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Project Summary

Research Planning Task Group Study—Thermal Destruction Final Report

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The objectives of this study were to determine the state-of-the-art for thermal destruction of industrial toxic waste, and to identify and prioritize research needs in this area. The study consisted of a literature search, discussions with EPA personnel and other authorities in the area of thermal destruction, and attendance at a national meeting on the subject. The state-of-the-art of thermal destruction of industrial toxic waste was determined, and research needs identified.

This Project Summary was developed by EPA's Industrial Environmental Research Laboratory, Cincinnati, OH, to announce key findings of the research project that is fully documented in a separate report of the same title (see Project Report ordering information at back).

Introduction

The modern technological society produces large quantities of industrial wastes Some typical industrial classifications and types of wastes generated are listed in Table 1. Typical industrial waste production rates are listed in Table 2 A sizable fraction of this waste is considered hazardous, i.e , an estimated 57 million metric tons in 1980.

Toxic chemical wastes in the environment represent one of today's most serious environmental problems. The ever increasing quantities of these toxic residues have overburdened the receiving environment (air, water, and land) Lack of adequate process waste disposal facilities is aggravating environmental problems, forcing some industries to close or restrict certain operations.

Although the need for proper disposal and control of toxic wastes is widely recognized, in many instances effective control techniques available have not been adequately applied. Land disposal and ocean dumping of toxic substances have contaminated and interfered with the biological systems of streams, rivers, lakes, and oceans.

Alternative methods for disposal of industrial toxic wastes include a number of thermal destruction techniques in which the pollutant is oxidized or pyrolized at a high temperature to produce benign products. As a hazardous waste disposal technology, thermal destruction techniques offer several advantages:

- Toxic components of hazardous wastes can be converted to harmless compounds or, at least, to less harmful compounds.
- Ultimate disposal of hazardous wastes eliminates the possibility of problems resurfacing in the future.
- The volume of hazardous waste is greatly reduced.
- Heat recovery makes it possible to recover some of the energy produced by the combustion process.

The Congress of the United States via Section 3004 of Subtitle C of the Resource Conservation and Recovery Act (RCRA) of 1976 (PL94-580) mandated that the Administrator of the U.S. Environmental Protection Agency promulgate regulations establishing performance standards applicable to owners and operators of hazardous waste treatment, storage, and disposal facilities necessary to protect human health and the environment. These standards are to

Table 1. *Combustible Wastes Generated by Various Industries*

Industry	*Wastes*
Ordnance and accessories	*Plastics, rubber, paper, wood, cloth, and chemical residues*
Food and kindred products	*Meats, fats, oils, offal, vegetables, fruits, nuts and shells, and cereals*
Textile mill products	*Cloth and fiber residues*
Lumber and wood products	*Scrap wood, shavings, sawdust, plastics, fibers, glues, sealers, paints, and solvents*
Apparel and finished products	*Cloth, fibers, plastics, and rubber*
Furniture (wood)	*Same as lumber plus cloth and padding residues*
Furniture (metal)	*Plastics, resins, rubber, adhesives, cloth, and paper*
Paper and allied products	*Paper, fiber residues, chemicals, coatings, filler, inks, and glues*
Printing and Publishing	*Paper, newsprint, cardboard, chemicals, cloth, inks, and glues*
Chemicals	*Organic chemicals, plastics, rubber, oils, paints, solvents, and pigments*
Petroleum	*Asphalt, tars, felts, paper, cloth, and fiber*
Rubber and miscellaneous plastics	*Scrap rubber and plastics, curing compounds and dyes*
Leather	*Scrap leather, thread, dyes, oils, and processing and curring compounds*
Fabricated metal products	*Coatings, solvents, lubricants, and pickling liquors*
Machinery (except electrical)	*Wood, plastics, rubber, cloth, paints, solvents, and petroleum products*
Electrical	*Rubber, plastics, resins, fibers, and cloth residues*
Transportation	*Fiber, wood, rubber, plastics, cloth, paints, solvents, and petroleum products*
Professional, scientific controlling instruments	*Plastics, resins, wood, rubber, and fibers*
Miscellaneous manufacturing	*Plastics, resins, leather, rubber, cloth, straw, adhesives, paints, and solvents*

Table 2. *Industrial Solid-Waste Production Rates*

Industry	*Waste Production Rate (tons/employee/year)*
Meat processing	*6.2*
Cannery	*55.6*
Frozen foods	*18.3*
Preserved foods	*12.9*
Food processing	*5.8*
Textile-mill products	*0.26*
Apparel	*0.31*
Sawmills and planning mills	*162.0*
Wood products	*10.3*
Furniture	*0.52*
Paper and allied products	*2.00*
Printing and publishing	*0.49*
Basic chemicals	*10.00*
Chemical and allied products	*0.63*
Petroleum.	*14.8*
Rubber and plastic	*2.6*
Leather	*0.17*
Stone, clay	*2.4*
Primary metals	*24.*
Fabricated metals	*1.7*
Nonelectrical machinery	*2.6*
Electrical machinery	*1.7*
Transportation equipment	*1.3*
Professional and scientific instruments	*0.12*
Miscellaneous manufacturing	*0.14*

include, but need not be limited to, requirements concerned with (1) operating methods, techniques, and practices; (2) location, design, and construction; and (3) contingency plans for effective action to minimize unanticipated damage that might occur at these facilities. As applied to the incineration of toxic industrial wastes, present regulations require incinerators to achieve a destruction and removal efficiency (DRE) of 99.99 percent for each designated principal organic hazardous constituent (POHC) in the waste feed. Destruction and removal efficiency for an incinerator/air pollution control system is defined by the following formula:

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

where

DRE = destruction and removal efficiency, percent;

W_{in} = mass feed rate of the principal organic hazardous constituent(s) to the incinerator;

W_{out} = mass emission rate of the principal organic hazardous constituent(s) to the atmosphere (as measured in the stack prior to discharge).

Thus, DRE calculations are based on the combined efficiences of destruction in the incinerator and removal from the gas stream in the air pollution control system. Specification of the principal organic hazardous constituents in a waste is subject to best engineering judgment, considering the toxicity, thermal stability, and quantity of each organic waste constituent. POHC's are identified on the incinerator permit application. To allow for the formation of any hazardous combustion byproducts, the EPA has proposed an amendment that the amount of the byproducts must not exceed 0.01 percent of the total mass feedrate.

For fundamental studies of thermal oxidation processes, a thermal oxidation destruction efficiency (DE) is of more use than the DRE. The DE is defined in a fashion similar to the DRE with the exception that W_{out} is defined to be the mass emission rate of the POHC's out of the incinerator combustion stack. Thus, the DE is a thermal oxidation destruction efficiency only and does not include removal by any air pollution control system as does the DRE used in the EPA incinerator regulations.

A great deal of effort is currently being focused on the subject of thermal destruction of toxic industrial wastes. A number of studies, reviews, conferences, and courses dedicated to this topic have appeared recently. A listing of these recent efforts is given in the Appendix to the final report. The specific objectives of this task group study were to examine the literature on thermal destruction processes in depth in order to determine how well the fundamentals of the processes are understood and to prioritize research needs in the areas of thermal destruction of industrial toxic wastes.

Classification and Characterization of Hazardous Wastes Potentially Treatable by Thermal Destruction

The term "hazardous wastes" covers a wide range of chemicals. Heavy metals, pesticide residues, organic solvents, acids, inorganic salts, explosives—all of these may fall under the heading of "hazardous." Each has its own chemical characteristics; each must be handled differently. Analysis and characterization of wastes is vitally important both from the standpoint of determining the best treatment or disposal strategy and of preventing dangerous reactions which could result from mixing incompatible materials. The most basic chemical waste classification is based on elemental composition. For those wastes potentially treatable by any of the various thermal destruction techniques, four classifications are used. These are listed in Table 3. Difficulty in treating the waste by thermal destruction techniques increases as one progresses from Waste Class 1 to Waste Class 4.

There are two basic types of hazardous wastes which are organic, or partially organic, in nature and which can be incinerated:

(1) Combustible wastes, which will sustain combustion without the use of auxiliary fuel; and
(2) Noncombustible wastes, which will not sustain combustion without auxiliary fuel.

Noncombustible types usually contain significant amounts of water or other inert compounds. Either of these two types of wastes may contain small or large amounts of inorganic salts, halogen compounds, nitrogen compounds, sulfur compounds, or phosphorus compounds. The final report fully describes the technology for thermal destruction of all compounds of hazardous wastes.

Table 3. Chemical Waste Classifications

Waste Class	Elemental Composition	Example
1	C,H and/or C,H,O	Tars from production of styrene Off-specification phenol
2	C,H,N and/or C,H,N,O	Solid residue from manufacture of aromatic amines TDI manufacture reactor tar bottoms
3	C,H,Cl and/or C,H,Cl,O	Vinyl chloride monomer manufacturing wastes Phenolic tar from 2, 4-D manufacture
4	C,H,N,Cl and/or C,H,Cl,N,O	Nitrochlorobenzene manufacturing wastes
	C,H,S and/or C,H,S,O	Petroleum refining sour waste
	C,H,F and/or C,H,F,O	Fluorinated herbicide wastes
	C,H,Br and/or C,H,Br,O	Ethylene bromide manufacturing wastes
	C,H,P and/or C,H,P,O	Malathion
	C,H,Si and/or C,H,Si,O	Tetraethyl orthosilicate wastes
	C,H,Na and/or C,H,Na,O	Refinery spent caustic

Thermal Destruction Devices

A survey of commercial incinerator installations reported in the literature, showed that the methods of incineration most commonly used are liquid injection incineration, fluidized bed incineration, multiple hearth incineration, rotary kiln incineration, catalytic combustion, molten salt combustion, pyrolysis/starved-air combustion, and wet air oxidation. An excellent review of the state-of-the-art of these incineration processes may be found in a recent publication produced by the Noyes Data Corporation (1). A technical resource document entitled *Engineering Handbook for Hazardous Waste Incineration*, was prepared for the U.S. Environmental Protection Agency by Monsanto Research Corporation (2). The latter document provides technical information for use in the design and performance evaluation of hazardous waste incineration facilities. Topics covered include a state-of-the-art survey of incineration and air pollution control design evaluations, overall incineration facility considerations, capital and operating costs, and trial burn summary data. Because rotary kiln and liquid injection are at present the most highly developed and most commonly used incinerators for hazardous waste incineration, primary emphasis has been given in the handbook to these two incineration processes. The final report of the current study presents a brief description of the various commonly used hazardous waste incineration devices. The interested reader is urged to consult the above two references for more detailed information.

Commercial Scale Hazardous Waste Thermal Destruction Tests

In order to provide a broad assessment of the capabilities of commercially available thermal destruction units, the U.S. Environmental Protection Agency awarded a two-phase contract to the team of TRW Defense and Space Systems Group and Arthur D. Little, Inc. (3). The first phase was the development of an operational plan for selecting chemical wastes and thermal destruction units that could be tested for their capabilities to destroy chemical wastes containing hazardous components. This encompassed the following tasks:

(1) Classification, identification, prioritization and selection of wastes which provided a reasonable cross-section of currently generated industrial wastes with particular attention to quantities and hazardous properties of the waste.
(2) Selection of units chosen to be representative of the most advanced engineering methods of thermal destruction.
(3) Assignment of top priority wastes to specific units on the basis that the wastes could be expected to be destroyed effectively, the transportation and handling of the wastes would be feasible, and all units would be tested with at least one priority waste.

The second phase of the project used the results from the first phase and encompassed the following tasks:

(1) Development of a testing and analytical protocol and outfitting a mobile laboratory for field testing.

(2) Obtaining wastes from generating sources and arranging for shipment to the thermal destruction units.

(3) Contracting with the operators of thermal destruction facilities for the tests.

(4) Preparing a detailed test and analytical program for each facility and carrying out the program at the thermal destruction facility.

(5) Analyzing samples in the mobile laboratory and interpreting data.

(6) Preparing a report on each unit tested

Two criteria were developed with which to prioritize candidate waste materials These were:

(1) *Hazard Rating* (r_{max}) - A given compound or waste may have a number of properties for which it is considered hazardous (flammability, oral toxicity, inhalation toxicity, carcinogenicity, etc) For each hazardous property, four ratings were established with assigned values of 1, 10, 100, 1,000—the higher the rating, the more hazardous the waste. In assigning a hazard rating to an individual waste with several hazardous properties, the highest hazard rating was used irrespective of which hazardous property the rating represented

(2) *Quantity Rating* (Q) - Four ranges of waste generation volume were chosen The ranges selected were over 45,400 metric tons per year, 4,540 to 45,400 metric tons per year, 454 to 4,540 metric tons per year and less than 454 metric tons per year These volume ranges were assigned ratings of 1,000, 100, 10, and 1, respectively

After hazard and quantity ratings were assigned to a waste, the priority category was determined by multiplying the two ratings together A total of 50 wastes were selected and ranked as prime candidates for consideration for the thermal destruction tests The distribution among priority categories for these 50 wastes and brief description of the wastes finally chosen for the actual thermal destruction tests are presented in the final report

Laboratory Scale Thermal Destruction Tests

When individual toxic organic substances or multicomponent industrial organic wastes are subjected to thermal destruction, the technique used may be quite successful in bringing about the destruction of the parent molecule; however, other secondary or intermediate reaction products may be produced that are more toxic or more thermally stable than the parent substance. Thus, in order to determine the thermal requirements necessary for environmentally acceptable disposal of hazardous materials, it is essential that fundamental thermal decomposition data for these toxic substances be obtained.

There are several advantages to generating fundamental thermal decomposition data in the laboratory. First, thermal decomposition experiments can be conducted much more safely in a properly equipped laboratory than in larger throughput units. Second, data generated in the laboratory can be much more precise and comprehensive than thermal decomposition data can be obtained economically and in a shorter period of time.

Once the thermal decomposition properties of a particular material have been characterized in the laboratory, the preliminary decision can be made as to whether high-temperature incineration is a viable disposal route for that particular material. If no adverse characteristics are detected during the laboratory experiments, then the material may be subjected to larger-scale thermal decomposition studies. However, if the laboratory data indicate difficulties or problem areas, then thermal decomposition is probably not a viable disposal method for that particular substance

Laboratory-scale thermal decomposition studies of various organic materials are being performed at the University of Dayton Research Institute These experiments are being performed using recently developed second generation thermal decomposition instrumentation, (4,5). The present instrumentation is referred to as a thermal decomposition analytical system (TDAS). This system incorporates a versatile in-line thermal decomposition unit with sophisticated analytical instrumentation capable of analyzing the various decomposition products.

The TDAS is designed to evaluate the thermochemical behavior of volatile materials under controlled conditions. The TDAS consists of a modular control panel (where the operating parameters for tests are established), several gas cylinders (that supply reaction atmospheres with known compositions), a sample insertion and vaporization chamber, a special quartz tube reactor, in a furnace (for the decomposition of samples), a product collection trap, a gas chromatograph, a mass spectrometer, and a minicomputer.

In operation, several micrograms of a solid sample (or several microliters of a liquid or gaseous sample) are introduced into a sample injection chamber. The chamber is then sealed and flushed with the controlled atmosphere to be used for the experiment. Solid and liquid samples are heated, vaporized at temperatures up to 300°C (over a controlled time interval), and mixed with a continuous stream of the reaction atmosphere. Samples may be flash pyrolyzed or gradually vaporized, depending on the desired reaction conditions. The mixture than passes through a reactor (location M) consisting of a 98 cm long, 0.097 mm inside diameter, thin walled, helical quartz tube enclosed in an electric furnace. The furnace and tube can be operated at temperatures up to 1150°C (±2°). The temperature of the reaction is monitored by a thermocouple located at a point representing the mean temperature for the reactor furnace. The final report presents a fuller, more detailed discussion of the laboratory scale thermal destruction tests.

Extension of Laboratory Scale Test Data to Commercial Scale Units

Pilot plant scale thermal destruction efficiency tests have been performed by the Swedish Water and Air Pollution Laboratory (6). The pilot plant thermal oxidation system used for these studies has primary and secondary combustion chambers, followed by a sampling duct and a variable speed fan. The primary combustion chamber is a cylindrical, refractory-lined vertical furnace with a stationary grate at the bottom. The chamber has the capability to handle liquid waste and/or solid waste. The furnace can use either sawmill chips or liquid petroleum gas (LPG) as auxiliary fuel or both. The system's secondary combustion chamber has a cyclonic separator configuration with a tangentially-tired LPG burner of the same type and size as the primary chamber. Destruction efficiency tests were carried out using PCB Pyraline 3010, PCB Arochlor 1254, and hexachlorobenzene. Test conditions, which are results of the pilot plant studies for these compounds, are shown in the final report. Destruction efficiencies of greater than 99.99 percent were obtained for seven of the nine PCB Pyralene 3010 samples, six of 13 PCB Arochlor 1254 samples, and 11 of 13 hexachlorobenzene samples. Multiple linear regression analysis was used to investigate the reaction of this analysis which, indicates that the data did not follow the Arrhenius equation and hence could not be described by using first-order kinetics.

Since the pilot plant data did not fit first-order kinetics, no direct comparison of T99.99/2 values can be made between pilot and bench-scale data (e.g. TDAS data). However, it appears that the temperatures required for 99.99 percent destruction at a 2-second residence time in the pilot plant studies are 200°C to 300°C higher than the temperatures required for the same degree of destruction in the laboratory bench scale unit. The final report presents a fuller discussion of all phases of extending laboratory scale data to commercial scale units.

Theoretical Analysis of Chemical Reaction Mechanisms

Equilibrium Considerations

While mixing and kinetic rate processes determine the overall rate at which thermal destruction occurs, the ultimate products of the thermal destruction processes is controlled by equilibrium considerations. It is true that virtually all toxic materials are thermodynamically unstable at high temperatures. However, the persistance of carbon monoxide and hydrogen cyanide, for example, in the high temperature effluent from a fuel rich oxidation process is one reason why virtually all thermal oxidation processes are carried out in the presence of a large excess of oxygen. It is also true that the high temperature stability of sulfur dioxide, sulfur trioxide, hydrochloric acid gas and hydrobromic acid gas require that some type of alkaline scrubbing be used when the elements sulfur, chlorine, or bromine are present in the toxic waste that is being destroyed using a thermal method.

The above mentioned equilibrium considerations, while important to the subject of thermal destruction, are very well understood at the present time, and there appears to be no need for new research in the area of high temperature equilibrium chemistry.

Studies of Detailed Chemical Reaction Kinetic Mechanisms

At the present time, the detailed reaction processes that lead to the oxidation of simple molecules are reasonably well understood and developed. The literature reports several studies of the oxidation of hydrogen, carbon monoxide, methane, and methanol. The reaction sequences developed for these simple compounds are relatively complex and are fully described in the final report.

Overall Kinetic Studies

The detailed kinetics of the pyrolysis and oxidation of more complex hydrocarbons than methane (a C_1 hydrocarbon) are considerably more difficult to model using elementary reaction kinetic steps (particularly on the fuel rich side). Nevertheless, these studies do show the complexity of higher molecular weight hydrocarbon oxidation processes and lead one to the general conclusion that detailed chemical mechanisms for the oxidation of higher molecular weight hydrocarbons (and substituted higher hydrocarbons which may be toxic) will not be forthcoming in the near future.

Mathematical Modeling of Combustion Processes

Problems with Mathematical Modeling

Efficient thermal destruction requires that the toxic fuel and the oxidizer air be rapidly mixed to the molecular level at high temperature so that the oxidation chemistry required for destruction can occur rapidly. This problem is exemplified by the discussion in the final report which indicated that reactor contact times for the TDAS experiments were much less than those required in larger, full-scale devices where turbulent mixing must be used to obtain the intimate contact which is necessary for chemical destruction to occur. The key to this problem is the attainment of high levels of turbulence in the reactor without paying the penalty of excessive pressure drop, which requires higher power levels for the operation of the device. A general solution to this problem is not available at the present time and the current understanding of the turbulent mixing problem, particularly when the system is chemically reactive, is really not well developed at all. The final report presents a full description of current research efforts in the area of turbulent reactive mixing as applied to combustion problems, particularly in jet engines or diesel combustion. Very little systematic work has been done on the improvement of incinerator design. At the present, the approach is to search for the solution by continually adjusting the configuration of an incinerator until optimum incineration is obtained.

Conclusions and Recommendations

The objectives of this study were to determine the state-of-the-art of thermal destruction of industrial toxic waste and to identify and prioritize research needs in this area. The study consisted of a literature search, discussions with Environmental Protection Agency (EPA) personnel, discussions with other authorities in the area of thermal destruction, and attendance at a national meeting on the subject. The state-of-the-art of thermal destruction of industrial toxic waste was determined, and the following research needs were identified:

1. Continue and expand the thermal decomposition analytical system (TDAS) studies to determine values of the temperature required to obtain a 99.99 percent destruction efficiency at a residence time of two seconds and general temperature/residence time thermal decomposition data for a variety of hazardous compounds representing different molecular structures.
2. Generate auto ignition temperature (AIT) values for the substances studied in (1) and determine the degree of correlation between AIT and T99.99/2.
3. Generate ionization energy data for the substances studies in (1) and determine the degree of correlation between ionization energy and T99.99/2.
4. Determine the effects of molecular structure of T99.99/2 values.
5. As a part of the TDAS study, examine the concentration of carbon monoxide (CO) as a function of temperature and residence time to determine if regulations governing the thermal destruction of CO will successfully govern the thermal destruction of all products of incomplete combustion (PICs).
6. Investigate the possibility of monitoring only CO to certify an incinerator for burning toxic wastes.
7. Continue development and implement the EPA rotary kiln pilot plant in Arkansas and use the generated data to develop scale-up laws for rotary kiln incinerators.
8. Develop a pilot plant as in step (6) of the generation of scale-up laws for liquid injection incineration.
9. Pursue the newer approaches to reactive turbulent flow modeling in the presence of large density gradients. Virtually all of the extant turbulent modeling is not predictive

when applied to a turbulent diffusion flame.

10. Fundamental kinetic studies, in which individual reaction steps are identified and each of their rates measured, would not be useful at this time, because in practical incineration, turbulence so restricts the rate of the chemistry that it controls the conversion rate. Also, the combustion chemistry of large organic molecules is a very complex subject and detailed mechanisms have not been identified as yet. Thus it appears that the simple first-order kinetic approach that has been used in the TDAS studies will be adequate for a considerable period of time.

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The complete report, entitled "Research Planning Task Group Study—Thermal Destruction Final Report," (Order No. PB 84-145 119; Cost: $14.50, subject to change) will be available only from:

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