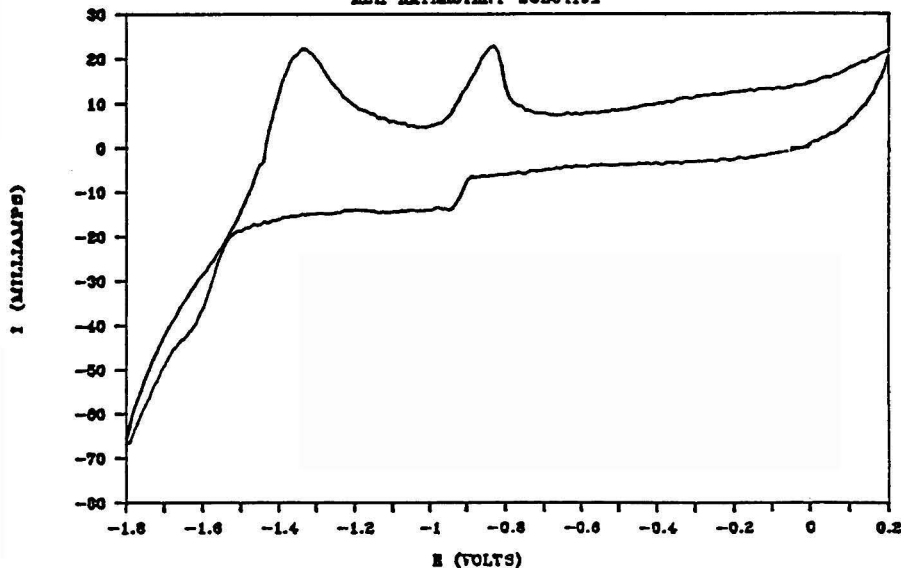


Figure 7. Ash extractant solution.

the aqueous extracts in order to determine the operating parameters for Pb recovery.

Materials and Methods

Cyclic voltammetric studies were carried out to determine the characteristic peak of Pb, and to determine the recoverability of lead from the extract solutions. Standard solutions of 180 mg Pb/L in a 1 N NaCl solution (acidified with HCl acid) were prepared. Five grams of ash (dry weight) were extracted with 100 ml of the acidified 1 N NaCl solution. Both the standards and the extractants were subjected to a voltage range of -1.8 to $+0.2$ volts, a specified scan rate of 50 millivolts/sec, and the current response was recorded. The anode and cathode in these preliminary experiments were both carbon rods. The solutions were analyzed prior to and after experimentation via atomic absorption spectroscopy for the presence of Pb, and the pH was also measured.

Experimental Results

The current response observed for the 180 mg Pb/l standard solution is shown in Figure 6. This cyclic voltammogram reveals a plating potential range of -0.95 V to -0.70 V for lead in this solution. Cyclic voltammetry was carried out utilizing an extract solution with a pH of 3.0 and a concentration level of 175 mg Pb/l (Figure 7). Results from this cyclic run exhibited a peak within this range, indicating that lead may be plated out of the extract solution.

The presence of a second peak in Figure 7 indicates the occurrence of another process. Identification of the peak is currently underway, and Cd, Fe, Zn, and Cr have already been eliminated as possibilities through comparative cyclic runs of their corresponding standard solutions.

It should be noted that the acidified, 1 N NaCl extractant solution was also exposed to a similar voltage range in order to isolate and identify any effects that could be attributed to the solution itself, as opposed to the ash. The voltage curve for the salt solution did not exhibit any additional peaks.

CONCLUSIONS

The residual ashes from MSW incineration contain high levels of hazardous metals, and leachable concentrations of these materials often surpass the EP Tox test limits mandated by the USEPA. The classification of these materials may be considered hazardous, warranting costly landfilling. This led to the investigation of the extraction and recovery of Pb, Cd, Cr from the residual ashes. A series of kinetics experiments were carried out, developing the characteristic extraction trends of the various ashes. The extraction kinetics of CF3 ash exhibited a peak in the lead concentration curve at an unsteady state time period of 10 minutes, indicating that the ash/extractant reaction should be halted at this time period in order to remove a maximum quantity of lead from the ash particulates. Optimum extent of reaction, in terms of unsteady state time periods, for the various ashes are 90, 90, 10, and 10 minutes for the CB, MF, MB, and MM ashes, respectively. Cyclic voltammetric experimentation exhibited the potential for metals recovery in a relatively pure form through plating techniques.

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