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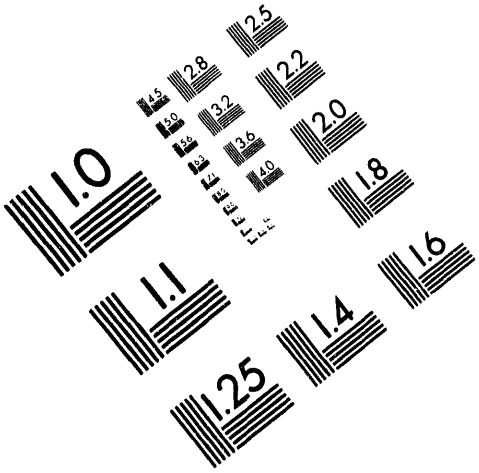

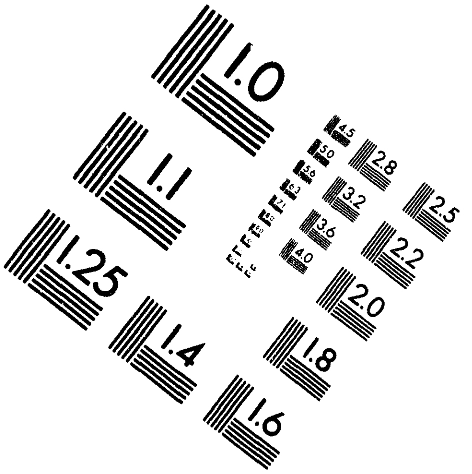

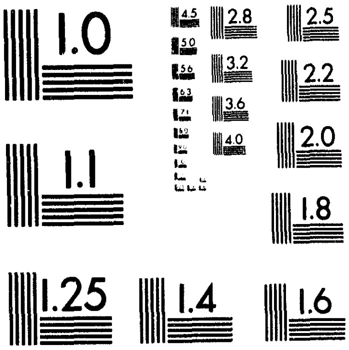

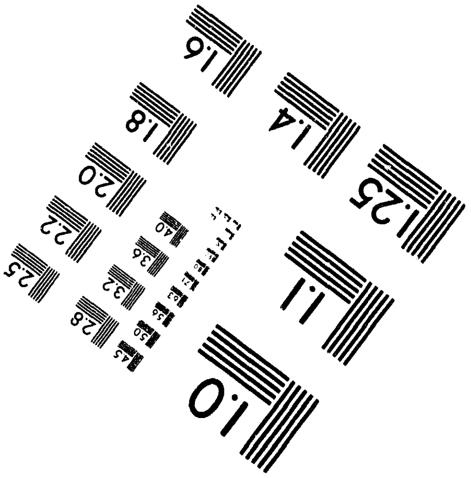

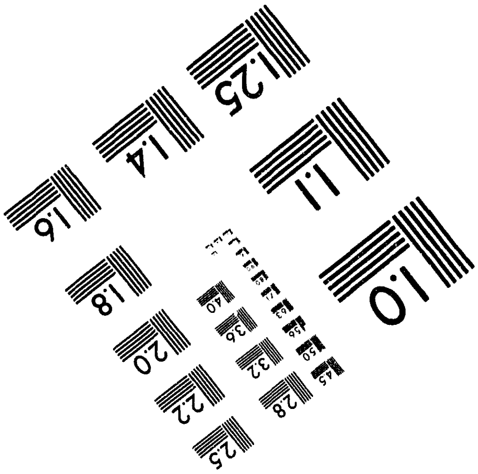

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DOE/MWIP-19

Guideline for Benchmarking Thermal Treatment for Low-Level Mixed Mixed Waste

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TABLES

ABBREVIATIONS AND ACRONYMS

APC	Air Pollution Control System
ARAR	applicable relevant and appropriate requirements
ASTM	American Society for Testing and Materials
BDAT	best demonstrated available technology
BIF	boilers and industrial furnaces
CAA	Clean Air Act
CEMS	continuous emissions monitoring systems
CWA	Clean Water Act
D&D	decontamination and decommissioning
DOE	U.S. Department of Energy
DQO	data quality objective
DRE	destruction and removal efficiency
EDE	effective dose equivalent
EPA	U.S. Environmental Protection Agency
ER	environmental restoration
FID	flame ionization detector
H&S	Health and Safety
HCl	hydrochloric acid
HEPA	high-efficiency particulate air
HSWA	Hazardous and Solid Waste Amendments
HWI	hazardous waste industry
ICP	inductively coupled plasma
LLMW	low-level mixed waste
MW	mixed waste
MWIP	Mixed Waste Integrated Program
NDIR	nondispersive infrared
NESHAPs	National Emissions Standards for Hazardous Air Pollutants
NRC	Nuclear Regulatory Commission
PA	phthalic anhydride
PCB	polychlorinated biphenyl
PCC	primary combustion chamber
PCDD	polychlorinated dibenzo dioxin
PCDF	polychlorinated dibenzo furan
PIC	product of incomplete combustion
POHC	principle organic hazardous constituent
ppm	parts per million
QA	quality assurance
QC	quality control
RAC	reference air concentration
RCRA	Resource Conservation and Recovery Act
RMA	relative molar abundance
SCC	secondary combustion chamber
TCLP	Toxic Characteristic Leaching Procedure

ABBREVIATIONS AND ACRONYMS (continued)

TEI	total employee involvement
THC	total hydrocarbons
TQM	total quality management
TSCA	Toxic Substance Control Act
ZD	zero defect

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EXECUTIVE SUMMARY

A process for benchmarking low-level mixed waste (LLMW) treatment technologies has been developed. When used in conjunction with the identification and preparation of surrogate waste mixtures, and with defined quality assurance and quality control procedures, the benchmarking process will effectively streamline the selection of treatment technologies being considered by the U.S. Department of Energy (DOE) for LLMW cleanup and management. Following the quantitative template provided in the benchmarking process will greatly increase the technical information available for the decision-making process. The additional technical information will remove a large part of the uncertainty in the selection of treatment technologies. It is anticipated that the use of the benchmarking process will minimize technology development costs and overall treatment costs. In addition, the benchmarking process will enhance development of the most promising LLMW treatment processes and aid in transferring the technology to the private sector.

The benchmarking process is intended for use during any stage (bench, pilot, or full scale) in the development of a treatment technology. The process can also be used for continuing improvement of a mature technology.

For any LLMW treatment technology to be considered for development or demonstration, it is anticipated that DOE would require that the technology be benchmarked according to the guidance provided in this document. The benchmarking process provides a comprehensive technical base for making decisions on the selection of alternative processes and on improvement of an individual treatment process. Flexibility in the decision-making process is maintained by allowing the decision-making team to assign the weighing of each benchmarking criteria.

To instill inherent quality, the benchmarking process is based on defined criteria and a structured evaluation format, which are independent of any specific conventional treatment or emerging process technology. Five categories of benchmarking criteria have been developed for the evaluation:

- operation/design
- personnel health and safety
- economics
- product quality
- environmental quality.

For thermal processes under consideration, data and other information collected and presented in each of the benchmarking categories interrelate the unit operations, to the effluent steams from the processes.

This benchmarking document gives specific guidance on what information should be included and how it should be presented. A standard format for reporting is included in Appendix A and B of this document. Special considerations for LLMW are presented and included in each of the benchmarking categories.

The five benchmarking categories can be further broken down into systems and performance evaluations. The systems evaluation is related to unit operations and the performance evaluation is related to quantification of effluent streams. The systems evaluation categories address how the system operates and what is required to make it operate. The operations criteria provide information on the history and ease of operation and on the mechanics of operation. The system design criteria document the standard and unique aspects of various unit operations. The health and safety criteria provide insight into the environmental and health risks for the operation and maintenance of the system. The economic criteria are used to evaluate annualized capital and operating costs of the system.

Performance evaluation categories address how well the system operates. Product quality criteria provide information on product or residue stream(s), which are used to assess how well objectives—such as reduction of mass or volume, capture of leachable constituents, and conversion of usable products—have been met. Environmental quality criteria are used to assess multimedia emissions of selected constituents and they are compared to acceptable emission levels cited in government regulations. Quantitative measures of these criteria are developed for comparison of treatment technology alternatives on a standard basis. To allow for direct comparisons of alternative treatment systems performances, certain Resource Conservation and Recover Act (RCRA) hazardous organics (principal organics hazardous constituents - POHCs), Clean Air Act and RCRA metals, and radioactive surrogate metals have been recommended for use in test waste feed streams.

The subtopics included in each benchmarking criteria category are listed below:

- operations/design criteria
  - process flow diagram
  - hardware specifications
  - complex and unique design
  - materials of construction
  - scale of operations
  - feed systems
  - thermal treatment process
  - auxiliary fuel/heat input
  - air pollution control equipment
  - residue/product handling
  - process monitoring and control
  - equipment/operations history

- personnel health and safety criteria
  - fugitive emissions
  - external contract with product and emission
  - maintenance
  - risk assessment

- economic criteria
  - capital investment
  - operating costs

- product quality criteria
  - measure of mass reduction
  - measure of volume reduction
  - measure of resource recovery

- environmental quality criteria
  - measure of emissions to each media
  - measure of pass/fail

Checklists of the above criteria subtopics are provided in Appendix A and B for the convenience of the benchmarking process user.

1. INTRODUCTION

When a waste contains both hazardous and radiological materials, it is classified as a mixed waste (MW). When the radiological activity is below a defined criterion, based upon the nature of the radionuclide present, the waste is determined to be low level. The evaluation of thermal treatment processes for low-level mixed wastes (LLMW) by benchmarking each process against established criteria is the subject of this report. Criteria are developed as a guideline for comparison (i.e., benchmarking, alternative thermal processes). Several reports have recently provided inventory information for LLMW currently in storage at the U.S. Department of Energy (DOE) facilities.[1,2] It is currently estimated that there is 250,000 m^3 of LLMW in storage. It is expected that a larger volume of LLMW may be generated during the decontamination and decommissioning (D&D), environmental restoration (ER), and facility compliance activities in order to ensure that DOE sites are in compliance with all regulations.

There are a wide variety of LLMW contaminant/matrix combinations and hence a wide variety of rules and regulations that define clean-up criteria and treatment process performance requirements. Hazardous organics and toxic metals are covered by the Resource Conservation and Recovery Act (RCRA) and Clean Air Act (CAA) and are regulated by the U.S. Environmental Protection Agency (EPA). Asbestos and polychlorinated biphenyls (PCB) are covered by the Toxic Substances Control Act (TSCA) and are regulated by EPA. The disposition, handling, and classification of radiological materials are controlled by the Nuclear Regulatory Commission (NRC) and DOE. These various requirements are utilized as a basis for process and system evaluation criteria in benchmarking.

In order to reduce the amount of waste in inventory and treat any new waste that is generated, treatment methods must be either used or developed to handle the wide range of anticipated waste streams. The objective is to transform the physical and chemical nature of the waste into residual products that significantly reduce the risk associated with the management of the waste material. Additional concerns are safety and reliability, volume reduction, minimization of secondary waste streams, and final product characterization that are factors in selecting feasible treatment technologies.

One class of waste treatment technology is thermal treatment. Thermal treatment is an engineered process that uses thermal oxidation to destroy the organic fraction of a waste stream. The thermal processes volatilize and destroy any hazardous organic component and leave a solid residual (e.g., ash, slag, glass, and metal). This residual inorganic product (hazardous and radiological contaminants) should contain minimal hazardous organic contaminants. This residue can either be the final waste form or require additional treatment to obtain a more desirable form. This treatment scheme allows volume reduction, waste destruction, waste-form conditioning, and risk management of the waste stream. Thermal treatment technologies show great potential in handling many of the waste streams that currently exist within DOE.

In order to realize that potential, technology modification and development programs are underway for various alternative treatment technologies (e.g., rotary kiln, vitrification, molten metal, and plasma arc) of thermal waste treatment. Some methods, such as rotary kiln incineration, have been fully permitted and licensed to handle LLMW within the DOE system.[3-6] Other technologies, such as vitrification and plasma arc, are in a development and design stage to demonstrate their applicability to various DOE LLMW streams.[7-10]

The use of consistent criteria for evaluating these technologies by using surrogate formulations[11-14] and benchmarking and defining the data quality objectives[15] (DQOs) will provide the means of comparison and selection to meet the treatment and disposal needs of LLMW within the DOE complex, both for waste that are in storage now and the waste that will be generated during the remediation and decontamination of the various DOE sites.

The benchmarking process can be applied but is not limited to the following alternative thermal treatment processes:[16]

- incinerator technologies
  - rotary kiln incinerator
  - fluidized bed incinerator
  - agitated hearth incinerator
  - multiple-hearth incinerator
  - KFK excess air incinerator
  - liquid injection incinerator
  - controlled air incinerator
  - cyclone incinerator
  - indirect-fired pyrolysis incinerator

- miscellaneous technologies
  - infrared furnace
  - wet air oxidation
  - steam gasification detoxifier
  - supercritical water oxidation
  - ultraviolet photo—oxidation
  - plasma pyrolysis reactor
  - gas phase destruction

- melter technologies
  - molten salt furnace
  - Joule-heated melter
  - plasma arc furnace
  - microwave melter
  - slagging kiln
  - electric furnace melter
  - fuel-fired melter
  - high-temperature Joule melter
  - in-can resistance melter
  - stirred Joule melter
  - induction melter

In many development and demonstration applications, it is advisable to structure a pilot-scale test using surrogates. This allows for (1) monitoring the partitioning of metals and characterizing off-gas effluents to firm up the integrated mixed waste treatment baseline process design and associated economics; (2) filling in data gaps for trace emissions such as radioactive surrogate metals and RCRA/CAA metals, nitrogen oxide (NO_x), total hydrocarbons (THC), products of incomplete combustion (PICs), carbon monoxide (CO), product leachability metal-specific data; and (3) assessing operability/availability and maintenance issues for field-scale unit. One fundamental objective of this benchmarking process is to allow DOE to establish accurate performance data at the bench, pilot and field scale in a structured manner so that resources can be allocated equitably with overall system payback. This thermal treatment technology development "exact template" approach can be applied toward mature as well as emerging technologies.

The concept of pass/fail criteria for alternative emerging technologies being defined by ability to control trace constituents emissions (relatively new—not nearly as much of a concern even just 10 years ago) is real. The need to control PICs, dioxins, metals, etc., at nonrisk-based, extremely low mass release rates has created the need to benchmark the mixed waste treatment processes/technologies in those terms. Very similar needs exists in the private sector to support the hazardous waste combustion industries as exist in the mixed waste treatment arena to treat DOE waste.

The technical guidance defined herein is directly applicable to assessing the status of a given mixed and hazardous waste thermal treatment technology development program as well as advisability of accepting responsibilities of demonstration cosponsor. To a significant degree, the technical assessments will boil down to comparisons in the ability to control trace constituents as a function of economics.

2. BENCHMARKING PROCESS

The definition of benchmarking is shown in Fig. 1 in a menu adapted from Spendolini.[17] From the menu, it can be seen that there are many different ways to describe what the benchmarking process does and why it is done. But one of the most important features to notice is that it is a *process* (Fig. 1, box 3). It is also important to realize that the process is not done just once but should be a continual method of improvement and evaluation. The quality-based philosophies of total quality management (TQM), zero defect (ZD), and total employee involvement (TEI) are all consistent with the benchmarking process.

The process of benchmarking thermal treatment systems will combine the disciplines of process operations, quality assurance (QA), quality control (QC), and technical support (engineering, development, research) to ensure that the goals of the process are met and that the full capabilities of the process are known. The application of the benchmarking process to the evaluation of the unit operations allows a composite picture of the entire system operation to be obtained. It is through the consistent methods of benchmarking that meaningful evaluations and comparisons of alternative thermal treatment processes and the processing of different waste streams can occur. From Fig. 1, the baseline definition for benchmarking thermal treatment systems can be read as follows:

> A continuous, systematic process for evaluating and understanding the operations of systems that are developed as representing best practices for the purposes of LLMW treatment.

It can be difficult to balance the objectives of economical treatment of LLMW and detailed process and/or regulatory oversight. The benchmarking process is not meant to be an every day process but a tool that is readily available and readily implemented when variations in the systems operations are expected. It can also be used on a routine basis to monitor the performance of the system. Documentation of defined benchmark parameters can provide a regulatory, QA/QC, and system performance criteria that will support the use of a particular thermal treatment system as a generally accepted and proven method of LLMW treatment.

Five categories of benchmarking criteria have been developed for the evaluation of thermal processes suitable to the treatment of LLMW. These categories include (1) operations/design, (2) personnel health and safety, (3) economic, (4) product quality, and (5) environmental quality. The first three categories relate to the systems evaluation described in Sect. 2.4. The remaining two categories relate to the process evaluation described in Sect. 2.5.

2.1 THERMAL TREATMENT SYSTEMS

Thermal treatment systems are normally composed of a series of unit operations. This combination of operations can generally be broken down into 4 unit operations: waste acceptance and pretreatment, primary combustion chamber (PCC), secondary combustion chamber (SCC), and Air Pollution Control System (APC). Each of these unit operations has input and output streams that must be controlled and evaluated. Although the initial waste

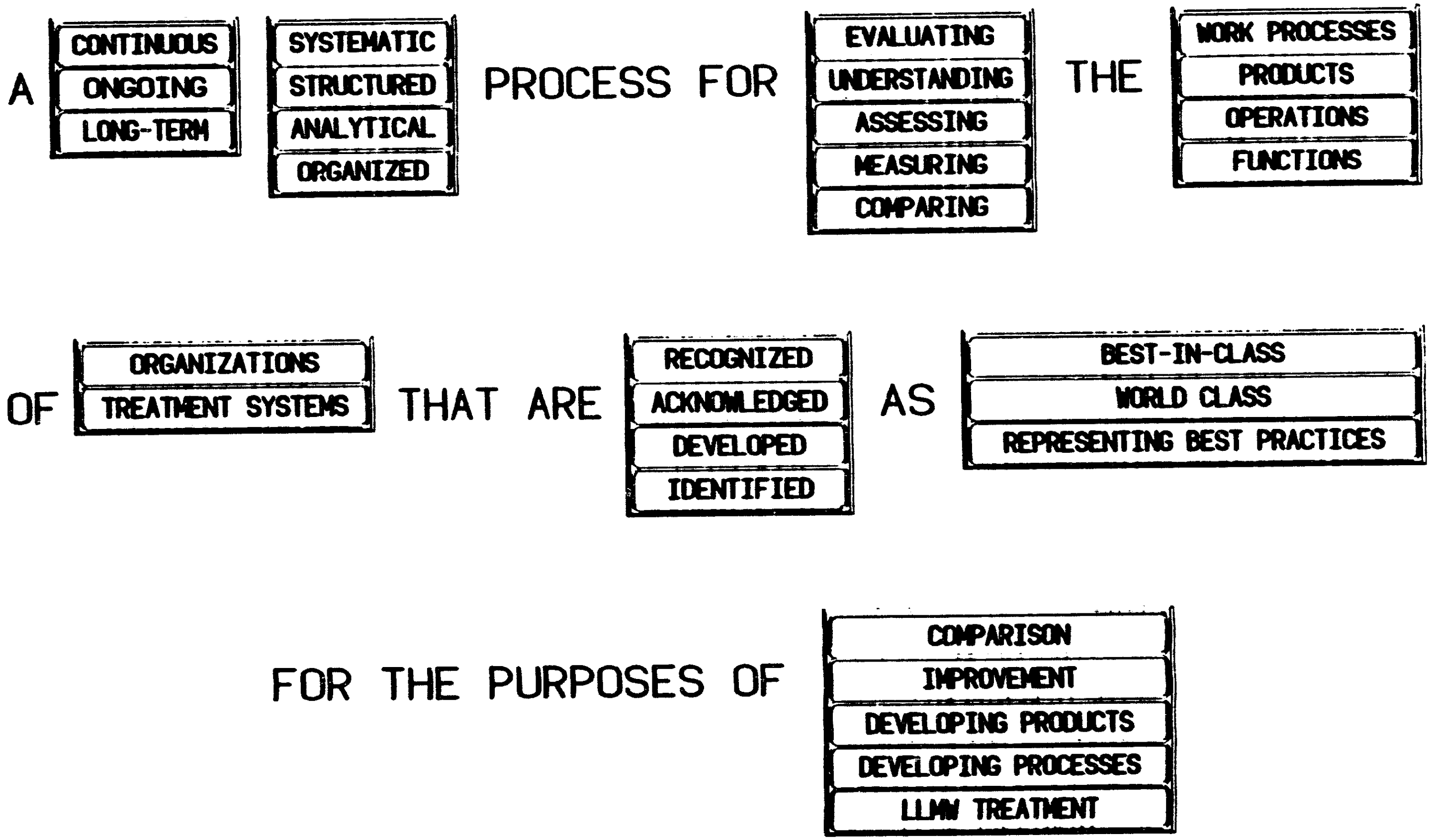

Fig. 1. The Benchmarking Menu (adapted from M.J. Spendolini (29), *The Benchmarking Book*, Amacom, 1992).

input stream, along with the final product (solid) and gaseous emissions, are the major areas of regulatory concern, all emission sources are of importance to obtain a good material balance on the system. Figure 2 shows a schematic diagram of the interrelationship between the unit operations (system evaluation) and the effluent streams (performance evaluation). It is this adaptability that allows tailoring of system operations to meet a specific set of needs for the treatment of various waste streams.

It is important to realize that there are a large number of possible permutations of these unit operations for thermal treatment systems. While this adaptability allows "custom" design of a process, it makes the comparison and evaluation process more difficult. The use of consistent methods and means of benchmarking the various unit operations and the overall systems operations will allow the performance capabilities of the various thermal treatment processes to be more accurately determined.

Defined herein are the methods and means by which the various thermal treatment technologies should be evaluated, i.e., benchmarked. This document will outline the various parameters that will allow a detailed understanding and interpretation of the process strengths and weaknesses. It is very important to have *consistent* methods of evaluation of the efficacy of techniques for various waste streams as well as for methods of comparison for various techniques for a given waste stream.

Benchmarking parameters can in part be developed from applicable regulatory requirements that thermal treatment technologies must meet. Therefore regulatory requirements for incinerators, boiler or industrial furnaces (BIFs), other thermal treatment processes, or miscellaneous units have been used in determining benchmarking criteria.

The following issues provide some insight into the regulatory drivers that must be addressed to permit a thermal treatment unit. Although there are various classifications for thermal treatment units, the following points require consideration:

- Normal steady-state operating conditions must be achieved before waste addition, unless the device is a batch process with a complete thermal cycle required to treat a discrete quantity of hazardous waste.
- Instrumentation measuring/documenting waste-feed flow and auxiliary fuel/air feed, treatment process temperature(s), off-gas flow, and other relevant process flow, pressure drop and level controls must be monitored. Appropriate process control adjustments and maintenance of steady-state thermal treatment conditions must be made automatically and/or by the operator. For example, each unit operation typically has one to two waste-feed cutoff control circuits with operating limits defined during controlled testing. A stack plume must be observed for normal color and opacity.
- The process and associated equipment must be inspected daily for leaks, spills, and fugitive emissions. Emergency shutdown controls and system alarms must be checked periodically. At closure, all hazardous waste and hazardous waste residues must be removed from the process or equipment.
- Performance standards for incinerators must be met.[18] For example, these standards include 99.99% destruction and removal efficiency (DRE) of selected principal organic hazardous constituents (POHCs) but 99.9999% DRE of dioxin listed and solid PCB-contaminated wastes; 99% removal of hydrochloric acid (HCl) or 4 lb/h HCl emissions, whichever is greater; and particulate emissions of no greater than 0.08 grain per dry

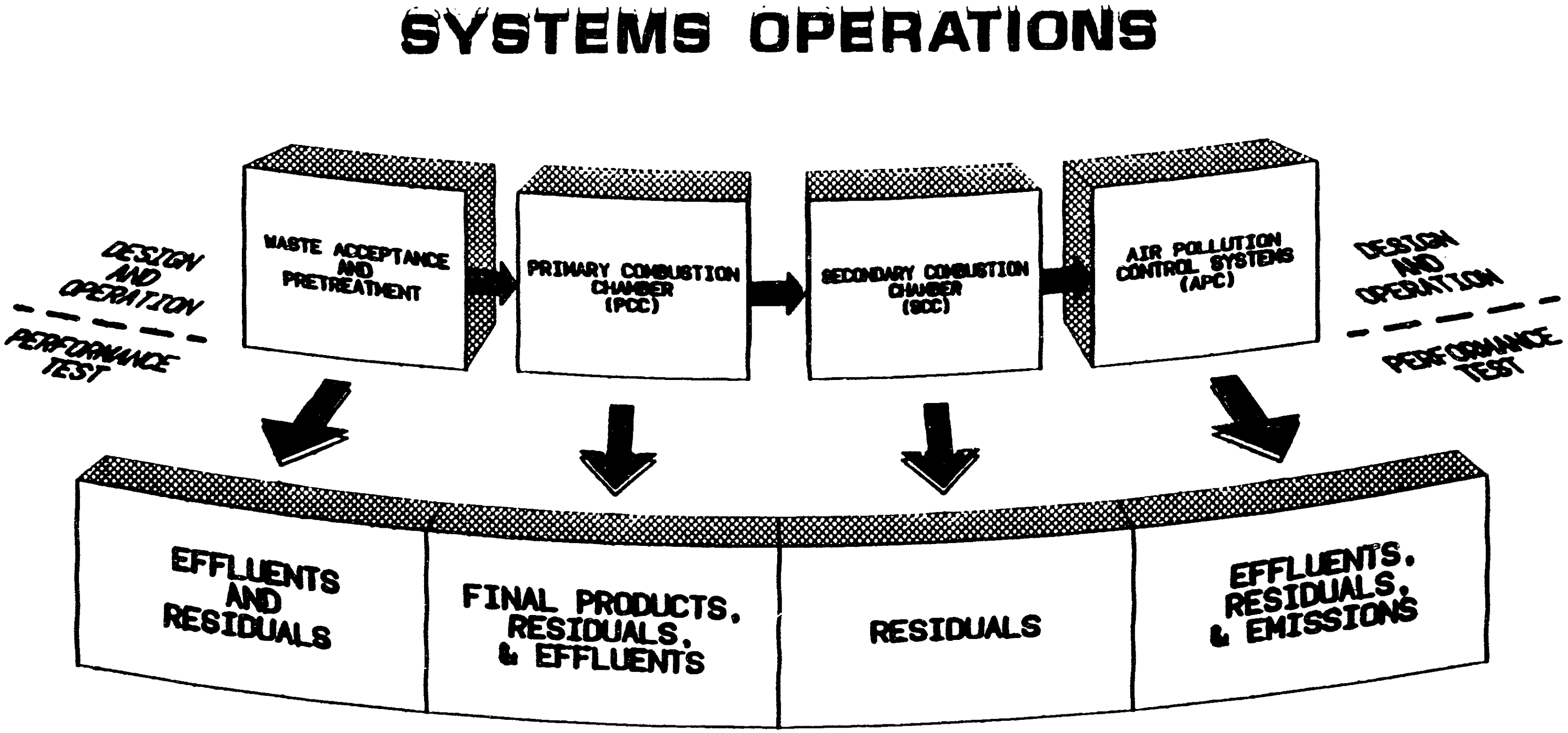

Fig. 2. Schematic diagram of the relationship between system and unit operations of thermal treatment processes.

standard cubic foot (corrected to 7% O_2). Under the Toxic Substances Control Act (TSCA), for treatment of PCBs, an operating temperature of at least 1,200°C at 3% O_2 with a minimum combustion gas residence time of 2 seconds is required. Regulatory permitting procedures include public notification and an open comment period.

- Additional regulatory complexity is introduced by various states. Several states incorporate the federal regulations on thermal treatment facilities directly within their individual state hazardous waste rules. Minnesota adds air flow, scrubber flow, and scrubber pH to partially specified federal monitoring and inspection requirements.[19] Wisconsin adds cadmium and chromium to baseline waste analysis and specifies adequate temperature and residence time to assure complete processing and necessary air pollution control equipment to produce a noncombustible residue and odor free operation.[20] In addition, National Emissions Standards for Hazardous Air Pollutants (NESHAPs), state air regulations, definitions of significant net emissions or source potential increases, and other standards promulgated for hazardous and toxic air pollutants may impose more stringent requirements than hazardous waste regulations. For example, significant pollutant and net emissions rate increases are defined by Tennessee for carbon monoxide, nitrogen oxides, sulfur dioxide, particulates, ozone, lead, asbestos, beryllium, mercury, vinyl chloride, fluorides, sulfuric acid mist, hydrogen sulfide, and reduced sulfur compounds.[21]
- The final rule for control of toxic metals from BIFs was effective August 21, 1991.[22,23] Standards are implemented through a three-tiered approach. Tier I feed-rate limits are based on an assumed reasonable, worst-case dispersion scenario with an assumption that all metals fed to the device are emitted. Under Tier II, credit for partitioning to bottom ash or product and air pollution control equipment removal is obtained in conjunction with emissions testing. Site-specific dispersion modeling and emission test results are used under Tier III to demonstrate that established health-based ambient concentrations are not exceeded.
- For the carcinogenic metals, arsenic, beryllium, cadmium, and (hexavalent) chromium, the hypothetical maximum exposed individual may not receive an increased cancer risk due to inhalation of more than 1 in 100,000. For the noncarcinogenic metals, antimony, barium, lead, mercury, silver, and thallium, predicted concentrations may not exceed reference air concentrations (RACs) designated by EPA. When the final rule was first effective, it did not limit emissions of nickel since the two carcinogenic nickel compounds (nickel carbonyl and subsulfide) are not likely under oxidizing conditions. Also at that time, adequate health data to establish RAC for selenium was not available to EPA.
- On May 18, 1993, the "EPA Draft Strategy for Combustion of Hazardous Waste in Incinerators and Boilers; Interim Final Guidance on Waste Minimization for Hazardous Waste Generators" was issued. A more stringent particulate matter standard of 0.015 grain per dry standard cubic foot, corrected to 7% oxygen, was recommended. An interim emission limit of 30 nanograms per dry standard cubic meter corrected to 7% oxygen for the total mass of tetra through octa dioxin and furan congeners was also proposed. EPA regions and states were strongly encouraged to impose these requirements through use of the omnibus permit authority.
- For superfund projects, the applicable relevant and appropriate requirements (ARARs) for hazardous waste incinerators and vitrification processes have been summarized by Staley.[24] In addition to the performance standards under RCRA for DRE for organic contaminants, HCl emissions, and particulate emissions, other requirements exist. [Any federal or state requirement that could be applied must be considered as a project—specific requirement.] Under RCRA, carbon monoxide emissions must be less than 100 ppm, or THC emissions less than 20 ppm at 7% O_2. A tiered approach similar

to metals is utilized. If CO is controlled to less than 100 ppm, no THC limit is imposed. If DRE performance is demonstrated at greater than 100 ppm CO, a THC limit of 20 ppm is imposed in addition to the CO limit. Metal emissions must be less than standards set using a three-tiered approach based on health risk to the most exposed individual.

- Under Hazardous and Solid Waste Amendments (HSWA), treatment process solid and liquid residues must meet best demonstrated available technology (BDAT) decontamination levels before disposal. The BDAT levels may be based on a performance standard or the use of a specific technology.[25] Incineration and stabilization are cited as BDAT for a number of DOE waste streams.[26]
- Under the Clean Air Act (CAA), an air permit that specifies emission limits for criteria and hazardous air pollutants must be obtained from the state. Under the Clean Water Act (CWA), permits may be required to discharge liquid effluents.

The standards and guidelines listed above, but not limited to, are recommended benchmarks that can be used to assess the performance of thermal treatment technologies proposed for the treatment of LLMW. These issues and others form the basis for the criteria selected for the benchmarking parameters to document, evaluate, and assess the performance of alternative thermal treatment technologies for LLMW.

2.2 WASTE STREAM CRITERIA

The physical form (gas, liquid, or solid), physical nature (e.g., heating value and viscosity), and chemical composition (e.g., concentration of hazardous components) are the three major parameters that determine the treatment options available for a specific waste stream. For many waste streams, some or all of these parameters must be determined through waste analysis in order to select appropriate operating conditions and to estimate the type and amount of pollutants emitted. Minimum waste analysis parameters typically include heating value, halogen and sulfur content, and concentrations of lead, mercury, and other RCRA and radiological metals of concern.

It is extremely important to be able to compare the performance capabilities of a given thermal treatment unit against another unit. To best establish standardization and make accurate comparisons, a common set of waste-feed constituents has been defined. Various DOE waste streams have been simulated. Companion documents[11-14] specify surrogate waste stream formulations for LLMW streams and simulations for waste water treatment sludges from within the DOE complex. Using these standardized surrogate formulations, the performance of the various thermal treatment technologies with respect to various waste stream types can be compiled. The use of surrogate wastes will provide for the evaluation of thermal treatment technologies being developed in the Mixed Waste Integrated Program (MWIP) and the hazardous waste industry.

Benchmarking thermal treatment technology development does not require using surrogate formulations[11-14] but can be greatly assisted by their use. These formulations were developed to provide a *consistent waste feed* for evaluating emerging, alternative thermal treatment technologies being developed to support the DOE's needs. Benchmarking provides a means for *consistent evaluation* of thermal treatment technologies. Benchmarking benefits from the use of the surrogate waste stream formulations but is not dependent upon them. It should be noted that if a technology is to be compared to other technologies then the waste stream selection can have a major effect on the ability to compare technologies. Thus the use of just the hazardous components portion (radiological surrogates, RCRA metals or RCRA metal surrogates, and RCRA organics) of the surrogate formulation can be added to the waste stream being treated to evaluate the process with respect to these materials. This is probably most beneficial with the use of the radiological surrogates. The recommended surrogates can be added to an existing hazardous waste stream without the need for a radiological license, without adding any additional hazards to the final product, and without generating a mixed waste residue.

2.3 SPECIAL CONSIDERATION FOR LOW-LEVEL MIXED WASTE

The DOE facilities must comply with 40 CFR Part 61, subpart H, which is the National Emissions Standards for Hazardous Air Pollutants (NESHAPs) for radionuclides. For a DOE facility, emissions of radionuclides other than radon shall not exceed amounts that would cause any member of the public to receive in any year an effective dose equivalent of 10 mrem/year.[27] A facility is defined as all buildings, structures, and operations, on a contiguous site and would include existing operations. Continuous sampling of vent discharges for radionuclides is required at all release points with a potential to emit radionuclides that would cause an effective dose equivalent of 1% of the standard. All radionuclides that could contribute greater than 10% of the potential effective dose equivalent for a release point shall be measured. Potential emissions are based on resulting discharges if all pollution control equipment did not exist but operations were otherwise normal.

Guidance is provided for the estimation of radionuclide emissions.[28] The amount of curies used in the process is multiplied by 1 if a gas, 10^{-3} if a liquid or particulate solid, or 10^{-6} if a solid. However, if heated to a temperature of 100°C, or boils at 100°C, or is intentionally dispersed, a radionuclide must be handled as a gas in absence of additional data. Adjustment to emission factors for effluent controls are provided.

The NESHAP radionuclide standards applicable to DOE facilities are summarized as follows:

- Dose standard of 10 mrem/year effective dose equivalent (EDE) to maximally exposed individual.
- Continuous sampling required for all emission point that would generate a potential dose of 0.1 mrem/year.
- "Periodic confirmatory measurements" required for sources that generate an EDE of less than 0.1 mrem/year.
- Approval for construction and modifications required for sources with an actual dose of greater than 0.1 mrem/year.
- Annual report required for submittal to EPA by June 30 of each year.

Materials handling, criticality safety, and exposure risks are the major differences between treating mixed waste and hazardous waste. Additonal documents provided by the Mixed Waste Integrated Program[29,30] provide special design and operating criteria for treating mixed waste.

For waste stream matrices containing LLMW, the process of optimizing thermal treatment throughput and maintaining low mixed and hazardous species emissions must be an integrated-systems approach that involves careful waste characterization assessment incorporated into the design, performance testing and permitted operation.

2.4 SYSTEM OPERATIONS EVALUATION

Each process will have site specific radiological requirements that impact the design and operation. Meeting the system evaluation (Sect. 2.4) and the performance evaluation (Sect. 2.5) criteria may require the following: (1) minimizing primary chamber operating temperature and related particulate and total inorganic carryover, (2) minimizing off-gas flow, (3) minimizing aqueous scrubber secondary liquid waste, and (4) overall optimization of the APC general process design with respect to controlling release of trace radioactive volatile and solid form constituents.

The first part of the benchmarking process (Chap. 3) is the overall systems evaluation. The operations criteria address *how* the system operates and *what* is required to make it operate. Much of the information documented in the systems evaluation section will not change as the system is benchmarked during various testing and evaluation procedures. This section provides documentation and detail of the system operations.

The system evaluation is broken into three sections that provide documentation and means of comparison of the performance test results. Some of these system evaluation benchmarking criteria are quantifiable, such as those shown in Fig. 3 (e.g., proven technology, operability, reliability, throughput, capital cost, and operating cost). More of a qualitative evaluation approach is required to assess such aspects as overall design complexity and risk assessment.

- operations/design criteria
    - process flow diagram
    - hardware specifications
    - complex and unique design
    - materials of construction

    - scale of operations
    - feed systems
    - thermal treatment process
    - auxiliary fuel/heat input
    - air pollution control equipment
    - residue/product handling
    - process monitoring and control
    - equipment/operations history

- personnel health and safety criteria
    - fugitive emissions
    - external contact with product and emission removal
    - maintenance
    - risk assessment

- economic criteria
  - capital investment
  - operating costs

The operations criteria provides background into the ease of operation, history of operation and the mechanics of how the system operates. The design criteria document the unique and standard aspects of the various unit operations and how, as a whole, they are combined to create a waste treatment system. The personnel health and safety criteria provide insight into the environmental and health risks for the operation and maintenance of the overall system. The economic criteria are used to evaluate the capital and operating costs associated with alternative treatment technologies.

The system operations information, detailed in Chap. 3, in combination with the performance test information obtained in Chap. 4, provides an overall prospective of the efficacy of the system. Thus as either engineering (hardware), operational, or waste stream acceptance criteria are varied, the overall performance of the system can be documented and evaluated. And, since a consistent format is used in this benchmarking and evaluation process, the results can be more equally compared with the performance results of other systems.

2.5 PERFORMANCE EVALUATION

In contrast to systems evaluation (Chap. 3), the performance evaluation (Chap. 4) provides insight into *how well* the system operates. The objective of using generic process performance testing for benchmarking processes is to apply standard techniques so data that is reliable and allows uniform comparison of product and environmental quality may be obtained. Such a performance evaluation is needed in order to compare technology alternatives and make site demonstration testing decisions in applying treatment of LLMW. Measurements made during a performance test on the thermal treatment process allow assessment of how well a process meets performance standards.

Figure 3 has been developed to illustrate the use of a process evaluation diagram to introduce and incorporate the following concepts for consideration in the benchmarking process:

- preprocessing,
- creating a useful product ("good product"),
- recovering and reusing of process waste,
- including subsequent treatment and disposal processes in the benchmarking evaluation ("cradle-to-grave concept"), and
- including a measure of utilities use, capital cost, human resource use, other supplies.

Potential product quality considerations include the following:

- physical form of the product (ease of handling),
- leachability of the product (organics, metals),
- presence of volatile organics in the product,
- volume reduction, and
- ratio of "good product" to "product for disposal."

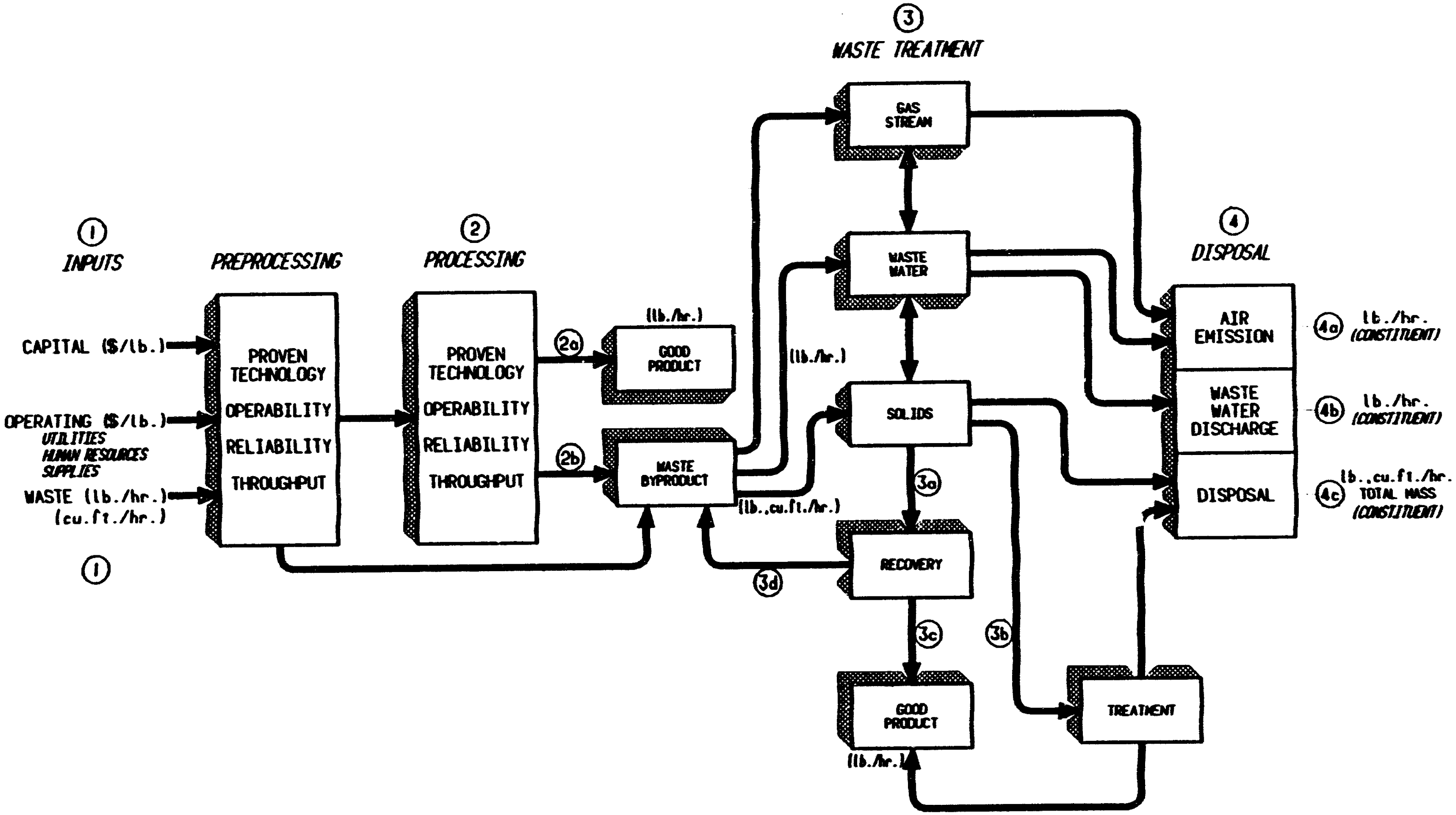

Fig. 3. Block diagram of thermal treatment benchmark processes.

Potential environmental quality criteria include the following:

- restrictions on leachate from ash products,
- degree of destruction of organic constituents,
- emission limitations, and
- impact of "secondary waste streams."

There are several categories and subcategories of mixed waste streams. In order that the performance test provides comparative, quantitative data on trace constituents present in the various mixed waste categories, eight surrogate constituents, representing organics (naphthalene, 1,2-dichlorobenzene, chlorobenzene), metals (Cd, Cr, Ni, and Pb) and radionuclide surrogates (Ce and Cs), will be added to representative waste mixtures for test purposes. The use of surrogate constituents and the preparation of waste mixtures has been described in companion documents.[11-14]

Measurements of surrogate constituents during the performance test will allow the following:

- comparison of surrogate mass emissions to all media to their corresponding mass feed
- evaluation against pass/fail environmental standards/guidelines.

Specific measurements during the test will

- determine emission rates for the eight surrogate constituents, particulates, HCl, SO_x, NO_x, CO, CO_2, and THC;
- determine capture and leachability of surrogate constituents in residue/product;
- establish system removal efficiency for each surrogate constituent;
- demonstrate the mixed-waste feed and process operating conditions "envelopes" that result in optimum product and environmental quality;
- identify/quantify PICs; and
- quantify emissions of "waste-specific" metals.

Standardization will be accomplished because

- common surrogate constituents will be included in all tested waste feed;
- standard sampling/analytical/monitoring methods will be used to measure the eight surrogate constituents and other parameters in all input, output, and appropriate in-process streams;
- DQOs will be established for waste feed, process residue, process product, and process emissions; and
- continuous process and emission monitoring measurements will be established and utilized.

Modeling the performance testing of alternative thermal treatment processes for LLMW after hazardous waste incinerator and BIF guidance for measurement allows the use of several existing EPA guidance documents and procedures and provides a comparison of alternative thermal technologies.

Following the data collection phase of the performance test, evaluation against the following quantitative measures would be calculated for benchmarking:

- product quality criteria
  - measure of mass reduction—(lb solid waste for disposal)/(lb waste fed)
  - measure of volume reduction—(ft^3 solid waste for disposal)/(ft^3 waste fed)
  - measure of resource recovery—(lb good product)/(lb waste fed)

- environmental quality criteria
  - measure of emissions to each media [for each constituent—(lb emitted/lb fed)]
  - measure of pass/fail [for each constituent—(comparison to standard)]

Since the performance testing process will be utilized for comparison of processes rather than establishment of process limits for permitting, use of alternative data collection procedures may be worth consideration. Several continuous emissions monitoring systems (CEMS) are under development and in some cases in use on combustion systems. The use of CEMS as part of a development program for process feedback and control is encouraged. However, standard sampling and analytical methods and certifiable instrumentation will be used during actual performance testing. This preserves the standardization of data for comparison of processes as is discussed in a companion document that describes the data quality objectives for the benchmarking process.[29]

2.6 QUALITY ASSURANCE/QUALITY CONTROL

In order for the benchmarking process performance test to create comparable data, a common minimum quality of that data must be assured. To accomplish this, consistent QA/QC procedures will be utilized. QA activities address delegation of program responsibilities to appropriate individuals and documentation, data review, and audits. These procedures allow assessment of the reliability of the data collected.[15,31-33]

The complementary activities of QC address sample collection and integrity, chemical analysis methods, and production and review of QC data. These QC procedures, when used continually during a sampling and analysis program, maintain the quality of data within control limits. Details on the goals and documentation of QA/QC related to performance test plans for alternative thermal treatment processes for the management of LLMW are developed in a companion document.[15] An overview of the QA/QC concepts for development and demonstration projects is presented below.

DQOs must be established for accuracy, precision, completeness, representativeness, and comparability for the process performance data collected. *Accuracy* is the degree of agreement of a measurement with the accepted reference or true value. Appropriate accuracy goals would include the use of high-purity reference materials for calibrations and spiking. This allows the correction of errors due to instrument response and incomplete preparation recoveries and minimizes uncertainties in the analytical data due to random errors. *Precision* is a measure of agreement among measurements of the same sample property. Example measures of precision would be the correlation coefficient for calibration curves and the relative standard deviation for analysis of surrogate compounds in replicate samples. *Completeness* is a measure of the number of samples for which analytical results are received during the performance test compared to the planned number (e.g., 95%). Factors that influence *representativeness* of a sample include the selection of appropriate sampling sites, sampling frequency, sample preservation, sampling procedures, sampling equipment, and sample preparation methods. The use of common units of measure will allow data to be *comparable.*

A key element of QA applicable to benchmarking of thermal processes involves the identification and establishment of roles and responsibilities for QA/QC within the testing and operation team for both development and demonstration projects. Suggested QA/QC roles and responsibilities include the following:

- project manager
  - ensure that proper materials, instruments, and qualified personnel are available
  - designate individuals to assist in QA/QC responsibilities

- quality assurance coordinator
  - assist the project manager in specifying QA/QC procedures
  - make on-site evaluations and submit audit samples (if applicable)
  - recommend corrective action as required

- analysis coordinator
  - train laboratory personnel in appropriate laboratory QC
  - receive samples and verify that samples received agree with packing list or chain of custody
  - verify that laboratory QC and analytical procedures are being followed

- sampling coordinator
  - determine appropriate sampling equipment
  - ensure appropriate sample collection, preservation, and transport
  - check all sample documentation

- QC and data manager
  - maintain records and track samples through subsequent processes
  - prepare QC samples
  - prepare QC data for review

Appropriate elements of QC can be incorporated into the benchmarking process through the use of standard methods. These include the use of

- standard sampling methods, handling, custody, and holding times;
- standard analytical methods on each sample from each input and output stream; and
- standard calibration procedures for sampling, analysis, and process monitoring equipment.

3. SYSTEMS EVALUATION

This section provides background operational information to allow the actual performance of the treatment system to be compared on a standardized bases. The following sections provide descriptions of the requested information. An organizational guide for compiling the requested information into a uniform package is provided in Appendix A. Any documentation or reference source should be included to ensure that all details of the system are documented and can be properly benchmarked. This will allow any reader or reviewer of the data to obtain additional vendor or literature data to further their understanding of the selected benchmarking parameters. If a benchmarking criteria is not documented, then an explanation should be provided as to why this criteria was not or could not be obtained.

3.1 OPERATION/DESIGN CRITERIA

This section provides information and background on the operation and design of the entire system. This information will assist not only in the interpretation of the data but also provide a detailed explanation of the technology for those unfamiliar with the technology. This technical and operational understanding will assist in the evaluation and comparison of the system performance.

3.1.1 Process Flow Diagram

A flow sheet of all components that form the current system under evaluation should be provided. This should include major components, monitoring points, feed back loops, sampling points, power and utility requirements, and their normal operating conditions (e.g., temperature, pressure and flow characteristics). For performance test planning and documentation purposes, process flow diagrams should illustrate the following:

- key unit operations,
- location of process instrumentation and sampling locations for the performance test, and
- material, energy balance, and performance criteria information.

This information should also clearly indicate any variations that have occurred since the last benchmark was performed (first benchmark excluded). One or more diagrams may be needed for these various purposes.

3.1.2 Hardware Specifications

This section should document the manufacturer's name and model number for all major process equipment. The purpose of this section is to allow the reviewer to obtain more detailed information from specified equipment vendors if desired.

3.1.3 Complex and Unique Design

A flow sheet of all components that are not commercially available and are either unique to the process or have been specially constructed to meet system criteria should be provided.

Discuss the advantages of the components that are unique to this system. How do they add to the overall efficacy of the process?

3.1.4 Materials of Construction

Materials of construction of the major process equipment used during the performance test or proposed for use in a demonstration test should be summarized in a table with the materials exposed to the process gas and residual product melts/ash highlighted.

3.1.5 Scale of Operations

This section is designed to

- document the current scale of operations with respect to the actual and/or anticipated maximum waste throughput (lb/h) for the system;
- document the "footprint" required for the system and the anticipated "footprint" of a full-scale system;
- state if this system could be made "portable" (e.g., size of unit and number of semi-trailers);
- provide documentation on what the various size limitations are for the various technologies;
- estimate the size the systems could be made (large or small); and
- state that unit operation is the limiting factor for scale-up or scale-down of the system.

3.1.6 Feed Systems

Many systems that are under development may not have dealt in much detail with the feed systems that would be required for management of large quantities of waste materials. In addition, some systems may require significant waste preparation prior to introduction into the primary thermal treatment operation. Both of these issues should be addressed in the documentation of the performance test in the description of the feed system utilized. Some areas to address may include the following:

- mixing and blending
- separation
- size reduction
- material transport
- feed rate monitoring and control

3.1.7 Thermal Treatment Process

Since the thermal treatment unit operation(s) is probably the most unique feature of the process when compared to alternative treatment processes, this section of the engineering description is extremely important for review of the performance test results. The description should promote understanding of thermal treatment process features that affect its performance relative to product and environmental quality criteria described in Sect. 2.4. Examples of process features to discuss include the following:

- principle of operation
- batch versus continuous operation, including associated throughput
- reactor dimensions, including associated volume
- reactor operating conditions, including temperature and pressure
- various operating modes that impact ability to meet performance and emissions standards
- the use of multiple thermal process steps

3.1.8 Auxiliary Fuel/Heat Input

Normally, as a consideration for economic criteria, auxiliary fuel/heat input needs to be quantified. The resource requirement (type of fuel/energy input) and an assessment of cost per pound of waste fed should be made. In addition to economic considerations, availability of utilities may be a site concern that needs to be addressed.

3.1.9 Air Pollution Control Equipment

Several alternatives for air pollution control equipment may be available for a given thermal treatment process. The specific system utilized for the process development should be described. If development has not reached a stage where the final air pollution control system(s) has been applied, the planned design air pollution control design should be described. With regard to both product and environmental quality, the effect of process emissions can be significantly affected by the choice of air pollution control equipment. When planning and documenting process performance results, the anticipated impact of planned air pollution control system improvements or changes should be considered.

Assessment factors that need to be discussed include those that affect mass and volume reduction (product quality criteria) and the multimedia (air, water, and ground) environmental emissions (environmental quality criteria).

Note that the current best design practice for the mixed waste incineration industry requires the use of high-efficiency particulate air (HEPA) filtration as a final (and "additional" relative to commercial sector) fine particulate removal unit operation in air pollution control trains. Besides HEPA incorporation in the baseline flowsheet, there is an economy of scale within the LLMW treatment industry to eliminate the need for maintenance and/or potential loss of overall availability due to such occurrences as caked lines; plugged valves; instrumentation calibration failure due to solids build-up; premature pump impeller degradation; suspended solids or high-dissolved level of solids in the scrubber liquor, and administratively controlled solids removal due to hold-up in process vessels and sumps.

3.1.10 Residue/Product Handling

As with feed systems, many processes in the development stage may not have dealt with the management of residue and products from the various unit operations. Significant benefits or, in some cases, drawbacks to a given project may be related to issues relative to product/residue handling. In the case of thermal systems, special consideration will be required because of the presence of radionuclides. Although the performance test may deal with surrogate constituents for the radionuclide,[11] residue/product handling with regard to these constituents should be discussed. In addition, any residue preparation and/or treatment processes (e.g., shredding and vitrifying) should be described.

3.1.11 Process Monitoring and Control

Critical operating parameters are monitored to optimize performance of any thermal treatment process. This section should discuss the system utilized to monitor and record key operating and emission parameters. Operating parameters are those related to the process (e.g., temperature, pressure, pH, and flow rates), while emission parameters are those related to stack gas emission to the environment and product or residue quality. It is suggested that this information be conveyed with reference to the process flow diagram, adding instrumentation and control information. The scope of the discussion should include feed and feed conditioning, thermal treatment, air pollution control, product removal; cooling/heat recovery systems; and special start-up and emergency shutdown systems.

In addition, the relationship of monitored parameters to the control of the process within normal specifications should be discussed. Specifically, the means for control within the range of measured and monitored process and emission parameters associated with performance testing that is planned or is being documented should be described. The system key parameter/system interlock relationships should also be discussed. The monitoring and control discussion should encompass start-up, normal operation, normal shutdown, and emergency shutdown operations.

3.1.12 Equipment/Operations History

Provide information and references that detail the following operational aspects.

3.1.12.1 Pilot experience

What level of pilot-scale design and operation was used? How long was/has the pilot unit been operated? What types of studies were performed with the pilot scale? Was radionuclide concentration buildup noted in refractory brick? What design and operational experiences will be carried into the next generation of this system?

3.1.12.2 Full-scale experience

What level of full-scale design and operation is being used? How long has the current full-scale system been in operation? If the system is not currently full scale, what are the anticipated hurdles and needs to go from pilot to full scale, and what full-scale systems are being used as design models to implement full-scale design?

3.1.12.3 Waste stream experience

What waste streams have been processed, and what results have been obtained for these studies? These results may reference any reports or documents that exist and any cost or risk studies that have been performed as part of the overall system operation.

3.1.12.4 Forecast availability

What percent of the time is it anticipated that the system could process waste on a fully operational day (e.g., batch waste feed versus continuous waste feed)? What is the expected maintenance down-time on a yearly basis? What is the anticipated or "theoretical" maximum continuous operation per year? Provide some basis and reasoning for the operational basis. Document the anticipated requirements to maintain the system in operational status. The expected daily or yearly throughput should be stated. Factors to consider include the following:

- refractory life/replacement
- mechanical equipment (pumps, blowers, fans, etc.)
- instrument calibration and interlock testing
- lubrication
- filter/strainer changeout/cleaning

3.1.12.5 Unit operations background

What is the operational experience or vendor experience for the various unit operations that are commercially available system? Provide any technical documents or vendor literature and contacts that discuss the operational aspects and track record of the unit operation.

3.2 PERSONNEL HEALTH AND SAFETY CRITERIA

This section provides insight into the health and safety (H&S) issues involved in the operation of the treatment system. This information may be either objective or subjective. In either case some documentation or insight should be provided. For those areas in which no information exists, provide information as to why it is felt that there are no H&S issues or when the issues will be addressed.

3.2.1 Fugitive Emissions

State all areas in which fugitive emissions may exist. This would cover all aspects of the operation from the waste acceptance and handling to the final product handling and packaging area. Document the typical nature of the emissions; reference any results from the performance test where applicable. State the expected release in lb/h for lb of waste treated if this can be determined. Make a qualitative statement if quantitative information cannot be generated. Document any continuous monitors that are currently being used to either document or control the release of the fugitive emissions. State areas in which design improvements could reduce fugitive emissions.

3.2.2 Contact/Exposure

Provide information concerning the exposure or contact to radiological and/or hazardous constituents associated with routine and periodic interaction with the system.

3.2.2.1 Routine contact

Document the anticipated routine contact with the hazardous waste stream (i.e., where and what hazards are expected to exist, and how long is the anticipated contact time). What areas of routine contact could be reduced through further development of the operational system?

3.2.2.2 External contact with product and emission removal

Document the system needs for the removal of the final product and for cleaning or removing any of the emissions from any auxiliary process components. Discuss any engineering improvements that could be made to reduce the exposure risk.

3.2.3 Hazards and Permits

What permits and hazards are anticipated for the system? What environmental assessments and permits have been obtained for the system? What permits are anticipated for full-scale implementation? What limitations does the current system have for testing and evaluation due to lack of permitting or regulatory compliance issues?

3.2.4 Risk Assessment

Provide the method of risk assessment used, the base assumptions, and the results of the risk assessment for the two following majors areas of consideration. It should be noted that the risks associated with radionuclides and their potential release should be included in the assessment.

3.2.4.1 Routine operations

Provide a risk assessment of all aspects of the overall operations. It is not necessary to include the anticipated waste storage facilities unless there are special needs. The risk of the individual unit operations as well as the overall system operations should be discussed. Upgrades or engineering designs to reduce risks that could be included in the full-scale or next generation system should be discussed.

3.2.4.2 Fail-safe emergency shutdown

Risks associated with loss of utilities such as electrical power and process cooling water should be considered. The operation and annual emission source term of thermal relief devices should be defined.

3.3 ECONOMIC CRITERIA

For pilot- and full-scale levels, an important consideration is the cost of capital equipment, both one time and disposable, for the overall system as well as the cost of operations. These costs will be compared on an expected waste throughput basis to assist in evaluating the economic potential that the technology provides for the specified waste streams.

3.3.1 Capital Investment

Provide a breakdown of the various units of operation and their associated costs. For those units that have been specially constructed for the system, provide a cost estimate and justification. Cost comparison with commercially available components should be provided to get an estimate of the cost to purchase the components at current market value.

3.3.2 Operating Costs

Provide cost information for both the consumable, noncapital, equipment (e.g., filter coatings) and the labor requirements for the system. The consumable goods, including utilities (e.g., fuel, water, steam, electricity, cooling water, and chemicals), should be averaged over a one year period; this is true for the readily consumed materials as well as the materials with an expected multiyear lifetime. The labor costs should break down the number of people required during process operation for start-up, steady-state operations, and shutdown. All labor and other operating costs should be reported on an annualized basis and per pound of waste treated.

4. PERFORMANCE TEST

As introduced in Sect. 2.5, data for benchmarking the performance of alternative processes for the treatment of LLMW is to be collected through a performance testing process. The overall objective is a standard measurement of product and environmental quality criteria. To ensure that consistent and comparable data is collected and reported, the performance test will require planning and reporting as outlined in this section. The important elements of the performance test plan and report include a detailed engineering description of the process; a summary of the process performance criteria; documentation of sampling, analysis, and monitoring methods that were used; and reporting of results. Note that the organics (i.e., naphthalene; 1,2-dichlorobenzene; and chlorobenzene) and inorganics (i.e., cerium, cesium, cadmium, chromium, nickel, and lead) are from the suggested surrogate formulation that have been compiled for several DOE LLMW streams.[12,13] Site- or test-specific organic and/or metals treatment will follow the same format with documentation describing the types of analysis performed.

Appendix B is an organizational guide for compiling the requested information into a uniform package. Any documentation or reference source should be included to ensure that all details of the system are documented and can be properly benchmarked. If a benchmarking criteria is not documented, then an explanation should be provided as to why this criteria was not or could not be obtained.

4.1 DETAILED ENGINEERING DESCRIPTION

The purpose of including a test-specific engineering description of the process is to allow the reviewer of the performance test results to understand the thermal processing unit operation(s), requirements for air pollution control equipment, key process control parameters, unique design features that affect process performance, degree of development of auxiliary equipment such as feed and residue handling systems, and selection of performance measurement parameter locations. This information is complementary to the information provided in Sect. 3.1.

4.2 SAMPLING, ANALYSIS, AND MONITORING

Performance and demonstration test procedures incorporate the use of standard sampling, analysis, and monitoring methods that have been used in measuring performance of other thermal systems managing hazardous waste. These standard methods include American Society of Testing and Materials (ASTM), Annual Book of Standards, Annual Series, New Source Performance Standards, Test Methods and Procedures (EPA Methods), 40 CFR 60, National Emissions Standards for Hazardous Air Pollutants, 40 CFR 61, Appendix B Test Methods, Test Methods for Evaluating Solid Waste (SW846), Third Edition, 1986, update I 1992, and Methods Manual for Compliance with the BIF Regulations - Burning Hazardous Waste in Boilers and Industrial Furnaces, (BIF Guidance), EPA/530-SW-91-010, December, 1990.

4.2.1 Sampling Locations and Procedures

The locations where test samples are to be collected are shown schematically on Fig. 3. Depending upon the level of process development, planning and reporting results of a performance test specific to given process technology could include measurement at some or all of the locations. Example sampling equipment and the procedures for collecting samples at each location are summarized in Table 1. The information discussed in "DOE Methods for Evaluating Environmental and Waste Management samples" and supplements should be reviewed for effects of radionuclides on conventional sample preparation for organics and metals analysis.[34] Procedures developed within single laboratories that have analyzed unique mixed wastes are being compiled and undergoing validation. Actual equipment and procedures would depend upon the physical form of the sample streams. Example sampling frequency and appropriate reference methods are also included. For the specific performance test, the actual sampling method at each location should be described in detail. Table 2 shows an example for stack gas particulate and hydrogen chloride sampling.

4.2.2 Analytical Procedures

Suggested minimum analysis for each performance test sample is summarized in Table 3. The analytical procedures and reference methods for these analyses are summarized in Table 4. For a specific performance test, detailed procedures for preparing and analyzing the collected samples should be described. An example for analysis of metals in feed and residue streams is presented in Table 5.

4.2.3 Continuous Emission Monitors

As described previously, CEMS would be utilized during a performance test for the measurement of carbon monoxide, carbon dioxide, total hydrocarbons, and oxygen. Procedures summarizing the use of a typical system are presented in Table 6.

4.2.4 Process Monitoring

In addition to determining the performance of the system relative to product and environmental quality criteria, the performance test also establishes the operating "envelope" that relates to the performance demonstrated. Normally this operating "envelope" is defined by test period process parameters that describe typical operating conditions such as,

- maximum feed rate of waste
- auxiliary fuel or heat input rate
- minimum and maximum temperatures (exit gas and product/residue) for waste processing unit operations and applicable waste treatment unit operations
- minimum and maximum pressures for waste processing and waste treatment
- maximum gas flow rate(s) within the process or exiting the stack

Prior to conducting the performance test, the planned operating conditions should be documented. During the test, appropriate parameters should be measured at a frequency that allows calculation of the test average, rolling-hour average, and variability of each parameter.

Table 1. Performance test sample collection locations, equipment, and methods

Location	Sample name	Sampling location	Sampling equipment	Sample size	General procedure/frequency	Reference^a method
1	Feed (organics)	Waste feed	scoop, 4-ounce wide mouth jars with lids	4-ounce (2)	Grab sample every 30 minutes; split into 2 samples.	SW-846, Chapter 9
	Feed (metals)	Waste feed	scoop, 2-gallon plastic bucket, 2 wide-mouth 8-ounce glass jars with lids, ceramic pestle	8-ounce (2)	Grab sample every 30 minutes; composite samples from each run; fill two 8-ounce glass jars from well-mixed composite in 2-gallon bucket at the end of each run.	SW-846, Chapter 9
	Feed (physical characteristics)	Waste feed	scoop, 5-gallon bucket	25 pounds	Grab sample every 30 minutes; composite sample of all runs.	SW-846, Chapter 9
2, 3	Residual/Product (organics)	Waste feed	scoop, 4-ounce wide mouth jars	4-ounce (2)	Grab sample every 30 minutes; split into 2 samples.	SW-846, Chapter 9
	Residue/Product (metals)	Waste feed	plastic scoop, 2-gallon plastic bucket, 2 wide-mouth 8-ounce glass jars with lids, ceramic pestle	8-ounce (2)	Grab sample every 30 minutes; composite samples from each run; fill two 8-ounce glass jars from well-mixed composite in 2-gallon bucket at the end of each run.	SW-846, Chapter 9
4a	Stack gas M5	Stack Port	EPA M5 sampling train modified for collection of HCl/Cl_2	At least 60–100 dry standard cubic feet	Collect integrated sample for particulates, HCl/Cl^2, moisture, measure stack gas velocity, pressure and temperature, collect bag samples for oxygen and carbon dioxide.	EPA Methods 1 to 5; Method 0050; BIF guidance not in SW-846 proposed updates

Table 1 (continued)

Location	Sample name	Sampling location	Sampling equipment	Sample size	General procedure/frequency	Reference[a] method
4a	Stack gas VOST	Stack Port	EPA VOST sampling train	At least 20 minutes per tube pair at selected sampling rate	Collect four pairs of sorbent tubes for volatile organics during each run.	SW-846 Method 0030
4a	Stack gas M23	Stack port	EPA M23 sampling train	At least 100–110 dry standard cubic feet	Collect integrated sample for PCDDs/PCDFs, semivolatile organics and moisture; measure stack gas velocity, pressure and temperature; collect bag samples for oxygen and carbon dioxide.	EPA Methods 1 through 5 and Method 23
4a	Stack gas MMT	Stack port	EPA multi-metals sampling train	60–100 dry standard cubic feet	Collect integrated sample for metals and moisture; measure stack gas velocity, pressure and temperature; collect bag samples for oxygen and carbon dioxide.	EPA Methods 1 through 5; BIF Guidance
4a	Stack gas radionuclides	Stack port	Based on principle of measurement	Based on principle of measurement	Flexible to allow most appropriate combination of sampling collection and analysis	EPA Method 114

Table 1 (continued)

Location	Sample name	Sampling location	Sampling equipment	Sample size	General procedure/frequency	Reference[a] method
4a	Stack gas CEMS	Stack port	Continuous emissions monitoring system	Continuous	Continuously monitor stack gas for carbon monoxide, carbon dioxide. Continuously monitor stack gas for total hydrocarbons. Continuously monitor stack gas for oxygen.	EPA Method 10 EPA Method 25A EPA Method 3A

[a] Reference method abbreviations are taken from the following sources:

"EPA Method"—New Source Performance Standards, Test Methods and Procedures, Appendix A, 40 CFR 60 and National Emission Standards for Hazardous Air Pollutants, Appendix B, 40 CFR 61; "SW846"—Test Methods for Evaluating Solid Wastes, Third Edition, 1986, revised 1990; and "BIF guidance"—Methods Manual for Compliance with the BIF Regulations—Burning Hazardous Waste in Boilers and Industrial Furnaces, EPA/530-SW-91-010, December 1990.

Table 2. Stack gas particulate and hydrogen chloride sampling procedure

Sample name:	Stack gas M5
Sampler:	Stack sampling team
Locations:	Stack
Equipment:	EPA Method 5 sampling train; petri dish with tared particulate filter; polyethylene sample jars with lids, graduated cylinder, balance.
Frequency:	Continuous during a test run; three runs to complete test. A minimum of 60-100 dry standard cubic feet of sample will be collected.
Procedures:	Stack gases will be isokinetically sampled to collect particulate matter on a filter, and to collect hydrogen chloride and chlorine in absorbing solutions. The particulate weight will be determined gravimetrically, and the chloride content of the absorbing solutions will be quantitatively determined by ion chromatography. Sample point locations are determined in accordance with EPA Method 1. An initial traverse is made with a pitot tube at each sample point following EPA Method 2 to establish stack gas velocity profile, temperature, and flow rate, and to check for cyclonic flow (cyclonic flow will be checked only on the first day of testing). EPA Method 3, employing an Orsat analyzer, CEMS, will be used to determine stack gas oxygen, carbon dioxide, and dry molecular weight. EPA Method 4 will be followed to determine the stack gas moisture content. EPA Method 5 procedures are followed for pretest and post-test leak checks, isokinetic sampling rate, filter changeouts (if needed), and data recording. The sampling train utilizes a heated particulate filter and a series of seven chilled impingers. Impinger 1 will be empty; impingers 2 and 3 will each contain 100 ml of a 0.1N sulfuric acid solution; impinger 4 will be empty; impingers 5 and 6 will each contain 100 ml of a 0.1 N sodium hydroxide solution; impinger 7 will contain 200 to 300 g of indicating silica gel, weighed to within 0.5 g. After sampling, the probe will be removed from the stack and the nozzle will be covered. External particulate matter will be wiped off the probe. It will then be disconnected from the train and both ends capped. The probe and the filter and impinger assembly are transported to the sample recovery area. The samples are recovered as follows:

Table 2 (continued)

- Particulate filter—The particulate filter is removed from its holder and placed into its original petri dish (Container No. 1), which is sealed with tape and placed in a plastic bag.

- Front half rinse—The internal surfaces of the nozzle, probe, and front half of the filter holder are cleaned by rinsing, brushing, and final rinsing with acetone into a separate sample jar (Container No. 2).

- Acid impinger liquid—The liquid contents of impingers 1, 2, 3, and 4 are measured to the nearest milliliter or weighed to the nearest 0.5 g and placed into a sample bottle (Container No. 3). Each acid impinger and all connecting glassware, including the back half of the filter holder, is rinsed with deionized water, and the rinse is added to Container No. 3.

- Alkaline impinger liquid—The liquid contents of impingers 5 and 6 are measured to the nearest milliliter or weighed to the nearest 0.5 g and placed into a sample bottle (Container No. 4). Each impinger and all connecting glassware is rinsed with deionized water, and the rinse is added to Container No. 4.

- Silica gel—The silica gel contents of impinger 7 are weighed to the nearest 0.5 g.

- Samples of the deionized water, acetone, sulfuric acid solution, and sodium hydroxide solution are taken for reagent blanks.

All of the sample containers will be assigned numbers and labeled with date and test-run number. The samples will be turned over to the sample coordinator who will record the appropriate data in the field logbook and pack the samples in shipping containers. Samples will be stored in the sample holding area separate from the container supply area.

Source: SPA Methods 1, 2, 3, 4, and 5, Appendix A, Test Methods and Procedures, New Source Performance Standards, 40 CFR 60, and Methods Manual for Complying with the BIF Regulations, EPA/530-SW-91-010, December, 1990.

Table 3. Analyses planned for performance test samples

Sample Name	Analyses
Feed	Organics, total metals (Cs, Ce, Cd, Cr, Ni, Pb), physical characteristics (particle size analysis, density, moisture content, percent volatile, percent inert), ultimate analysis, heating value, viscosity, and chlorine content.
Residue/product	Organics, total metals (Cs, Ce, Cd, Cr, Ni, Pb), Toxic Characteristic Leaching Procedure (TCLP) metals (Cd, Cr, Pb), moisture-density relations, grain size analysis, pH.
Stack gas M5	Particulate, HCl, Cl_2, moisture, oxygen, carbon dioxide, temperature, flow rate
Stack gas VOST	Volatile organics, moisture, oxygen, carbon dioxide, temperature, flow rate
Stack gas M23	Semivolatile organics, PCDDs/PCDFs, moisture, oxygen, carbon dioxide, temperature, flow rate
Stack gas MMT	Metals (Cs, Cd, Ce, Cr, Ni, Pb)
Stack gas radionuclides	Site specific radionuclides
Stack gas CEMS	Carbon monoxide, carbon dioxide, total hydrocarbons, oxygen

Table 4. Summary of analytical procedures and methods

Sample name	Analysis	Total field samples for analysis	Preparation method[a]	Analytical method[a]	Analytical[a] responsibility
Feed	Organics	24	SW846 Method 3540 or 3550	SW846: 8000 series	ACL
	Total metals (Ce, Cs, Cd, Cr, Ni, Pb)	3	Acid digestion (SW846-3050 or 3051)	SW846: 6000 & 7000 series	ACL
	Physical characteristics	1	N/A	ASTM D422, D4318, D1556, E870	ACL
Residue/ product	Organics	24	Solvent extraction (SW846-3500 series)	SW846: 8000 series	ACL
	Total metals (Ce, Cs, Cd, Cr, Ni, Pb)	3	Acid digestion (SW846-3050)	SW846: 6000 & 7000 series	ACL
	TCLP metals	3	TCLP extraction (SW846-1311)	SW846: 6000 & 7000 series	ACL
	Moisture-density relations	3	N/A	ASTM D1557	ACL
	Particle size analysis	3	N/A	ASTM D422	ACL
Stack gas M5	Particulate	3		Gravimetric (EPA Method 5)	SSC
	HCl/Cl_2	3	Evaporate/dessicate N/A	Ion chromatography (Method 9057 – BIF guidance)	ACL
	Moisture	3		Gravimetric (EPA Method 5)	SSC
	Temperature	N/A	N/A	Thermocouple (EPA Method 5)	SSC

Table 4 (continued)

Sample name	Analysis	Total field samples for analysis	Preparation method[a]	Analytical method[a]	Analytical[a] responsibility
Stack gas M5	Velocity	N/A	N/A	Pitot tube (EPA Method 5)	SSC
	Oxygen, carbon dioxide	(c)	N/A	Orsat (EPA Method 3)	SSC
Stack gas VOST	Organics	Four tube pairs	Thermal desorption, trap (SW846-5040)	GC/MS (SW846-8240)	ACL
Stack gas M23	Semivolatile organics, PCDDs and PCDFs (filter, XAD-2, acetone/ methylene chloride rinse)	3	Solvent extraction (EPA Method 23)	GC/MS (EPA Method 23)	ACL
	PCDDs and PCDFs (toluene rinse)	3	Rotary evaporator (EPA Method 23)	GC/MS (EPA Method 23)	ACL
	Moisture	3	N/A	Gravimetric (EPA Method 5)	SSC
Stack gas M23	Temperature	N/A	N/A	Thermocouple (EPA Method 5)	SSC
	Velocity	N/A	N/A	Pitot tube (EPA Method 5)	SSC
	Oxygen, carbon dioxide	(c)	N/A	Orsat (EPA Method 3)	SSC
Stack gas MMT	Metals	3	Acid digestion (SW846-3010/3050)	SW846: 6000 & 7000 series	ACL
	Moisture	3	N/A	Gravimetric (EPA Method 5)	SSC
	Temperature	N/A	N/A	Thermocouple (EPA Method 5)	SSC

Table 4 (continued)

Sample name	Analysis	Total field samples for analysis	Preparation method[a]	Analytical method[a]	Analytical[a] responsibility
Stack gas MMT	Velocity	N/A	N/A	Pitot tube (EPA Method 5)	SSC
Stack gas MMT	Oxygen, carbon dioxide	(c)	N/A	Orsat (EPA Method 3)	SSC
Stack gas radionuclides	Radionuclides	3	EPA Method 114	EPA Method 114	ACL
Stack gas CEMs	CO	(d)	N/A	Continuous NDIR (EPA Method 10)	Operator
	THC	(d)	N/A	Continuous flame ionization detector (FID) (EPA Method 25A)	Operator
	O2	(d)	N/A	Continuous zirconium oxide cell (EPA Method 3A)	Operator

Abbreviations in the Preparation method, Analytical method, and Analytical responsibility columns mean the following:

- "SW846" refers to Test Methods for Evaluating Solid Waste, Third Edition, 1986 revised 1990.
- "EPA Method" refers to New Source Performance Standards, Test Methods and Procedures, Appendix A, 40 CFR 60.
- "BIF Method" refers to Methods Manual for Compliance with the BIF Regulations—Burning Hazardous Waste in Boilers and Industrial Furnaces, EPA/530-SW-91-010.
- Gas bag samples collected during each stack traverse for Orsat analysis.
- CEMS sampling and analysis is continuous during each run.

Table 5. Analysis of metals feed materials and residue/product streams

Matrices:	Feed Residue/Product
Holding Time:	40 days
Procedures:	**Total Metals** Feed and residue soil samples will be acid digested according to SW-846 Method 3050. As an alternate, microwave-assisted acid digestion may be used according to SW-846 Method 3051. The digestion solutions will be analyzed for Ce, Cs, Cr, Cd, Ni, and Pb by inductively coupled argon plasma emission spectroscopy inductively coupled plasma (ICP) using SW-846 Methods 6000 and 7000 series. If individual metals are found at concentrations below approximately 2ug/ml, the digestion solutions will be analyzed by graphite furnace atomic absorption (GFAA) spectroscopy according to SW-846 7000-series methods referenced below. **TCLP Metals** Treated residue streams will be extracted according to the Toxicity Characteristic Leaching Procedure (SW-846 Method 1311). The extraction solution will be analyzed by inductively coupled argon plasma emission spectroscopy ICP using SW-846 Method 6000 series. If individual metals are found at concentrations below approximately 2ug/ml, the extraction solutions will be analyzed by graphite furnace atomic absorption (GFAA) spectroscopy according to SW-846 7000-series methods referenced below.

Source: Methods 1311, 3050, 3051, 6000-series, and 7000-series, Test Methods for Evaluating Solid Waste, SW-846, Third Edition, November 1986, and Updates.

Table 6. Stack gas continuous emissions monitoring procedure

Sample name:	Stack gas CEMS
Sampler:	Monitoring system operator
Components:	Probe, sample conditioning system, analyzer
Location:	Stack
Frequency:	Continuous during each sampling run; three runs to complete each test.
Procedures:	Continuously monitor the following stack gas constituents: • Carbon monoxide by nondispersive infrared (NDIR) analyzer (EPA Method 10) • Total hydrocarbons by FID (EPA Method 25A) • Oxygen by zirconium oxide cell (EPA Method 3A)

Source: EPA Performance Specifications 2, 3, and 4, Appendix B, Test Methods and Procedures, New Source Performance Standards, 40 CFR 60.

4.2.5 Quality Assurance and Quality Control

As described in Sect. 2.6, consistent QA/QC procedures must be utilized during the data collection process within the performance test. QA is accomplished through delegation of program responsibilities to appropriate individuals, documentation, data review, and audits. Complementary activities of QC address sample integrity, chemical analysis methods, and production and review of QC data. Further detail on DQOs and their documentation within the performance testing process are discussed in a companion document[15]. A Performance Test Quality Assurance Project Plan should be included as an attachment to the Performance Test Plan and/or Report.

4.3 PERFORMANCE CRITERIA

This section describes the information to be obtained for each process or constituent performance criteria. The data collected to calculate various performance criteria measures require a performance test plan protocol that measures performance of the process while treating a waste mixture that contains the following surrogate constituents:

- organic constituents (naphthalene, 1,2-dichlorobenzene, and chlorobenzene)
- metal constituents (cadmium, chromium, nickel, and lead)
- surrogate radionuclide constituents (cerium and cesium)

For demonstration testing, a site-specific waste mixture would be evaluated. This would involve evaluation of waste-specific constituents (e.g., metals, other organics, radionuclides).

The data collected in the performance test will

- determine emission rates for surrogate constituents, particulate, acid gases, CO, and THC;
- determine capture and leachability of surrogate constituents in the residue/product;
- establish system removal efficiency for each surrogate constituent;
- demonstrate the mixed waste-feed and process operating "envelope" that result in acceptable product and environmental quality;
- quantify polychlorinated dibenzo dioxin (PCDD), polychlorinated dibenzo furan (PCDF) emissions; and
- quantify emissions of "waste-specific" metals.

Specific performance criteria are described in this section for the following:

- organic constituent
- metal constituents
- radionuclide constituent
- particulate
- acid gases
- SO_x, NO_x
- product/residue
- continuous emission monitored constituents (CO, CO_2, O_2, THC)

Tables 7-10 illustrate the product and environmental quality criteria as they relate to data collected during the performance test. Measures of product quality are related to resource recovery (converting waste to a useful product) and to mass and volume reduction (for land disposal consideration). Measures of environmental quality are related to normalized waste surrogate constituent multimedia impact on a mass basis and comparison of constituent and other process emissions against appropriate environmental guidelines or standards. Figure 3 shows the location where measurements will be required to calculate the various benchmarking criteria. Measurements to be obtained at these designated locations are summarized in Table 11.

4.3.1 Organic Constituents

Thermal treatment processes are normally designed to either separate or convert organic constituents so that they are no longer present in process streams that would potentially impact the environment. An overall objective of the performance test is to demonstrate minimization of any organic constituent in emission or residue/product streams. Table 8 illustrates data collection and summary relative to organic constituents. Three criteria will be evaluated relative to organic constituents:

- DRE of the three organic POHCs as compared to requirements under RCRA (99.99% for hazardous waste, 99.9999% for PCB-contaminated and dioxin-listed waste).
- Quantification of surrogate organic constituents contained in all emissions and products, normalized for the amount of the specific constituent fed to the system.
- Identification and quantification PCDD/PCDF in the stack emissions.

Depending upon the scale of operation (bench, pilot, or full) and whether the performance test is part of demonstration for a specific site, testing may also need to incorporate quantification of additional PICs. A discussion of PICs and some specific compounds that would be expected PICs is provided in Appendix C. As can be seen from the discussion provided, the three surrogate organics compounds to be quantified (naphthalene, 1,2-dichlorobenzene, and chlorobenzene) as POHCs are also potential PICs from thermal processing of other organic compounds that may be present in the waste being treated at a specific site. In addition, one POHC may be a PIC of another POHC (e.g., chlorobenzene from 1,2-dichlorobenzene). Since all processes to be compared must deal with the same common constituent performance criteria, based on both quantification and demonstration of DRE, it is felt these POHC selections are appropriate for initial or "Phase I" testing of all alternative processes [see "Surrogate Formulations for Thermal Treatment of Low-Level Mixed Waste: Part II Selected Mixed Waste Treatment Project Waste Streams" (1)].

Note that for POHC selection, we used the EPA approved sampling methods to define whether the compound is classified as volatile (VOL) or semivolatile (S-VOL). Technically, all three compounds (naphthalene, DCB, and MCB) are S-VOL (SW846, BP >100°C). The VOST, however, can be used for MCB because its BP is <140°C. Therefore, MCB could be considered either VOL or S-VOL.

4.3.2 Metal Constituents

With metal constituents, the overall objective remains to minimize emissions to the environment by either separation of the metal from the waste stream to render a useful product or capturing the metal in the residue, such that is not leachable to the environment.

Four criteria will be evaluated relative to metal (waste-specific and surrogate) constituents:

- quantity of each metal constituent captured as "good product" normalized to the quantity of that constituent fed to the process
- quantity of each metal emitted from the stack normalized to the quantity of that constituent fed to the process
- concentration of each metal constituent in the stack gas
- quantity of each metal constituent in the residue/product stream(s) (total and leachable) normalized to the quantity of that constituent fed to the process

Table 7. Product quality criteria

Criteria	Method of calculation[a]	Benchmark
Mass reduction	Output mass (4C)/sum of input mass (1)	0.0 - 1.0
Volume reduction	$\frac{\text{Output mass (4C)/density (4C)}}{\text{sum of input volume (1)}}$	0.0 - 1.0
Resource recovery	$\frac{\text{Good product mass [(2a)+(3c)]}}{\text{Sum of input mass (1)}}$	0.0 - 1.0

[a] Refer to Fig. 3 for sampling locations.

Table 8. Environmental criteria for organic constituents (POHCs)

Constituent	Disposal	Criteria	Air	Criteria
Naphthalene	Concentration		Concentration	Site specific
	residue	N/A (minimize)		
	extract	N/A (minimize)		
	Mass		Mass	0.01% of feed
	residue	N/A (minimize)		
	extract	N/A (minimize)		
1,2-Dichlorobenzene	Concentration		Concentration	Site specific
	residue	6.2 mg/kg		
	extract	N/A (minimize)		
	Mass		Mass	0.01% of feed
	residue	N/A (minimize)		
	extract	N/A (minimize)		
Chlorobenzene	Concentration		Concentration	Site specific
	residue	5.7 mg/kg		
	extract	N/A (minimize)		
	Mass		Mass	0.01% of feed
	residue	N/A (minimize)		
	extract	N/A (minimize)		

Table 9. Environmental criteria for metal constituents

Constituent	Disposal	Criteria	Air	Criteria
Cadmium	Concentration		Concentration	BIF guidance
	residue	N/A		
	extract	1.0 mg/l		
	Mass		Mass	BIF guidance
	residue	N/A		
	extract	Minimize		
Chromium	Concentration		Concentration	BIF guidance
	residue	N/A		
	extract	5.0 mg/l		
	Mass		Mass	BIF guidance
	residue	N/A		
	extract	Minimize		
Nickel	Concentration		Concentration	BIF guidance
	residue	N/A		
	extract	Minimize		
	Mass		Mass	BIF guidance
	residue	N/A		
	extract	Minimize		
Lead	Concentration		Concentration	BIF guidance
	residue	N/A		
	extract	1.0 mg/l		
	Mass		Mass	BIF guidance
	residue	N/A		
	extract	Minimize		
Cerium	Concentration		Concentration	
	residue	N/A		
	extract			
	Mass		Mass	
	residue	N/A		
	extract	Minimize		
Cesium	Concentration		Concentration	
	residue	N/A		
	extract			
	Mass		Mass	
	residue	N/A		
	extract	Minimize		

Table 10. Environmental criteria air emissions

Constituent	Criteria
CO	100 ppm corrected to 7% Oxygen
THC	20 ppm corrected to 7% Oxygen
PCDD/PCDF	0.1 ng/dscm corrected to 11% Oxygen (as 2,3,7,8-TCDD equivalents)
Particulate	0.015 gr/dscf corrected to 7% Oxygen
HCl	4 lb/h or 99% removal by APCD
SO_x	Must meet National Ambient Air Quality Criteria
NO_x	Must meet National Ambient Air Quality Criteria

Table 11. Material flow measurements

Inputs (1)[a]	Combustion (2)[a]	Waste Treatment (3)[a]	Disposal (4)[a]
Mass flow rate(s) of all inputs Density of all waste inputs Constituent concentrations	Mass flow rate(s): solid usable product (2a) waste product (2b)	Mass flow rate(s): solid products to recovery (3a) solid products to treatment (3b) usable good recovered product (3c) waste from recovery (3d)	Mass flow rate(s): air emission (4a) wastewater (4b) solid residue for disposal (4c) Density of residue (4c) Constituent concentrations in: air (4a) wastewater (4b) solid (4c) Constituent concentrations in extract (TCLP) of solid residue (4c)

[a] Refer to Fig. 3 for sampling locations.

4.3.3 Radionuclide Constituents

The primary objective in treatment of radiological waste is to reduce the mass and volume of the waste such that the concentration of the radionuclide is maximized in the residue/product and minimized in all other process emissions. Three criteria will be evaluated on the metals surrogates for radionuclides:

- quantity of each radionuclide metal emitted from the stack normalized to the quantity of that constituent fed to the process
- concentration of each radionuclide metal in the stack gas
- quantity of each radionuclide metal constituent in the residue/product stream(s) (total and leachable) normalized to the quantity of that constituent fed to the process

4.3.4 Particulate

Since the process to be evaluated is treating mixed waste, the objective is to minimize emission of particulate to the environment. At a minimum, particulate emissions will be compared to allowable emissions for hazardous waste incinerators that are currently limited to 0.08 grains/dscf corrected to 7% oxygen. It is expected that this limit will be reduced. Current EPA combustion strategy guidance is 0.015 grains/dscf.

4.3.5 Acid Gases

Several LLMW sites are contaminated with chlorinated organics that yield HCl during combustion. Two of the POHCs utilized in the performance test are chlorinated organics. The objective is to demonstrate removal of HCl to achieve emission limits required by RCRA for hazardous waste incinerators. This would require demonstration of less than 4 pounds/h emission and/or 99% removal of HCl by the air pollution control equipment used in the process.

4.3.6 Sulfur Dioxide and Nitrogen Oxides

Emissions of sulfur dioxide and nitrogen oxides should be quantified and reported on a mass and concentration basis.

4.3.7 Product/Residue

Constituent performance criteria for the produce/residue have been addressed in Sects. 4.2.1, 4.2.2, and 4.2.3. Measures of product/residue quality that are not constituent related include mass reduction, volume reduction, and waste reduction. These three product quality criteria will involve the following:

- measurement and summation of the mass (pounds) of all solid waste product/residue streams and comparison to the mass of waste fed to the process
- measurement and summation of the volume (cubic feet) of all solid waste product/residue streams and comparison to the volume of the waste fed to the process
- measurement and summation of the mass of all reusable product and comparison to the mass of waste fed to the process

4.3.8 Continuous Emission Monitored Constituents

Continuous emission monitors are typically used to monitor carbon monoxide, carbon dioxide, oxygen, and THC emissions from thermal combustion systems treating wastes. Performance criteria for these constituents are based upon regulatory guidance for hazardous waste incinerators. Carbon monoxide is expected to be controlled such that the rolling-hour average concentration leaving the stack does not exceed 100 ppm corrected to 7% oxygen. THC concentration leaving the stack may be controlled at 20 ppm corrected to 7% oxygen if the CO concentration is greater than 100 ppm.

4.3.9 Process Parameters

Process parameters are monitored and recorded to establish the appropriate operating "envelope" that results in the environmental and product quality demonstrated in the performance test.

4.4 REPORTING OF RESULTS

The results of a performance test should document the quantity of waste treated during the test and the duration of each test and its individual test runs. A minimum of three replicate test runs are required for each reported test condition. Test results should include the following information at a minimum:

- product quality criteria summary (per Table 7) for each run and the test average
- environmental quality criteria summary (per Tables 8 and 9) for each run and the test average
- air emissions summary (per Table 10)
- summary of measurements of performance (per Table 11)
- process operating condition summary

5. SUMMARY

The information presented in this report details a process that allows technical comparison of thermal treatment systems for the management of LLMW. Three other reports, "Surrogate Formulations for Thermal Treatment of Low-Level Mixed Waste: Part II: Selected Mixed Waste Treatment Project Waste Streams,"[12] "Surrogate Formulations for Thermal Treatment of Low-Level Mixed Waste: Part III: Plasma Hearth Process Testing,"[13] and "Data Quality Objectives: Evaluation of Thermal Treatment Processes,"[15] when used in conjunction with the benchmarking criteria developed in this report, provide a means for consistency and high-quality comparison. This comparison may be for the same waste stream (i.e., surrogate constituent formulations) on different thermal treatment techniques or it may be on a variety of waste streams treated by the same technique.

The purpose of applying the quality technique of benchmarking to the several potential processes applicable to the treatment of LLMW was to put forth a logical and scientific means for comparison and selection. This process is meant to provide direction to DOE and industry for development and selection of appropriate thermal treatment technologies, recognizing that there are limited resources available to accomplish process development, site cleanup, and waste management. It is also recognized that some latitude may need to be provided in the collection and reporting of the required benchmarking data and that site-specific concerns would need to be incorporated into the decision process.

The benchmarking of the performance of a given process that is accomplished using the guidance provided is based upon sound engineering and scientific practices. Quality-based performance testing can be documented and—in conjunction with a standard comparison of system design, operation, health, safety, and economic criteria—consistent benchmarking of various thermal processes for several LLMW-contaminated sites can be accomplished. The DOE will use the information from this benchmarking process to provide a technically based direction that ensures the development and procurement of thermal systems that best meet the agency's need for cleanup of contaminated sites and management of LLMW.

For the five categories of benchmarking criteria, standard formats have been presented that allow technology developers and vendors to summarize data to be evaluated for operations/design, personnel health and safety, economics, product quality, and environmental quality. The information to be provided is both quantitative and qualitative form.

Most quantitative information is provided based upon the results of performance testing conducted according to the guidance provided in this report. Quantitative results for product and environmental quality—as well as insight and some quantitative information relative to operations, personnel health and safety, and economics—are outputs of this testing. Other operating experience can be used to complete the benchmarking process in the system evaluation categories.

The decision process remains flexible since the decision process can weight the various benchmarking categories to suit site- and waste-specific concerns. The process establishes a fair comparison since common data are collected for various waste stream matrices or various thermal treatment processes. It is recognized that elements of the benchmarking criteria may require modification over time as data are collected and utilization of the benchmarking process for decision making is implemented.

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Appendix A

SYSTEMS EVALUATION CHECKLIST

SYSTEMS EVALUATION CHECKLIST

Benchmarked technology:

System location:

Principle contact: **Organization:**

Phone number: **FAX number:**

Mail address: **Fed-ex address:**

Customer/funding organization(s):

Date of last benchmarking:

Date of current benchmarking:

BENCHMARKING CHECKLIST FOR QUALITATIVE SYSTEM EVALUATION CRITERIA

Document section	General description of benchmarked parameter(s)	Benchmarking performed?		Reference or attachment number for documentation
		YES	NO	
3.1	OPERATIONS/DESIGN CRITERIA			
3.1.1	Process Flow diagram			
3.1.2	Hardware Specifications			
3.1.3	Complex and Unique Design			
3.1.4	Materials of Construction			
3.1.6	Feed Systems			
3.1.7	Thermal Treatment Process			
3.1.8	Auxiliary Fuel/Heat Input			
3.1.9	Air Pollution Control Equipment			
3.1.10	Residue/Product Handling			
3.1.11	Process Monitoring and Control			
3.1.12.5	Unit operations background			

OPERATION CRITERIA

(Provide additional documentation as needed)

Scale (3.1.5)	**Throughput (lb/h)**	**Footprint (ft^2)**	**Portable (Y/N)**
Pilot experience (3.1.12.1)	**Throughput (lb/h)**	**Hours operated**	
Full experience (3.1.12.2)	**Throughput (lb/h)**	**Hours operated**	
Waste streams (3.1.12.3)	**Throughput (lb/h)**	**Hours operated**	
Availability (3.1.12.4)	**Hours/day**	**Maintenance (h/year)**	**Expected availability (h/year)**

PERSONNEL HEALTH AND SAFETY CRITERIA

(Provide additional documentation as needed)

Fugitive Emissions (3.2.1)	Source	Constituent	Mass emission rate
Contact (3.2.2)	Source	Constituent	Hours/year
Permits (3.2.3)	Agency	Existing/obtained previously	Test required
Air			
Waste			
Wastewater			
Risk (3.2.4.1)	Assessment provided (Y/N)	Constituents	Pathway
Emission impact			
Emergency shutdown			

ECONOMIC CRITERIA
(Provide additional documentation as needed)

CAPITAL (3.3.1)	Purchase	Annualized	Annualized/lb waste feed/year
Preprocess			
Feed			
Thermal process			
Air pollution control			
Total system (estd)			
OPERATING (3.3.2)	Purchase	Annualized	Annualized/lb waste/year
Materials			
Utilities			
Labor			
Total operations (estd)			

Appendix B

PERFORMANCE TEST PLAN CHECKLIST

PERFORMANCE TEST PLAN CHECKLIST

Benchmarked technology:

System location:

Principle contact: **Organization:**

Phone number: **FAX number:**

Mail address: **Fed-ex address:**

Customer/funding organization(s):

Date of last benchmarking:

Date of current benchmarking:

BENCHMARKING CHECKLIST FOR PERFORMANCE TEST CRITERIA

Document section	General description of benchmarked parameter(s)	Benchmarking performed?		Reference or attachment number for documentation
		YES	NO	
4.1	**ENGINEERING DESCRIPTION**			
4.2	**SAMPLING, ANALYSIS, AND MONITORING**			
4.2.1	Sampling Locations and Procedures			
4.2.2	Analytical Procedures			
4.2.3	Continuous Emission Monitors			
4.2.4	Process Monitoring			
4.2.5	QA/QC			
4.3	**PERFORMANCE CRITERIA**			
4.3.1	Organic Constituents			
4.3.2	Metal Constituents			
4.3.3	Radionuclide Constituents			
4.3.4	Particulate			
4.3.5	Acid Gases			
4.3.6	Sulfur Oxide and Nitrogen Oxides			
4.3.7	Product/Residue			
4.3.8	CEM Constituents			
4.3.9	Process Parameters			

ENVIRONMENTAL CRITERIA ORGANIC (POHCs) CONSTITUENTS (4.3.1)

(Provide additional documentation as needed)

Constituent	Disposal		Air	System removal efficiency
	Residue	Extract	Emission	
Naphthalene: Concentration Mass				
1,2-Dichlorobenzene: Concentration Mass				
Chlorobenzene: Concentration Mass				

ENVIRONMENTAL CRITERIA METAL CONSTITUENTS (4.3.2–4.3.4)

(Provide additional documentation as needed)

Constituent	Disposal		Air	System removal efficiency
	Residue	Extract	Emission	
Cadmium: *Concentration* Mass				
Chromium: Concentration Mass				
Nickel: Concentration Mass				
Lead: Concentration Mass				
Cerium: Concentration Mass				
Cesium: Concentration Mass				

ENVIRONMENTAL CRITERIA AIR EMISSIONS (4.3.4–4.3.6, 4.3.8)

(Provide additional documentation as needed)

Constituent	Results
CO (ppm)	
THC (ppm)	
PCDD/PCDF (ng/dscm)	
Particulate (gr/dscm)	
HCl (lb/h) (% Removed)	
SO_x (lb/h)	
NO_x (lb/h)	

PRODUCT QUALITY CRITERIA (4.3.7)

(Provide additional documentation as needed)

Criteria	Results
Mass reduction	
Volume reduction	
Resource recovery	

Appendix C

PRODUCTS OF INCOMPLETE COMBUSTION ASSOCIATED WITH SPECIFIC SURROGATE PRINCIPAL ORGANIC HAZARDOUS CONSTITUENTS: A LITERATURE REVIEW

Introduction

The thermal destruction of Principal Organic Hazardous Constituents (POHCs) requires that the constituent be destroyed or removed with a minimum destruction and removal efficiency (DRE) of 99.99%. Although the POHC may be destroyed at a DRE of 99.99%$^+$, products of incomplete combustion (PICs) may be formed. While monitoring of the emission level of the POHC determines whether or not the design DRE has been achieved, it is also beneficial to identify and to measure the PICs as these are also a measure of the performance, or lack of performance, of the thermal destructor. In this light, a literature review was conducted to determine the PICs associated with hazardous waste incineration and in particular for the three surrogate POHCs[1,2]: naphthalene ($C_{10}H_8$), chlorobenzene (C_6H_5Cl), and 1,2-dichlorobenzene ($Cl_2C_6H_4$).

As a general indication of the types of PICs that are formed in hazardous waste incinerators, Trenholm, Kapella, and Hinshaw[3] summarized the most common RCRA Appendix VIII PICs observed in the emissions from over 20 research tests conducted on full-scale hazardous waste combustion systems. Figure C.1, taken from that study[3], shows the typical concentration ranges of eleven of the fifteen most common contaminants. Four other compounds, all phthalates were not included; they were reported to be ubiquitous and suspected of being common contaminants that are typically found in analyses of organic compounds. Table C.1, also taken from the same source[3], summarizes additional Non-Appendix VIII compounds commonly found in combustion stack gases.

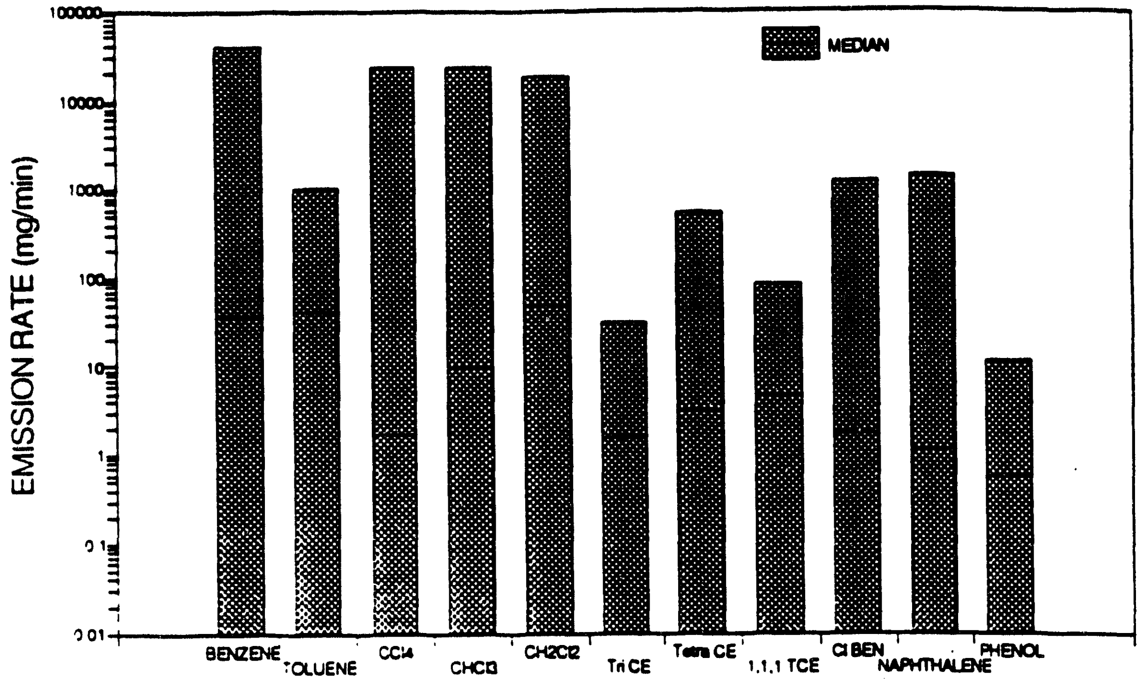

Fig. C.1. Common PICs observed in incineration tests.

Table C.1. Common Appendix VIII and Non-Appendix VIII Compounds found in Combustion Gases

Most common RCRA Appendix VIII PICs	
Volatile compounds	**Semivolatile compounds**
Benzene	Naphthalene
Toluene	Phenol
Carbon tetrachloride	Bis (2-ethylhexyl)-phthalate
Chloroform	Diethylphthalate
Methylene chloride	Butylbenzylphthalate
Trichloroethylene	Dibutylphthalate
Tetrachloroethylene	
1,1,1-Trichloroethane	
Chlorobenzene	
Non-Appendix VIII compounds found in combustion gases	
Acetone	Ethylbenzene
Acetophenone	Ethylbenzoic acid
Benzaldehyde	Ethylphenol
Benzenedicarboxaldehyde	(ethylphenyl) ethanone
Benzoic acid	Ethynylbenzene
Chlorocyclohexanol	Phenylacetylene
Cyclohexane	Phynylbutenone
Cyclohexanol	1,1'-(1,4-Phenylene)-bisethanone
Cyclohexene	Phenylpropenol
Dioctyl adipate	Propenylmethylbenzene
Ethenylethylbenzene	Tetramethyloxirane
Ethylbenzaldehyde	Trimethylhexane

Source: Trenholm et. al.

In an effort to rank wastes by their ability to be incinerated, a Thermal Stability Ranking System was recently developed at the University of Dayton[4]. The system used a numerical ranking system from 1 to 320 with 1 being the most difficult to incinerate and 320 being the easiest. In this ranking system, which was based on a laboratory scale flow reactor, the rankings were found to be as follows for the three specific POHCs that were the focus of this review:

POHC	RANK
naphthalene ($C_{10}H_8$)	5
chlorobenzene (C_6H_5Cl)	19
1,2-dichlorobenzene ($Cl_2C_6H_4$)	23-24

Only cyanogen (ethanedinitrile)-Rank 1, hydrogen cyanide-Rank 2, benzene-Rank 3, and sulfur hexafluoride-Rank 4 had rankings greater than naphthalene.

The destruction of the POHCs in the first stability category consisting of the first 77 rankings were characterized by bi-molecular decomposition processes that dominated the decomposition with a multiplicity of pathways.[4] For the majority of these compounds, degradation was dominated by H-atom metathesis and Cl atom displacement reactions. In the case of the chlorinated benzenes, these were believed to be dominated by Cl displacement reactions under oxygen starved conditions. Dellinger[5] reported that the PICs were formed by several different mechanisms, including (1) fragmentation of POHCs to form smaller, less complex molecules, (2) reactions involving fuel and POHCs, and (3) formation of PICs of higher molecular weight than the POHCs due to complex radical-molecular reaction pathways.

Dellinger, Taylor and Lee[6] and Lee, Whitworth and Waterland[7] have conducted tests on full-scale and pilot scale combustors to evaluate the Thermal Stability Ranking System. In general, these studies have shown that the ranking system is in good agreement with the tests. The statistical success of the thermal stability ranking system in predicting PICs led Dellinger et. al[6] to conclude that chemical kinetics controlled the relative emission rates of organic compounds and that reaction kinetic approaches could be used to predict the relative emissions of POHCs and PICs. As a result, studies reviewed in the following sections involving reaction kinetics should provide at least a qualitative indication of the PICs associated with the POHCs of interest.

In thermal destruction tests[5] conducted on a mixture of benzene, chlorobenzene, tetrachloroethylene, dioxane, and tribromomethane at a temperature of 1050°C in a laboratory reactor it was found that the ratio of PICs to POHCs was 500:1 at a DRE of 99.9, and in excess of 1000:1 at 99.99. These results clearly indicate the need for a better understanding of the thermal destruction process, and the need to identify the primary PICs that might be associated with a particular surrogate POHC.

The information in the following three sections summarizes data found in the literature related to the formation of PICs during the thermal oxidation of the three surrogate POHCs: naphthalene ($C_{10}H_8$), chlorobenzene (C_6H_5Cl), and 1,2-dichlorobenzene ($Cl_2C_6H_4$).

Naphthalene

The literature review conducted to date did not identify any specific thermal destruction studies conducted on laboratory scale or full scale incinerators burning naphthalene. However, naphthalene is used as the feedstock in the manufacture of phthalic anhydride. In this process, the naphthalene undergoes either air oxidation or catalytic oxidation to produce the phthalic anhydride (PA). Although catalytic oxidation is generally performed at lower temperatures than occur in incinerators, the reaction products formed in catalytic oxidation may provide some insight into the possible products that might form in thermal destructors, as both are conducted under oxidizing conditions.

Moores[8] reported that the primary organic waste gas emissions from fluidized bed PA plants included phthalic anhydride, maleic anhydride, and benzoic acid in decreasing order of concentration. Johnsson et. al.[9] reported on the emissions from a fluidized bed reactor that was operated at 636 K. At the outlet of the reactor, the principal organic concentrations were 89% phthalic anhydride, 3.2% maleic anhydride, and 1.3% 1,4-naphthoquinone. Medimagh et. al.[10] found the same products in a catalytic oxidation reactor in which naphthalene was oxidized in molten sulphate pyrosulphate at 698 K with a vanadium pentoxide catalyst. Unreacted naphthalene was also found in this later study.

Chlorobenzene

Valeiras et. al.[11] reported the results of laboratory flame studies in which they studied a variety of chlorinated hydrocarbons. In general their conclusions were that

> highly chlorinated hydrocarbons do not burn in normal air. Therefore they require the use of either oxygen-enriched air ..or an auxiliary fuel such as methane...in order to generate stable open flames. The use of methane is particularly advantageous because: a) it is widely available and relatively inexpensive, b) it has sufficiently high heat of combustion, and c) it has a high hydrogen content. Methane because of its high hydrogen-to-carbon ratio, insures the formation of HCl as the primary chlorinated combustion product instead of Cl_2.

In the case of chlorobenzene, however, Valeiras concluded that it could be burned as a stable flame without the presence of methane due to the relatively low chorine content[11]. No reporting was made on the products of combustion of the chlorobenzene, however.

More recently, kinetic studies have been conducted using chlorobenzene to develop a better understanding of the chemical kinetics of the combustion of this POHC.[12]-14 Tsang and Burgess[12] reported on the results of computer simulations of the destruction of chlorobenzene in systems using formaldehyde, ethane, or methane as the pure fuel. The study used a chemical kinetics data base and concentrated on the roles of the OH radicals and H atoms as the key agents for destruction. The study addressed the predicted products of incomplete combustion associated with fragmentation and destruction of the POHC, but did not address the PICs associated with bi-molecular processes that could have created PICs with a higher molecular weight than the parent compound. Rate expressions were summarized for chlorobenzene destruction by OH radical attack, H-atom attack, and Oxygen atom and CH_3 radical attack, and unimolecular decomposition. The computer simulations suggested that the later three of these were not significant contributors to the destruction, and that OH radical attack was most likely responsible:

$$OH + C_6H_5Cl \rightarrow H_2O + C_6H_4Cl$$

No identification of the specific PICs associated with the further destruction of the C_6H_4Cl were presented.

Sethuraman, Senkan, and Gutman[13] reported on a detailed study of the oxidation of chlorobenzene (5000 ppmv or 0.005 mole fraction) in a laboratory flow reactor at a temperature of 630-850°C, 0.4-1.94 seconds of residence time, and an oxygen content of 1.8-3.3%. For these conditions, the equivalence ratio (based on fuel to air ratio) was 1.94 at 1.8% O_2 to 1.17 at 3%, which constituted fuel-rich conditions. Figures 2a and 2b, taken from their study[13], show typical results of their study, and illustrate the importance of the oxygen content and the temperature on the reaction products. Under the starved air condition (see Fig. 2a), the initial oxygen concentration of 1.8% decreased and the CO and CO_2 concentrations increased as the temperature was increased from 650 up to 850°C and the chlorobenzene began to be destroyed. Figure 2b shows that PICs began to appear concurrently with the decrease in chlorobenzene since insufficient oxygen was present to completely oxidize all of the hydrocarbons. While this operating condition is atypical of the overall operation of an incinerator, the data are probably representative of the types of PICs that would be formed in those sections of the incinerator in which oxygen deficiencies occur. As stated previously, it is such areas within the incinerator that are suspected to be the primary source of PICs that are emitted from incinerators, even though the overall system is operated in an excess air mode. For the data taken at 850°C and an O_2 content of 1.8%, the PICs in order of decreasing concentration follow:

PICs	Mole Fraction	Name
C_2H_2	10×10^{-4}	acetylene
C_6H_6	3×10^{-4}	benzene
CH_4	4×10^{-4}	methane
C_4H_4	3×10^{-4}	vinylacetylene
C_2H_4	1×10^{-4}	ethylene
$C_{10}H_8$	$.5 \times 10^{-4}$	naphthalene

No chlorinated hydrocarbon intermediates were observed in the study within the limits of detection of the particular GC/MS. It should be noted that Sethuraman, Senkan, and Gutman[13] did not find the presence of C_6H_4Cl or any of the anticipated by-products of further OH attack of this compound suggesting that the probable mode of attack was more likely by H atom attack of the chlorobenzene molecule resulting in formation of HCl, followed by further attack of the C_6H_5 molecule by H, O, Cl, or HO_2 radical attack. The authors provided a detailed discussion of possible mechanisms whereby the above HC molecules were formed.

More recently, Cicek and Senkan[14] have reported on the destruction of chlorobenzene in fuel-rich mixtures in which a more sophisticated microprobe was used with a GC/MS to study the concentration of PICs within a pre-mixed laminar flame. In these latest studies it was possible to detect the presence of hydrocarbon compounds in the mole fraction range of 1×10^{-5} (10 ppmv) to 1×10^{-4} (100 ppmv). In this more sensitive study a number of additional compounds were identified with concentrations ranging from 10 to 150 ppm, and include the following:

Formula	Name	Formula	Name
CCl_4	carbon tetrachloride	$C_6H_5C_2H$	ethynylbenzene
$C2H_6$	ethane	C_6H_5OH	phenol
C_2HCl_3	trichlorethylene	$C_6H_4Cl_2$	dichlorobenzene
C_2Cl_4	tetrachloroethylene	$ClC_6H_4CH_3$	chlorotoluene
C_4H_2	biacetylene	ClC_6H_4OH	chlorophenol
C_5H_6	cyclopentadiene	$Cl_2C_6H_3OH$	dichlorophenol
C_5HCl_4	tetrachloropentadiene	$Cl_3C_6H_2OH$	trichlorophenol
$C_6H_5CH_3$	toluene	$C_5H_5C_2H_3$	styrene
$ClC_6H_4C_2H_3$	1-chloro-4-ethynylbenzene		

1,2-Dichlorobenzene

Three studies were identified in which 1,2-dichlorobenzene ($C_6H_4Cl_2$) was oxidized and destructed. The first study was conducted by Atalay and Alpay (1987) in which the 1,2-dichlorobenzene was oxidized by catalytic oxidation at temperatures of 285-355°C over a vanadium pentoxide catalyst. The study was conducted primarily to determine the reaction rate coefficients of the oxidation of the 1,2-dichlorobenzene and subsequent reaction products. Due to the low temperature and catalytic conditions the products observed may only provide an initial indication of potential PICs associated with incineration of 1,2-dichlorobenzene. Potential oxidation schemes included the following:

$$C_6H_4Cl_2 + 4.5\ O_2 \rightarrow C_4Cl_2O_3 + 2CO_2 + 2H_2O$$

$$C_6H_4Cl_2 + 4O_2 \rightarrow C_4HClO_3 + 2CO_2 + 2HCl + H_2O$$

$$C_6H_4Cl_2 + 3.5O_2 \rightarrow C_4H_2O_3 + 2CO_2 + 2HCl$$

$$C_6H_4Cl_2 + 6.5O_2 \rightarrow 6CO_2 + 2HCl + H_2O$$

Products identified in the experiments included 2,3-dichloromaleic anhydride ($C_4Cl_2O_3$), 2-chloromaleic anhydride (C_4HClO_3), maleic anhydride ($C_4H_2O_3$), 1,2,3-trichlorobenzene ($Cl_3C_6H_3$), 1,2,4-trichlorobenzene ($Cl_3C_6H_3$), and hydrochloric acid (HCL). While reaction rate coefficients for the reactions were presented, actual concentration data were not presented.

Van Dell and Mahle[16] conducted a study of the PICs and precursors produced from the combustion of 1,2-dichlorobenzene in the flame and the post flame of a laboratory thermal oxidizer that was operated at a flame temperature of 800°C and at post flame temperatures of 150 to 800°C. The system was operated at a fuel-rich fuel to air equivalence ratio of 1.46. Actual concentrations of the PICs were not identified, however the relative molar abundance (RMA) of the compounds was calculated by analyzing the areas under the curves of the response on the GC/MS. As such the RMA indicates the relative number of moles of each constituent, i.e., an RMA of 10 contains twice as many moles than an RMA of 5. The RMA of each observed constituent was reported in graphical and tabular form. Van Dell and Mahle[16] summarized the major PICs that were observed by decreasing concentration for post flame temperatures ranging from 150°C to 800°C. The effect of the post flame temperature on the RMA of each PIC was complex. In some cases the RMA decreased from observable values to near zero or negligible values as the post flame temperature was increased from 150° to 800°C. In other cases, the RMA peaked at an intermediate temperature of 400 to 500°C, indicating the complex behavior of the PICs. Specific compounds with the highest RMAs included:

1,2-dichlorobenzene	(RMA=24.3)
benzene	(RMA=17.1)
1,2,4-trichlorobenzene	(RMA=10.3)
chlorobenzene	(RMA=6.2)
1,2,3-trichlorobenzene	(RMA=4.8)
2,3,4-chlorobiphenyl	(RMA=3.6)
3,4-dichlorophenol	(RMA=3.6)
biphenyl	(RMA=2.5)
pentachlorophenol	(RMA=2.3)
naphthalene	(RMA=2.2)

An additional 65 chlorinated compounds were observed at lower RMAs including -benzenes, -biphenyls, -naphthalenes, and -phenols.

Altwicker, Konduri, and Milligan[17] conducted a study in which 1,2-dichlorobenzene was combusted in a laboratory combustor. The combustor was followed by two post combustion zones with separate temperature controls. A fuel-rich fuel to air equivalence ratio of 1.82 was used to favor formation of PICs. The temperature of the sand-bed within the combustor was maintained at 605°C. Although the primary objective of the study was to determine if polychlorinated dibenzo-p-dioxins and dibenzofurans (PCDD and PCDF) were formed, the authors also measured and found chlorobenzenes (299-553 $\mu g/m^3$) and chlorophenols (117-192 $\mu g/m^3$). Assuming temperature of 300°C, these concentrations are equivalent to 125-230 and 43-70 ppmv as chlorobenzene and chlorophenol. The higher concentration of the chlorobenzenes was consistent with the data reported above by Van Dell and Mahle[16]. For post combustion temperatures of 125-325°C, the concentrations of PCDD and PCDF were nondetectible ($\leq$ 1 ng/m^3). However, for postcombustion temperatures of 390–410°C, concentrations of PCDD and PCDF of 22-23 and 56-76 ng/m^3 were observed, respectively. The formation of these PICs occurred in the post combustion zones of the combustor. The exact mechanisms of formation, i.e., whether by gas phase formation or by a surface-induced effect, were uncertain.

It is evident from the types of PICs formed in the combustion of 1,2-dichlorobenzene that a combination of mechanisms including attack by H, O, OH, and Cl radicals as well as bimolecular reactions all take place in the complex combustion zone and post flame zones.

Final Comment

Based on the literature conducted, it is apparent that a number of compounds are formed due to bi-molecular reactions involving molecules or radicals as well as from attack by specific radicals. While PICs have been identified that were associated with the three surrogate POHCs, the studies indicated that the products formed were also dependent on the type of fuel, if any, being burned along with the POHC. In the case where multiple surrogate POHCs are to be burned in the same test, it is also highly probable that additional bi-molecular reactions and fragmented molecular reactions are likely to occur between POHCs and their fragmented or bi-molecular products. This may create PICs that have not been identified in the above review, as most of the tests reported herein were conducted with a single initial POHC or a single POHC plus fuel.

It is also noteworthy that some of the PICs identified in the combustion of chlorobenzene and dichlorobenzene are actually rated as having a greater thermal stability rating than the POHCs themselves. For example, the PICs include benzene (Rank=3) and naphthalene (Rank=5), while chlorobenzene and dichlorobenzene had rankings of 19 and 23-24, respectively. Other PICs high in the ranking system include tri- and tetra-chlorobenzene (26-27 and 28) and toluene (35).

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