



Project Summary

Guidelines for the Disposal of PCBs and PCB Items by Thermal Destruction

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This is a resource and guidelines report intended to aid the U.S. Environmental Protection Agency Regional Offices in evaluating facilities which apply for approval of thermal destruction of polychlorinated biphenyls (PCBs). Annex I incinerators and high efficiency boilers (40 CFR 761) are emphasized.

Information is provided on: fundamental combustion processes as they relate to incineration efficiency and the formation of organic compounds not originally present; thermal destruction technologies that have been or could be used for disposal of PCBs; thermal destruction tests on PCBs and other relevant materials; and a description and evaluation of sampling and analysis methods for PCBs.

Guidelines and criteria are provided for: interpreting those parts of the PCB Regulations governing Annex I incinerators and high efficiency boilers; establishing the consistency of disposal operations with the regulations; evaluating Annex I incinerators and high efficiency boilers: Initial Reports, Notifications, Trial Burn plans, and Trial Burn data; issuance of approvals and monitoring compliance; and facilitating coordinated Agency review of PCB disposal operations.

This Project Summary was developed by EPA's Industrial Environmental Research Laboratory, Research Triangle Park, NC, 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

Polychlorinated biphenyls (PCBs) are derivatives of the compound biphenyl in which from 1 to 10 hydrogen atoms have been replaced with chlorine atoms. PCBs are characterized by extremely high thermal and chemical stability. These characteristics made PCBs highly useful in a wide variety of commercial applications. The wide use of PCBs coupled with a lack of recognition of their hazards led to the present ubiquitous distribution of PCBs in the environment. EPA estimated that up to 1975, between 136,000 and 181,000 metric tons (300 to 400 million pounds) of PCBs had entered the environment.

Although PCBs have low acute toxicities, other adverse effects have been found in humans, laboratory animals, and other organisms. There is evidence that PCBs are carcinogenic, oncogenic, and teratogenic. PCBs are also known to bioaccumulate and biomagnify.

In 1976, growing evidence of the problem of PCB contamination led to an inclusion in the Toxic Substances Control Act (TSCA) of a provision that would require the eventual elimination of PCB usage in the United States. The PCB Regulations (40 CFR 761), promulgated under TSCA do not require removal of PCBs and PCB items from service earlier than would otherwise be required; but when PCBs and PCB items are removed from service, disposal must be in ac-

cordance with the PCB Regulations. Other acts which govern the disposal of PCBs include the Resource Conservation and Recovery Act; the Clean Water Act; the Marine Protection, Research, and Sanctuaries Act; and the Occupational Safety and Health Act.

Large amounts of PCBs are in service and will eventually require disposal. The Electric Power Research Institute projects a shortfall of utility waste PCB disposal capacity (landfill and incinerator) in most EPA regions after January 1, 1981 (EPRI, 1980). Additionally, there will be a smaller quantity of PCB wastes from commercial and industrial uses which will require disposal.

The full report is a resource and guidelines document. It is intended to aid EPA Regional Offices in evaluating facilities which apply for review and/or approval of thermal PCB destruction activities.

Thermal Destruction of PCBs

The physical form of the PCB waste (i.e., liquid or solid) is the most important factor influencing the mechanisms of its combustion. Other important physical properties are viscosity, solids content, and moisture content. The fuel's chemical properties also are important and include its elemental composition and heating value. The efficiency of destruction for a given fuel will depend upon unit operating parameters: combustion air, waste feed rate, temperature, residence time, and mixing.

Thermal Destruction Systems

The thermal destruction processes described in this report can be grouped into one of two general categories: Annex I incinerators or high efficiency boilers. Table 1 lists the incineration systems which were cited most often in the literature for disposal of hazardous wastes. Not all of these systems are suitable for the thermal destruction of PCBs. PCBs have been successfully incinerated in rotary kilns (coupled with afterburners) and liquid injection incinerators. Also, several successful tests have been performed in cement kilns. A test in a municipal sludge incinerator was partially successful but demonstrated a need for a change in the method of feed.

In addition to incinerators, which are designed to combust hazardous materials, conventional boilers also can be used to destroy PCBs if proper combus-

Table 1. Incineration System Summary

Type	Applicability	Reasons
Rotary kiln	Liquids - Yes Solids - Yes	Best system for PCB Items. Requires an afterburner.
Liquid injection	Liquids - Yes Solids - No	Best system for liquid PCBs. May be used as afterburner following a solids incinerator.
Multiple hearth	Liquids - Yes Solids - Yes	Design is suitable, but may require operation at higher temperatures than currently used. Afterburner required. Scrubber may be required.
Fluidized bed	Liquids - Potential Solids - No	Future consideration warranted for liquids. Hard to remove shredded noncombustibles. Temperatures probably too low.
Multiple chamber	Liquids - Yes Solids - No	Liquids may be suitable if liquid burner is installed above grates. Insufficient air/solid mixing.
Catalytic combustion	Liquids - No Solids - No	Primarily designed for gases and vapors.
Pyrolysis	Liquids - No Solids - No	High probability of forming toxic combustion products.
Starved air combustion	Liquids - No Solids - No	High probability of forming toxic combustion products.
Molten salt	Liquids - Potential Solids - No	Future consideration warranted for liquids. Not proven commercial technology. Temperatures probably too low. Hard to remove shredded noncombustibles.

tion conditions are maintained. The PCB Regulations permit, under certain conditions, burning of PCB liquids with concentrations in the range of 50 to 500 ppm in boilers with at least a 50 million Btu/hr heat input rate. PCB liquids below 50 ppm are not subject to the disposal regulations. PCB liquids above 500 ppm must be disposed of in Annex I incinerators.

Sampling Methods

For the initial use, or after substantial modification of a facility for burning PCBs, the stack gas may be monitored for carbon monoxide (CO), carbon dioxide (CO₂), oxygen (O₂), hydrogen (H₂), nitrogen oxides (NO_x), PCBs, organochlorines (RCLs), hydrogen chloride (HCl), and total particulate matter (TPM). Scrubber effluent and solid residues also may be monitored. Other process parameters that may be measured are PCB and auxiliary fuel feed rates and combustion zone temperatures.

Carbon monoxide and oxygen must be measured continuously and maintained in accordance with the PCB Regulations. Sampling for PCBs, RCL, HCl, NO_x, and TPM are not specified in the PCB Regulations and are subject to the require-

ments of the cognizant EPA Regional Administrator. During the four recent Trial Burns, from four to five stack gas samples (4-hour duration) were required. Variable numbers of samples for RCLs, HCl, TPM, and NO_x also were required. Sampling intervals for scrubber effluent and other process influent and effluent streams have ranged from 15- to 30-minute intervals (Rollins, 1980; EPRI, 1980; Tennessee Eastman, 1979; and Zelenski and Haupt, 1979).

A critical factor in all sampling activities is obtaining a representative sample because the accuracy and precision of an analytical result can be no greater than the accuracy and precision of the sampling. EPA (1980) has described in detail (Method 5, 40 CFR 60) how to obtain representative samples of particulate and gases in stacks and ducts. Many of the sampling methods described in this section are based on modified Method 5 sampling trains. Methods for sampling aqueous streams are described in: (Grant, 1978; and "Standard Methods," 1975). The American Society for Testing and Materials (1978) gives a procedure for obtaining representative samples of bulk solids. EPA recently published a manual (EPA, 1980) for

sampling and analysis for hazardous materials.

Gas sampling methods (stack or ambient air) can be grouped into three general categories: 1) liquid absorption systems, 2) liquid phase absorbents coated on solid supports, and 3) solid adsorbents. For sampling PCBs in stack gas from Annex I incinerators, use of a Florisil-trap-modified Method 5 train is recommended, as described in EPA's interim sampling and analysis manual (Beard and Schaum 1978). For other RCLs and organics, use of a Method 5 train modified with an XAD-2 trap is recommended. Tenax adsorption tubes have also been used. If ambient air monitoring for PCBs is to be performed during a PCB Trial Burn, it is recommended that a high volume sampler incorporating polyurethane foam be used.

There are suitable commercial instruments for continuous monitoring of O₂, CO, and CO₂. The reference method for NO_x is Method 7 (40 CFR 60), but there are equivalent near-continuous instrumental methods. Hydrogen chloride and TPM are sampled by a modified Method 5 technique.

Liquids are often taken by single "grab samples"; however, these samples may not be representative of a stream during process variations, and thus composite sampling is appropriate. Modified Mine Safety Appliances Model 5 samplers have been used when personnel or work space monitoring for PCBs or RCLs is necessary.

Analytical Methods

Data on airborne PCB levels and on PCB emissions from combustion sources are limited, partly because the assessment and interpretation of PCB emission data is complicated. One of the complicating factors is the fact that there are 209 possible PCB isomers, and most PCBs were made and marketed as mixtures. Interpretation is also complicated by the fact that the combustion process alters the relative amounts of isomers, and thus ambient air samples tend to be enriched in higher volatility PCBs and deficient in the lower volatility PCBs. Interferences from compounds (e.g., pesticides) which exhibit analytical behavior similar to PCBs also can make the interpretation of results difficult.

The most commonly used analytical method for determining PCBs is gas chromatography (GC) which separates compounds in the vapor phase. After

separation, various detectors are used to measure compounds. The most widely used detector is the electron capture detector (ECD) although flame ionization detectors (FID) and mass spectrometry (MS) can also be used. Gas chromatography-mass spectrometry (GC/MS) is generally used for confirmatory purposes.

For quantifying PCBs, three general methods can be used individually or in combination. Pattern recognition is the most common method and involves comparing the areas under a multiplex chromatographic elution pattern generated by a sample to the areas under the elution pattern generated by a PCB mixture of known concentration. Another method, derivatization, involves converting all PCB isomers in a sample to the fully chlorinated isomer, deca-chlorobiphenyl (DCB), and then using ECD or GC/MS to measure the amount of DCB present. Quantification also can be achieved by the measurement of individual isomeric components using GC/ECD or GC/MS.

Several different analytical methods for the detection of PCBs are described in the literature, but it is recommended that the methodology specified in EPA's interim manual (Beard and Schaum, 1978) be employed for analysis of samples taken during PCB Trial Burns. Results are reported in terms of nanograms (ng) DCB per dry standard cubic meter of combustion effluent sampled. To verify the presence of PCBs, GC/MS and pattern matching with Aroclor mixtures is used. The precision of the DCB analysis is stated to be 10 to 15 percent, and recovery of PCBs through the entire sampling and analysis procedure is stated to be 85 to 95 percent.

Combustion of PCBs

The purpose of incinerating PCB-containing wastes is to destroy the PCBs so effectively that any emissions of undestroyed PCBs to the environment will be at such low concentrations that adverse environmental and health impacts are not expected to occur. Five combustion process parameters have major impacts on the destruction and/or formation of polycyclic organic matter (POM) such as PCBs: 1) reaction temperature within the combustion and post-combustion zones, 2) residence time of reactants (air and fuel) and products in the high temperature zone, 3) turbulence or mixing efficiency of fuel and air, 4) air/fuel ratio including the

effects of operating cycles on combustion air supply, and 5) fuel feed size. Thermal destruction tests on PCBs indicate that essentially complete destruction occurs in well designed incineration systems. The most important cause of incomplete combustion of fuel is lack of turbulence or incomplete mixing of fuel, air, and combustion products.

The potential for formation of polychlorinated dibenzofurans (PCDFs) and dibenzo-p-dioxins (PCDDs) during thermal destruction of PCBs can be examined by thermochemical equilibrium calculations. Because accurate thermodynamic data are unavailable for these compounds, the thermodynamic feasibility of formation of PCDFs and PCDDs was examined indirectly by investigating combustion conditions and waste types that would favor the formation of intermediates, such as chlorobenzenes and chlorophenols. The calculations predict that, under oxidizing conditions, formation of PCDFs and PCDDs is not thermodynamically favored. However, under pyrolytic conditions (i.e., the absence or near absence of oxygen), as may arise in an inadequately designed or operated incinerator, thermochemical equilibrium calculations indicate that trace amounts of possible precursors to PCDFs and PCDDs can form.

Theory and experiment indicate that essentially complete destruction of PCBs can be achieved in both Annex I incinerators and high efficiency boilers. However, inadequate design or operation can lead to inadequate destruction efficiency and/or formation of highly toxic compounds such as PCDFs and PCDDs.

Annex I Incinerators

One disposal option for PCBs and PCB items is thermal destruction in an approved incinerator. In general, incinerators must meet specific operating requirements set forth in Annex I of the PCB Regulations. An incinerator which meets these requirements or which, based on evidence, is capable of operating without presenting unreasonable health or environmental risks from PCBs when one or more of the Section 761.40 requirements is not met, is known as an Annex I incinerator.

The operator of an incinerator is required to obtain written approval from the cognizant EPA Regional Administrator prior to incineration of PCBs or PCB items. The requirements for approval of

incinerators for PCB disposal are stated in the PCB Regulations (40 CFR 761.40). The EPA Regional Administrator also may prescribe any additional requirements which are necessary to satisfy the intent of the regulations. For example, incinerator design and operational criteria are very broad, and more definitive restrictions may need to be imposed in an approval. The Regional Administrator also may want to waive existing requirements or specify additional requirements in the areas of monitoring and recordkeeping, sampling and analysis, restrictions on waste composition, or compliance assurance.

High Efficiency Boilers

One disposal option for liquids containing 50 ppm or greater of PCBs (but less than 500 ppm) is thermal destruction in a high efficiency boiler. In general, high efficiency boilers must meet specific design and operational requirements set forth in the PCB Regulations (40 CFR 761.10).

The notification and approval process for high efficiency boilers depends on the type of liquid being burned. Incineration of mineral oil dielectric fluid from PCB-contaminated transformers only requires that the cognizant EPA Regional Administrator be given written notice 30 days prior to the burn. Thermal destruction of other liquid wastes containing from 50 to 500 ppm PCBs in high efficiency boilers requires written notice as well as authorization by the EPA Regional Administrator.

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The complete report, entitled "Guidelines for the Disposal of PCBs and PCB Items by Thermal Destruction," (Order No. PB 81-182 339; Cost: \$23.00, subject to change) will be available only from.

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