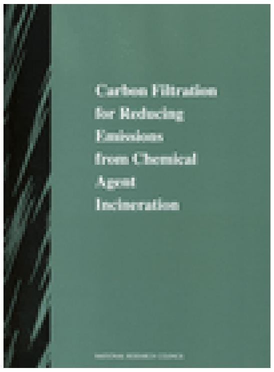

Carbon Filtration for Reducing Emissions from Chemical Agent Incineration

Committee on Review and Evaluation of the Army Chemical Stockpile Disposal Program, National Research Council

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THE NATIONAL ACADEMIES
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CARBON FILTRATION FOR REDUCING EMISSIONS FROM CHEMICAL AGENT INCINERATION

Committee on Review and Evaluation of the Army Chemical Stockpile Disposal Program
Board on Army Science and Technology
Commission on Engineering and Technical Systems
National Research Council

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Preface

The United States has maintained a stockpile of highly toxic chemical agents and munitions for more than half a century. In 1985, Public Law 99-145 mandated an "expedited" effort to dispose of M55 rockets containing unitary chemical warfare agents because of their unlikely, but plausible, potential for self-ignition. This program soon expanded into the Army Chemical Stockpile Disposal Program (CSDP), the mission of which is to eliminate the entire stockpile of unitary chemical agents and munitions. The current baseline incineration system was developed to carry out this mission.

Since 1987, the National Research Council (NRC), through its Committee on Review and Evaluation of the Army Chemical Stockpile Disposal Program (Stockpile Committee), has overseen the Army's disposal program and has endorsed the baseline incineration system for destroying the stockpile. In 1992, after setting several intermediate goals and dates, Congress enacted Public Law 102-484, which directed the Army to dispose of the entire stockpile of unitary chemical agents and munitions by December 31, 2004. As a result of the subsequent implementation, on April 29, 1997, of the international Chemical Weapons Convention, which the United States has ratified, the date has been reset to April 29, 2007.

Incineration processes raise concerns about potentially harmful emissions. Many people fear that substances in the exhaust gas could adversely affect their health and the environment, and some have remained resolutely opposed to the baseline incineration system. When properly operated, however, the incineration system with its pollution control devices releases mostly harmless products: carbon dioxide, water, and other completely oxidized products in their most stable state. However, incinerator emissions also contain small quantities of products of incomplete combustion and other trace contaminants, collectively known as substances of potential concern (SOPCs). For the CSDP, the presence of these SOPCs (and, potentially, trace quantities of chemical agents below the monitoring detection limits) have become matters of concern.

At a workshop sponsored by the Stockpile Committee in 1991, the committee suggested that the Army evaluate a number of modifications to the pollution abatement systems (PASs) for cleaning the incinerator off-gases at sites in the continental United States. One of these technologies involved using activated carbon to adsorb SOPCs. At the time, this technology was already being routinely used at chemical processing plants for the separation and recovery of trace organic products, although it had not been used as an air pollution control system for incinerators in the United States. Hence, activated carbon filters were not included in the PAS at the first full-scale chemical agent disposal facility, the Johnston Atoll Chemical Agent Disposal System (JACADS), or at the Tooele Chemical Agent Disposal Facility (TOCDF).

The Stockpile Committee described public concerns regarding emissions from the baseline incineration system in a 1992 letter report entitled, "Letter Report on Review of the Choice and Status of Incineration for Destruction of the Chemical Stockpile," and again in a February 1994 report, *Recommendations for the Disposal of Chemical Agents and Munitions*. The Stockpile Committee found the baseline system to be adequate for the safe disposal of the stockpile but noted that adding activated carbon filter beds to polish all facility exhaust gases could further protect against emissions of chemical agent or trace organic materials, even in the unlikely event of a major upset. Consequently, the committee recommended that the use of activated charcoal beds to filter the discharge from baseline system incinerators be evaluated. The assessment was to include estimates of the magnitude and potential consequences of upsets and site-specific estimates of benefits and risks. If carbon filtration was found to have site-specific advantages, the committee recommended that the equipment be installed.

This report reviews the Army's evaluation of carbon filters for use in the baseline incineration PAS, as well as the Army's change management process (the Army's tool for evaluating major equipment and operational changes to disposal facilities). In preparing this report, members of the Stockpile Committee evaluated exhaust gas emissions testing at the two operating baseline incineration systems, JACADS and the TOCDF; evaluated the development of the dilute SOPC carbon filter simulation model; and evaluated the conceptual design of a modified PAS with an activated carbon filter. The two major risk assessments conducted for each continental disposal site that use the baseline system, namely, (1) the quantitative risk assessment, which evaluates the risks and consequences of accidental agent releases, and (2) the health risk assessment, which evaluates the potential effects of nonagent emissions on human health and the environment, were also examined.

In a 1997 NRC report, *Risk Assessment and Management at Deseret Chemical Depot and the Tooele Chemical Agent Disposal Facility*, the Stockpile Committee first reviewed carbon filters and included findings and recommendations concerning the addition of carbon filters to the baseline PAS. In the present report, the Stockpile Committee has evaluated continuing developments pertaining to these findings and recommendations.

The committee greatly appreciates the support and assistance of NRC staff members, Donald L. Siebenaler, Harrison T. Pannella, William E. Campbell, Carol R. Arenberg, and Margo L. Francesco in the production of this report.

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Committee on Review and Evaluation of the
Army Chemical Stockpile Disposal Program

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This report has been reviewed by individuals chosen for their diverse perspectives and technical expertise, in accordance with procedures approved by the NRC's Report Review Committee. The purpose of this independent review is to provide candid and critical comments that will assist the authors and the NRC in making the published report as sound as possible and to ensure that the report meets institutional standards for objectivity, evidence, and responsiveness to the study charge. The content of the review comments and draft manuscript remain confidential to protect the integrity of the deliberative process. We wish to thank the following individuals for their participation in the review of this report:

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While the reviewers provided many constructive comments and suggestions, responsibility for the final content of this report rests solely with the authoring committee and the NRC.

Contents

Figures and Tables

FIGURES

TABLES

Abbreviations and Acronyms

ATV	acute threshold value
BIF	boiler and industrial furnace
CAMDS	Chemical Agent Munitions Disposal System (Deseret Chemical Depot)
CDF	chlorinated dioxin/furan
CFR	U.S. Code of Federal Regulations
CMP	change management process
CSDP	Chemical Stockpile Disposal Program
CWC	Chemical Weapons Convention
DCD	Deseret Chemical Depot
DFS	deactivation furnace system
D-R	Dubinin-Radushkevich (adsorption equilibrium relation)
DRE	destruction and removal efficiency
DUN	dunnage incinerator
EMPC	estimated maximum possible concentration
EPA	Environmental Protection Agency
GB	sarin (nerve agent)
HD	mustard agent (distilled)
HE	hazard evaluation
HEPA	high efficiency particulate air
HRA	health risk assessment
ITEQ	international toxic equivalence
JACADS	Johnston Atoll Chemical Agent Disposal System
LC_{50}	lethal concentration resulting in fatality of 50 percent of subjects in a given population
LIC	liquid incinerator
MACT	maximum achievable control technology
MPF	metal parts furnace
MWC	municipal waste incinerator
NODA	Notice of Data Availability
NRC	National Research Council
NSPS	new source performance standards
PAS	pollution abatement system
PFS	PAS (carbon) filter system
PIC	product of incomplete combustion
POHC	principal organic hazardous constituent
PQL	practical quantitation limit
QRA	quantitative risk assessment
RAC	reference air concentration
RCRA	Resource Conservation and Recovery Act
RfD	reference dose
RsD	Risk-Specific Dose
SOPC	substance of potential concern
SOPEC	substance of potential environmental concern
TOCDF	Tooele Chemical Agent Disposal Facility
VX	a type of nerve agent

ng/dnm^3 at 7% O_2	nanograms (10^{-9} grams) per dry normal (32°F [0°C], 1 atm) cubic meter adjusted to a diluent concentration of 7 percent oxygen
ng/dsm^3 at 7% O_2	nanograms (10^{-9} grams) per dry standard (68°F [20°C], 1 atm) cubic meter adjusted to a diluent concentration of 7 percent oxygen

Executive Summary

The Committee on Review and Evaluation of the Army Chemical Stockpile Disposal Program (Stockpile Committee) of the National Research Council has endorsed incineration (with comprehensive air pollution control systems) as a safe and effective procedure for destroying chemical agents and munitions. Recognizing, however, that some public opposition to incineration (based primarily on substances of potential concern [SOPCs] that could escape into the atmosphere with the combustion gas) has always existed, the committee also recommended that the Army study the addition of a carbon filtration system to improve the existing pollution abatement system. This recommendation reflected the committee's belief that (1) reductions in emissions resulting from carbon filtration systems, however small, could increase public confidence, and (2) a carbon filter would virtually eliminate the possibility of an accidental release of a chemical agent through the stack.

When the first recommendations were made in 1991 and 1992, carbon filters were being introduced in Europe. Since then, the Army has evaluated the European experience and decided to add carbon filters to the baseline incineration systems for the disposal of chemical weapons stockpiles at Anniston, Alabama; Umatilla, Oregon; and Pine Bluff, Arkansas. Carbon filters are called for in the Resource Conservation and Recovery Act (RCRA) permits for the Anniston, Umatilla, and Pine Bluff sites, where construction of the disposal facilities is already under way.

Since these decisions were made, data from trial burns conducted at the operating Tooele Chemical Agent Disposal Facility (TOCDF) near Tooele, Utah, have become available. Although this facility does not have a carbon filtration system, the data show very low emitted concentrations of SOPCs, including dioxins and metals. The concentrations measured at the TOCDF were either the lowest or among the lowest emitted concentrations in the Environmental Protection Agency's (EPA's) Hazardous Waste Combustor Emissions Database. Chemical agent, if present at all, was below the detection limit, which is also below the levels generally believed to have deleterious environmental or health effects. Nevertheless, an Army study modeling the performance of carbon filters concluded that they would reduce many SOPCs to even lower levels. The committee concurs with this judgment.

The carbon filter system, including associated gas conditioning equipment designs, had not been finalized at the time this report was prepared. Suggested design alternatives were available, however, and the committee concluded that an effective pollution abatement system carbon filter system (PFS) design could be implemented.

The Utah Department of Environmental Quality's Division of Solid and Hazardous Waste, which conducted the health risk assessment (HRA) for the Tooele facility, determined that the health risk to the public posed by the incinerator stack gas emissions was below the level of regulatory concern. HRAs have also been conducted by Army contractors for the Anniston and Umatilla facilities in which the effects of adding carbon filters to the baseline incineration system pollution abatement systems were considered, but only in terms of changes in the exhaust gas flow rate and temperature, not reduction in emissions of SOPCs. These studies did not quantitatively evaluate the potential benefits of the PFS, but even without carbon filtration systems, emissions are expected to be below the levels of regulatory concern.

Based on quantitative risk assessments (QRAs) (estimates of the probability and consequences of accident scenarios that could lead to a release of agent) completed at Tooele and under way at Anniston and Umatilla, the increased risk to the public from an accidental release of agent associated with carbon filters was found to be negligible (i.e., orders of magnitude below the risks people face every day). This was not so for worker risk. In the Anniston QRA analysis carried out using the Phase 2 QRA from the TOCDF, modified for the presence of a PFS, the only type of upset condition that would increase the risk of agent release was blockage of the exhaust gas flow by the PFS coupled with loss of the induced draft (which maintains the pressure drop for the exhaust gas flow). The risk of an explosion of agent vapor caused by blockage of the PFS represents 3 percent of the total worker risk. Individual worker fatality risk from agent over the facility life attributable to upsets in the pollution abatement system are estimated at 3.3×10^{-5} with the PFS and 1.1×10^{-5} without the PFS. This is in contrast to total worker risk from agent over the facility life of 4.1×10^{-4} as estimated for TOCDF. These findings also can be compared with the worker accidental death rates of 3×10^{-5} *per year* for manufacturing and 1.5×10^{-4} *per year* for construction industries during 1996. The increased risk at the TOCDF is within the range of the uncertainty of worker risk analysis at the facility but significant enough to warrant further evaluation.

The QRAs assess the risk of accidental releases of chemical agent, but they do not address "normal" industrial risk to workers. Hazards to workers from operating and maintaining an industrial facility (hazards not related to agent) will be evaluated during design and prior to commissioning, as part of the health, safety, and environmental evaluations for baseline facilities. If carbon filters are used, they will be included in these evaluations and the risk management and safety programs of each facility. Two risks that are frequently mentioned in this connection are risks associated with potential fires and risks during disposal of the carbon. PFS design and monitoring plans substantially mitigate the risk of potential carbon fires. The amount of potentially contaminated carbon from the PFS that will require disposal is small in comparison to the amount of agent-contaminated carbon that will require disposal from the treatment of the ventilation air for the facility.

The QRAs for three sites (Tooele, Anniston, and Umatilla) to date all confirm the committee's previous observations: (1) the major hazard to the public is from the stored agent and munitions in the stockpile itself; and (2) the risk introduced by stockpile disposal processing is relatively small (less than 1 percent of the stockpile storage risk). Major changes in a RCRA permit may engender a considerable delay that would increase the overall risk to the public. However, the magnitude of the increased storage risk depends on the length of the delay (which is uncertain). The increased risk from prolonged stockpile storage has been estimated on a *per year of storage* basis. For the population 2 to 5 km from the Anniston Chemical Agent Disposal Facility, the individual public fatality risk is 1.4×10^{-5} per year, and the societal public fatality risk is 2.6×10^{-2} per year. This risk is in contrast to the disposal processing risks for the same population of 3.8×10^{-8} per year (individual public fatality risk) and 1.8×10^{-5} (societal public fatality risk). Thus, the *per year* risk from storage is at least three orders of magnitude higher than the risk from disposal processing. Hence, very short delays would increase public risks more than the total public risk from disposal. A delay of approximately one year would result in increased individual public risks of the same order of magnitude as the estimated increase attributable to the PFS in individual worker fatality risk over the *entire* period of disposal processing. Consequently, public risk will be minimized by the expeditious safe destruction of the stockpile.

Conceptually, the committee agrees with the Army's decision to proceed with the current designs at Anniston and Umatilla and not to alter the operating configurations of JACADS and the TOCDF. Removing or adding carbon filters at this point is likely to cause delays that will increase the risk to workers and the public. However, potential increases in worker risk from the carbon filters, which were initially estimated to be small, require further evaluation. To mitigate the potential adverse consequences of adding carbon filters at Anniston and Umatilla, worker risk should be evaluated quickly and managed effectively, including changing the PFS design, if necessary.

The Army's initial attempts at public outreach using its change management process (CMP) in PFS decision making did not elicit meaningful public involvement or comment during the decision process, and several shortcomings of the CMP have now become apparent. First, public involvement must be initiated much earlier in the process of evaluating change. For example, public involvement could have helped the

Army formulate the questions to be answered during the PFS risk evaluation. Second, public involvement should allow for public input prior to making decisions on major process changes, even if initial assessments indicate that no change is preferred. Third, for the CMP public involvement process to be credible and engender public trust, the Army must provide clear guidelines for initiating the CMP, which should not be circumvented by executive decision.

The Army's decisions not to change the configurations at Tooele, Anniston, and Umatilla were made in the context that the original intent of the PFS was to reduce risk and increase public confidence. These goals were to be achieved by adding another air pollution control system component to polish the effluent and curb whatever pollutants would have been emitted without the PFS. However, the results of the Army's analysis showed that changes to risk would be small, that these changes could be improvements or degradations depending on the population considered and the uncertainty analysis, and that the risks could be different for the public and workers. In addition, the Army's presentation of the risk evaluations was difficult to understand and was not issued in a self-contained document delineating (1) comparisons of each risk component with and without the PFS and (2) the Army's rationale for making no changes to the current site configurations. These crucial lapses all but precluded the public from following the process or influencing the results.

FINDINGS AND RECOMMENDATIONS

The estimated concentrations and emission rates of SOPCs from chemical agent incinerator operations developed during the permitting processes for the Anniston Chemical Agent Disposal Facility and the Umatilla Chemical Agent Disposal Facility were below the thresholds of regulatory concern, whether or not a passive carbon filtration system (like the PFS) was included in the facility design. Therefore, the committee considers PFS to be risk neutral to off-site populations.

The addition of a PFS to the PAS would probably reduce the already low emissions of some SOPCs during normal, transient, and upset operating conditions. However, a PFS would also increase worker risk by making the facility more complex and by introducing new scenarios for potential facility upsets and failures. The extent of the increase in worker risk is not clear because all of the applicable risk evaluations (e.g., Phase 2 QRAs and health, safety, and environmental evaluations) and resulting risk mitigation measures have not yet been completed. Preliminary assessments, however, indicate that the increase in worker risk would be small.

Significant changes in permitted facility designs require permit modifications, which could cause substantial delays. Because risk analyses consistently indicate that the storage risk to the public and workers is much greater than the processing risk, changing the permitted configuration at any stockpile site is likely to increase the overall risk by delaying destruction of the stockpile.

Finding 1a. The reported emitted concentrations of SOPCs measured during trial burns at the JACADS and TOCDF incinerators are among the lowest reported to the EPA. TOCDF emissions are the lowest, or at least one of the lowest, in dioxins, mercury, cadmium, lead, arsenic, beryllium, and chromium. The reported emissions of some SOPCs were based on the analytical detection limit for the constituent, which means the actual concentration could be much lower than the reported concentration. Maximum emitted concentrations from JACADS were used for the HRAs for other baseline facilities to ensure that estimates of risks would be conservative.

Finding 1b. In 1992 and 1994, the NRC recommended that the Army investigate using carbon filters for two purposes: (1) to contain transient stack emissions or accidental releases of agent and (2) to increase public confidence in incineration. Activated carbon filters in use at several large incinerators in Europe meet very stringent regulations on emissions of chlorinated dioxins/furans and are considered to be the state-of-the-art technology for this purpose. Based on preliminary design evaluations, activated carbon in the PFS of the Army's baseline incineration system is likely to have sufficient adsorption capacity to reduce emitted concentrations of dioxins, furans, HD, VX, and GB for more than a year of normal operations before the activated carbon would have to be replaced. The activated carbon would also have the capacity to adsorb a chemical agent in case of a major upset; however, a major upset would necessitate the immediate replacement of the activated carbon.

The addition of carbon filters to a baseline incineration PAS does not appear to reduce the health risk to the surrounding population substantially because the health risk is already small (see Finding 1a). Nevertheless, reinforcing public and worker confidence is an important goal.

Recommendation 1. The Army should only consider removing the carbon filtration system from the permitted designs of the Anniston, Umatilla, or Pine Bluff facilities if, after a thorough implementation of the change management process to ensure meaningful public involvement, the public supports that decision.

Finding 2. Based on the evaluation of preliminary PFS design alternatives, an effective design for the PFS is feasible. Operating facilities in several countries now have significant experience in the design and operation of activated carbon filters.

Recommendation 2. The Army should take advantage of the experience of other users of carbon filters through appropriate consultation.

Finding 3. The Army has evaluated the implications of adding or removing passive carbon filter systems to the baseline incineration systems at the Tooele, Anniston, and Umatilla disposal facilities. Some of the impacts on risk to public health from stack emissions were evaluated by comparing the HRAs for the existing baseline facilities to estimates of the upper bound of public health risk posed by the addition of the PFS. However, the potential reductions in public health risk were not estimated, and the evaluations of impacts to off-site populations were incomplete.

An estimate of the impact on risk of accidents leading to agent-related public fatalities was made by expanding the Anniston and Umatilla Phase 1 QRAs to consider the addition of the PFS. The impact of the PFS on worker risk, which is not evaluated in the Anniston and Umatilla Phase 1 QRAs, was estimated by extrapolating the Tooele Phase 2 QRA results (which does include worker risk) to these other facilities. The Phase 1 QRAs for the Anniston and Umatilla facilities were also used to estimate increases in risk to the public from extended storage of the stockpile due to the PFS. Thus, the QRA evaluations completed to date are initial estimates of the magnitude of increased risk to the public from accidental releases of agent resulting from the addition of the PFS, but they are not complete evaluations of worker risk. Moreover, the range of potential delays to stockpile destruction caused by permit modifications and physical changes to the current site-specific baseline incineration configurations has not been defined.

Based on these estimates, the Army concluded that "[the] current plan to install and operate the PFS at the ANCDF [Anniston] and the UMCDF [Umatilla] remains the best course of action for maximizing human health and environmental protection," and that the TOCDF should continue to operate without a PFS. The decision to continue with the current configurations at permitted facilities eliminates increases in risks to the public and workers from potential delays in stockpile destruction caused by facility modifications or permit changes. Although worker risk from current PFS configurations is uncertain, based on the available risk estimates and projected schedules, the committee concurs with the Army's conclusion.

Recommendation 3. To minimize increased risks to off-site populations and on-site workers from delays in stockpile destruction, the Army should proceed with the current configurations, which include carbon filtration systems at Anniston and Umatilla, and should continue operations at Tooele, which does not have a carbon filtration system.

Finding 4. Only the Phase 1 Anniston and Umatilla QRAs have been completed. The risk of acute hazards to workers, probably the receptors at greatest risk from a mishap involving the PFS, has not been adequately characterized. Early initiation of the Phase 2 QRAs could identify these risks while facility design and construction are in progress and give the Army greater flexibility to modify facility designs and operating procedures, if necessary.

Recommendation 4a. The site-specific Phase 2 QRAs for Anniston, Umatilla, and Pine Bluff, which would identify and analyze specific failure modes, should include a complete evaluation of worker risk associated with the addition of the pollution abatement system filter system. The Phase 2 QRAs for each site should be initiated as soon as possible and should be completed and reviewed by independent technical experts before systemization of the facilities at Anniston, Umatilla, and Pine Bluff is completed.

Recommendation 4b. A risk management plan should be developed to minimize worker risk during the operation and maintenance of the pollution abatement system filter systems. The evaluation of operating and maintenance risks should include the operational experience of similar systems. If the increased risk to on-site workers is found to be substantial, the Army should consider making modifications, as long as they do not substantially increase overall worker or public risk from prolonged storage.

Finding 5. If increased worker risks and hazards are identified, it is not clear what steps the Army would take to mitigate them. Nor does the Army have a clear decision basis for balancing reductions in public risk and increases in worker risk.

Recommendation 5. The Army should clarify to the public and facility workers the risk management actions that would be taken if increased worker risks are identified. The Army should also clarify the decision basis for balancing reductions in public risk against increases in worker risk while fulfilling its mandate to protect both workers and the public.

Finding 6. The PFS was assumed to have no effect on concentrations of SOPCs in the HRA calculations for Anniston and Umatilla. The effects of SOPCs emitted from the stacks at these facilities have been estimated to be below the thresholds of regulatory concern without the benefit of the PFS. However, changes from installing a PFS have not been determined in a way that facilitates quantitative comparisons.

Recommendation 6. Future health risk assessments should include estimates of emitted and ambient concentrations of SOPCs, with and without the PFS, for all substances that contribute significantly to the overall risk. Because PFS performance cannot be based on actual measurements, the analysis should consider the implications of reducing emissions to both the method detection limit and the levels indicated by engineering calculations, including quantitative evaluations of the uncertainties associated with each risk estimate. The results, including the acute and latent risks, should be reviewed by independent technical experts. The results should then be presented in a way that facilitates public input to decision making.

Finding 7. Because of the length of time required to complete the preliminary PFS risk assessment, the fact that this evaluation is still incomplete, and the status of construction activities at Anniston and Umatilla, meaningful public involvement in the decision to include the PFS at these sites is no longer possible. The CMP Plan and the CMP Public Involvement Outreach Plan were not effectively implemented during the Army's analysis of the PFS. The lack of public involvement in this process represents a lost opportunity for the Army to develop its CMP and to implement the CMP public outreach process.

Recommendation 7a. The health risk assessment and quantitative risk assessment for Pine Bluff should be completed as quickly as possible and communicated to the public in a timely manner so that there can be meaningful public involvement in the decision process to retain or remove the carbon filter system. The risk assessments should be subject to independent expert review and the findings incorporated into the decision-making process.

Recommendation 7b. The Army should continue to refine its change management process and the change management process public involvement plan. Public involvement should be an integral part of future evaluations of the pollution abatement system filter system, especially at Pine Bluff. The committee repeats its recommendation that the Army involve the public meaningfully in the Chemical Stockpile Disposal Program as a whole.

1

Introduction and Background

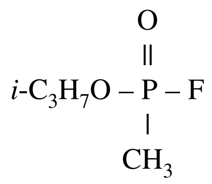
For more than half a century, the United States has maintained a stockpile of extremely hazardous chemical agents and munitions at eight sites in the continental United States and Johnston Atoll in the Pacific Ocean. The United States has decided to destroy this stockpile because of its age, its lack of utility as weapons or as a deterrent, the continuing costs of maintenance, and the potential for accidental release with resultant harm to human health and the environment.

In 1985, Congress passed Public Law 99-145, which directed the U.S. Department of Defense to destroy at least 90 percent of the stockpile of unitary[1] chemical agents and munitions, especially M55 rockets, which were deteriorating and becoming increasingly hazardous. After setting several intermediate goals and dates, on October 23, 1992, Congress passed the National Defense Authorization Act for fiscal year 1993 (Public Law 102-484), which directed the Army to dispose of the entire stockpile of unitary chemical warfare agents and munitions by December 31, 2004. Congress also directed that the Army's Chemical Stockpile Disposal Program (CSDP) ensure the maximum protection of workers, the public, and the environment.

The CSDP has evolved in parallel with worldwide attempts to control and eliminate chemical agents and munitions. Over the course of several decades, a broad, complex agreement known as the Chemical Weapons Convention (CWC) has been negotiated. This agreement, which went into effect on April 29, 1997, requires that all chemical agents and munitions be destroyed in ten years (i.e., by April 29, 2007); the congressional mandate has been modified to reflect the CWC deadline. The agreement allows each country to determine the method of destruction, as long as it ensures public safety and protects the environment.

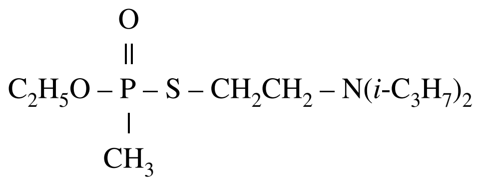
The chemical formulas for the three principal agents in the U.S. stockpile to be destroyed are given below. GB and VX are nerve agents; HD, commonly called "mustard," is a blister agent.

GB



$$i\text{-}C_3H_7O-\overset{\overset{\displaystyle O}{\|}}{\underset{\underset{\displaystyle CH_3}{|}}{P}}-F$$

VX



$$C_2H_5O-\overset{\overset{\displaystyle O}{\|}}{\underset{\underset{\displaystyle CH_3}{|}}{P}}-S-CH_2CH_2-N(i\text{-}C_3H_7)_2$$

HD $ClC_2H_4-S-C_2H_4Cl$

SELECTION AND DEVELOPMENT OF THE BASELINE INCINERATION SYSTEM

In the 1970s, the Army commissioned studies of many different disposal technologies and tested several

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[1] The term *unitary* refers to a single chemical loaded in munitions or stored as a lethal material. More recent *binary* munitions consist of two relatively safe chemicals loaded into separate compartments and mixed to form a lethal agent only after the munition is fired or released. Components of binary munitions are stockpiled in separate states and are not included in the present Chemical Stockpile Disposal Program. However, they are included in the munitions that will be destroyed under the international Chemical Weapons Convention.

of them. In 1982, disassembly followed by component incineration was selected as the method for disposing of agents and associated propellants and explosives and for thermally decontaminating metal parts. In 1984, the National Research Council (NRC) Committee on Demilitarizing Chemical Munitions and Agents reviewed a range of disposal technologies and endorsed the Army's selection of incineration as an adequate technology for the safe disposal of chemical warfare agents and munitions (NRC, 1984).

Pursuant to the enactment of Public Law 99-145, the Army developed and tested prototype components of the baseline incineration system at the Chemical Agent Munitions Disposal System (CAMDS) facility at Deseret Chemical Depot (DCD), formerly Tooele Army Depot South, Utah. To date, two baseline incineration systems are in operation: the Johnston Atoll Chemical Agent Disposal System (JACADS), located on Johnston Island about 700 miles southwest of Hawaii, and the Tooele Chemical Agent Disposal Facility (TOCDF) at DCD in Utah, about 50 miles west of Salt Lake City. JACADS, the first full-scale version of the baseline system, commenced operational verification testing in July 1990. Construction on the TOCDF, the first baseline incineration system disposal facility in the continental United States, began in 1989. The destruction of agent and munitions from the DCD stockpile at the TOCDF began in August 1996. JACADS is scheduled to complete the destruction of the stockpile at Johnston Island in 2000; the TOCDF is scheduled to operate until 2005. In 1997, the construction of baseline incineration system disposal facilities was begun at two other storage sites: Anniston Chemical Activity, Anniston, Alabama, and Umatilla Chemical Depot, Hermiston, Oregon. As of early March 1999, construction of these facilities was 36 percent and 40 percent complete, respectively. Construction of a baseline incineration system at Pine Bluff Chemical Activity, Pine Bluff, Arkansas, began in January 1999.

Incineration processes have raised concerns about potentially harmful emissions. People who fear that contaminants in the exhaust gas could have adverse effects on their health and the environment have remained resolutely opposed to the baseline incineration system. Properly operated, the incineration system produces mostly relatively harmless products: carbon dioxide, water, and other completely oxidized products in their most stable state. However, incinerator emissions also contain small quantities of products of incomplete combustion (PICs) and other trace contaminants, collectively known as substances of potential concern (SOPCs). The presence of SOPCs and trace quantities of agent at levels below the monitoring detection limits have become matters of concern to the public. The chemical agent is sometimes called the principal organic hazardous constituent (POHC) being incinerated. In keeping with normal practice for hazardous-waste incineration operations, stack emissions are continuously monitored for the presence of chemical agent. However, SOPCs (other than carbon monoxide), which include particulates, heavy metals, and acid gases, are not routinely monitored; and current monitoring techniques cannot provide real-time analysis. These substances are usually measured only during tests required to obtain or maintain federal and state operating permits.

There appear to be two levels of public concern. Some people are convinced that incinerator operations will not keep SOPCs at relatively benign levels. Others believe that the presence of any SOPCs—no matter how small—is unacceptable because any discharge adds to the pollution burden to which people are exposed. These well documented concerns are not limited to the incineration of chemical agents and munitions but have also been expressed about waste incineration, the burning of fossil fuels, other combustion processes, and industrial chemical processes in general.

ROLE OF THE NATIONAL RESEARCH COUNCIL

In 1987, at the request of the Undersecretary of the Army, the NRC Committee on Review and Evaluation of the Army Chemical Stockpile Disposal Program (Stockpile Committee) was established under the aegis of the Board on Army Science and Technology to provide the Army with technical advice and counsel on specific aspects of the disposal program. Under this charter, the Stockpile Committee has completed 17 reports evaluating various stages of progress and aspects of the program. See Appendix A for a list of these reports.

After a workshop sponsored by the Stockpile Committee in 1991, the Army was urged to evaluate a number of improvements in the pollution control systems for cleaning the incinerator off-gases at stockpile disposal sites in the continental United States (NRC, 1991). One of the technologies to be evaluated was the use of activated carbon to adsorb SOPCs:

> Use of an activated carbon filter downstream of the scrubbers would remove pulses of agent [puffs][2] and low-level organics...The ability to reduce mercury vapor and dioxin emissions is an additional feature of carbon. While such a system is currently considered redundant in municipal and industrial waste incineration, the use of redundant air pollution control could substantially enhance public confidence, particularly if the redundant system is independent of system operating conditions.

At the time, carbon filtration was routinely used for the separation and recovery of trace organic compounds from various sources (e.g., storage tanks, chemical process plants, automobiles, etc.), but it had not been used as an air pollution control system for incinerators in the United States. Hence, activated carbon filters were not included in the pollution abatement system (PAS) at JACADS, the first full-scale chemical agent disposal facility.

The workshop was followed by a letter report in 1992 by the Stockpile Committee that included several recommendations based on workshop discussions for improving the performance of the baseline system PAS (NRC, 1992). One of these mentioned carbon filters:

> The Army should consider incorporating passive controls, such as activated carbon beds, to ensure the lowest emissions even under temporary upsets (e.g., "puffs") that might not be controlled by the existing afterburner. (*Recommendation 2*, NRC, 1992).

The Army divided its consideration of the NRC recommendations into three subtasks:

- Subtask 1: a review of literature and existing data on PASs
- Subtask 2: a PAS plant survey and applicability study
- Subtask 3: a comparison of new and existing PAS technologies

The results of the Army's study were presented in three reports (U.S. Army, 1994a, 1994b, and 1994c), but no decision for change was made at that time.

Meanwhile, in March 1991, as a result of growing public concerns about and opposition to the baseline incineration system and the rising cost of the CSDP, the Stockpile Committee suggested, and the Army agreed, that a study be undertaken of alternatives to incineration for the destruction of the stockpile.

In January 1992, the NRC, at the request of the Office of the Assistant Secretary of the Army for Installations, Logistics and Environment, established the Committee on Alternative Chemical Demilitarization Technologies (Alternatives Committee) to develop a comprehensive list of alternative technologies, review their capabilities, and evaluate their potential for the disposal of agents and munitions. In June 1993, this committee published its report, *Alternative Technologies for the Destruction of Chemical Agents and Munitions* (NRC, 1993). Continuing public concerns about emissions from the baseline incineration system were expressed during a public forum on June 30, 1993, in Washington, D.C., sponsored jointly by the Alternatives Committee and the Stockpile Committee.

Based on the report of the Alternatives Committee and the Stockpile Committee's knowledge of the baseline system and disposal requirements, the Stockpile Committee recommended that alternatives to incineration be investigated. The recommendations were published in a report in February 1994, *Recommendations for the Disposal of Chemical Agents and Munitions* (NRC, 1994). Although the committee still considered the baseline system to be adequate for disposal of the stockpile, the committee included the following finding and recommendation for enhancing the performance of the baseline incineration system.

> **Finding 13.** The Stockpile Committee finds the baseline system to be adequate for disposal of the stockpile. Addition of activated carbon filter beds to treat all exhaust gases would add further protection against agent and trace organic emissions, even in the unlikely event of a substantial system upset. If the beds are designed with sufficient capacity to absorb the largest amount of agent that might be released during processing, addition of these beds could provide further protection against inadvertent release of agent.
>
> **Recommendation 13.** The application of activated charcoal filter beds to the discharge from baseline system incinerators should be evaluated in detail, including estimations of the magnitude and consequences of upsets, and site-specific estimates of benefits and risks. If warranted, in terms of site-specific advantages, such equipment should be installed.

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[2] *Puffs* refer to transient increases in concentration in the exhaust gas as distinguished from *pressure excursions*, which are sometimes also referred to as puffs. Pressure excursions cause gas to leak out of the incineration system into the containment area. Puffs are attenuated by the air pollution control system. Activated carbon beds are designed to eliminate or mitigate puffs.

The Army responded to the NRC finding and recommendation in two ways. First, the trial burns at JACADS and the TOCDF (required as part of the permitting process) showed, as expected, that numerous SOPCs were present at very low levels. Chlorinated dioxin concentrations measured at JACADS and the TOCDF were much lower than the levels reported for sources using activated carbon filters in Europe (Clarke, 1991). Because adsorption efficiency is a function of many parameters, including inlet concentrations, a question arose as to how effectively carbon beds would reduce SOPCs (e.g., chemical agent, dioxins, etc.) even further. The Army performed an experimental and theoretical study to determine what might be achieved by carbon adsorption with very dilute inlet concentrations (Mitretek Systems, 1997). The study also considered the risk of a sudden release of sorbed materials from the carbon in the event of an operational failure. Second, anticipating that the Mitretek study would show potential benefits, the Army included a carbon bed filter in the pollution abatement designs submitted for permitting of the baseline incineration systems at Umatilla, Oregon; Anniston, Alabama; and Pine Bluff, Arkansas.

Carbon filters have been shown to reduce emissions of some SOPCs (see for example, Hartenstein, 1994). The health benefits of reducing residual SOPC emissions may be inconsequential, however, because the emissions are already very low. However, further reductions may increase public confidence.

Carbon filters can introduce other types of risk. First, there is a possibility of a carbon fire, although to the committee's knowledge none has been reported in an incinerator application. Second, SOPCs from incinerator exhaust gas will accumulate and concentrate on the filters, and there is a possibility that the accumulated SOPCs could be driven off of the filters by a thermal transient or a sudden increase in the gas humidity. Third, the SOPC-loaded activated carbon could be considered contaminated and would, therefore, have to be treated as hazardous waste. Thus, carbon filters should be thoroughly evaluated in quantitative risk assessments (QRAs), health risk assessments (HRAs), and hazard evaluations (HEs) for their overall beneficial and harmful effects.

Carbon filters are already in the designs and permits for the Anniston and Umatilla plants, and construction of both of these facilities is well under way. A carbon filter is also included in the design submitted as part of the RCRA Part B permit application for the baseline facility at Pine Bluff, Arkansas, the fifth baseline facility to be built. Construction at Pine Bluff began in January 1999. If the decision to install or remove a carbon filter system is made after a permit has been issued, a permit modification would be required, which could delay the completion of the disposal program and increase the overall risk.

In response to NRC recommendations concerning the use of risk assessments and the need for public involvement, the Army established a formal procedure called the change management process (CMP) for making significant changes to a facility's configuration or operations (U.S. Army, 1997a). The CMP evaluates changes to the risk estimates in the QRA and HRA from proposed modifications to equipment or operations. The CMP also includes public input into decisions to make changes in equipment, operational procedures, or any aspect of the operation of concern to the public. The decision about carbon filters was intended to be an early application of the CMP.

PURPOSE OF THE REPORT

This report reviews the Army's evaluation of carbon filters, as well as its process for reaching decisions on their utilization. Members of the Stockpile Committee have been actively following the testing of stack gas emissions at JACADS and the TOCDF, the development of the carbon filter simulation model, the conceptual design of a PAS modified with an activated carbon filter system (the PFS), and the two major risk assessments conducted for each continental disposal site, namely, the QRA (a quantitative risk assessment of the likelihood and consequences of accidental agent releases) and the HRA (a health risk assessment of potential effects of facility emissions during mild and severe upset conditions on human health and the environment).

In the Statement of Task for this report, the committee was asked to do the following tasks:

- Gather and assess trial burn data from JACADS) and the TOCDF.
- Acquire from appropriate Army and contractor sources data and information regarding the design concept for a PFS for the Anniston and Umatilla Chemical Agent Disposal Facilities.
- Assess the PAS carbon filter simulation model.
- Review the changes in previous QRAs and HRAs after the addition of carbon filters to the PAS of the baseline incineration system.

- Travel to Umatilla Chemical Agent Disposal Facility to observe the change management process as applied to any design change that might affect the carbon filter system.
- Gather relevant data, information, and literature on carbon filters and carbon filter performance based on other (e.g., municipal and hazardous waste) incinerators.
- Produce a report that reflects the background of the Army's incineration program and previous relevant NRC recommendations; provides data on flue gas emissions and public concerns; details filter performance principles; and reviews the PAS carbon filter design, operation, maintenance, and disposal requirements.
- Assess the Army's QRAs and HRAs evaluating the addition of carbon filters and provide appropriate findings and recommendations.

The committee could only base its evaluation on the Anniston and Umatilla HRAs and Phase 1 QRAs because the Phase 2 QRAs[3] were not yet complete. Therefore, no formal characterization of worker risk was available. The committee has used the available information to suggest additional steps the Army could take to implement its decisions.

The Stockpile Committee had already initiated its review of carbon filters in a recent NRC report, *Risk Assessment and Management at Deseret Chemical Depot and the Tooele Chemical Agent Disposal Facility* (NRC, 1997a). That report included the following findings and recommendation concerning the addition of carbon filters to the PAS.

> The proposed methodology [using an HRA/QRA risk-based evaluation], if well implemented, is appropriate for evaluating whether or not to install a PFS on a site-specific basis.
>
> Carbon filters appear to be effective in reducing the level of dioxins/furans to below the limits of detection and to have a useful life of at least one year. Because these levels cannot be measured, however, credit only for reducing them to the detection limit appears in the HRA.
>
> **Recommendation 10.** The Army should proceed with the application of its proposed methodology for evaluating the use of PAS carbon filters on a site-specific basis. For consistency with the HRA assumptions, the QRA should take into account the possible sudden release of agent that may have accumulated on the filter at a gas concentration equal to the lower detection limit.

In preparing the present report, the Stockpile Committee evaluated developments pertaining to the findings and recommendation cited above. Chapters 2, 3, and 4 are focused on science and engineering aspects of carbon filters, particularly their application to flue gas emissions from chemical agent disposal by incineration. Detailed discussions in these chapters address the composition of trace gaseous emissions, the control of trace gas emissions with carbon filters, and the impact of carbon filters on facility design. Chapter 5 is focused on the risk assessments and public involvement in the Army's decisions about using PAS carbon filters. Chapter 6 contains the committee's findings and recommendations.

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[3] A Phase 2 QRA is a detailed evaluation of the risks and consequences of accidental releases of agent to workers and the community based on the site-specific design and operations. A Phase 1 QRA evaluates only public risks from a proposed facility before it is constructed.

2

Trace Gaseous Emissions from Agent Incineration

HISTORY OF THE REGULATION OF TRACE EMISSIONS

Trace emissions were essentially unregulated until 1977 when polychlorinated dibenzo-p-dioxins and dibenzofurans (collectively known as "dioxins") were first detected in the stack gases of a municipal waste incinerator in Sweden (Aslander, 1987). This was quickly followed by a similar discovery in the United States (New York State Legislative Commission on Solid Waste Management, 1986). Shortly thereafter, a moratorium on the construction of incinerators was imposed in Sweden. The Swedish moratorium was lifted in 1986 with the promulgation of a standard equal to 0.1 ng/dnm^3 at 11 percent O_2 ITEQ[1] dioxin. In the units commonly used by the Environmental Protection Agency (EPA), this is approximately 0.3 ng/dsm^3 at 7 percent O_2.

In the United States, the regulation of particulates from municipal and hazardous waste incinerators began in 1972 (40 CFR 60c).[2] Hazardous-waste incinerators were also required to control emissions of hydrogen chloride and demonstrate at least 99.99 percent destruction and removal efficiency (DRE) of hazardous organic compounds (40 CFR 263). For wastes contaminated with polychlorinated biphenyls (PCBs) and dioxins, the DRE requirement was 99.9999 percent.

In 1991, regulations covering boilers and industrial furnaces that burn hazardous waste were adopted (the BIF Rule) (EPA, 1991). The BIF Rule included maximum allowable concentrations for a host of trace organic and inorganic compounds in ambient air. Because ground-level atmospheric concentrations are related to stack concentrations through site-specific dispersion modeling, the BIF Rule effectively created emissions standards for all regulated trace organic and inorganic emissions. However, they establish a common ambient impact for specified emissions constituents rather than a constant emitted concentration standard for each source, which results in different localized ground-level concentrations.[3] This has led to considerable confusion and charges that facilities regulated under the BIF Rule may not be equipped with the best available control technologies, thus exposing some areas to more pollution than others.

In 1995, the Clean Air Act set standards for maximum achievable emissions control technology (MACT) for municipal waste combustors that incinerate more than 250 tons per day (40 CFR 60 Subpart Eb). These regulations restrict total dioxin emissions (i.e., the sum of the dioxin and furan homologues with 4 to 8 chlorine atoms per molecule) to 13 ng/dsm^3 at

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[1] ITEQ (international toxic equivalency) dioxin is the amount of 2,3,7,8 TCDD (2,3,7,8-tetrachlorodibenzo-p-dioxin) with toxicity equivalent to the complex mixture of 210 dioxin and furan isomers with 4 to 8 chlorine atoms found in flue gases. This equivalency is based on the International Toxic Equivalence Factor scheme adopted by the Environmental Protection Agency and most countries to simplify the reporting of dioxin emissions.

[2] CFR citations refer to the U.S. Code of Federal Regulations with the volume number preceding CFR and the section number following. Copies of volumes of the U.S. Code of Federal Regulations are available through the Government Printing Office outlets and commercial document and regulatory services.

[3] Examples of constant emitted concentration standards include the EPA's New Source Performance Standards (NSPS) and Maximum Achievable Emissions Control Technology (MACT) standards.

7 percent O_2 for new combustors. Using the EPA's rough equivalency factor (1 ng ITEQ dioxin equals 60 ng of total dioxins), this standard is 13/60 or 0.2 ng/dsm^3 at 7 percent O_2 for ITEQ dioxins (EPA, 1994). New municipal waste combustors that can incinerate more than 250 tons per day must also limit mercury emissions to 80 µg/dsm^3, lead to 200 µg/dsm^3, and cadmium to 20 µg/dsm^3, all concentrations corrected to 7 percent O_2.

The EPA has scheduled its release of MACT standards for hazardous waste combustors for the third quarter of 1999. The April 19, 1996, proposal included emissions limitations for dioxins expressed as the equivalent amount of 2,3,7,8 TCDD using the ITEQ Factors (EPA, 1989, 1996). The EPA proposed an ITEQ dioxin emissions limitation of 0.2 ng/dsm^3 at 7 percent O_2 in the May 2, 1997, Notice of Data Availability (NODA) for this rule (EPA, 1997a). Total hydrocarbon and carbon monoxide limitations were proposed to act as surrogates for the other trace organics listed as hazardous air pollutants in Clean Air Act Section 112. Regulations were also proposed for limiting emissions of mercury, "semivolatile" metals (defined as the sum of cadmium and lead), and "low volatile" metals (defined as the sum of arsenic, beryllium, and chromium). The May 2, 1997, NODA proposed limiting new hazardous waste incinerators to 40 µg/dsm^3 of mercury, 100 µg/dsm^3 of semivolatile metals (lead and cadmium), and 55 µg/dsm^3 of low volatile metals (arsenic, beryllium, and chromium), all at 7 percent O_2.

Emissions limitations for some trace SOPCs are specified in site-specific construction and operating permits. Although environmental impact and HRA guidelines adopted by regulatory authorities are intended to limit emissions to levels that are unlikely to harm human health or the environment, public perception sometimes induces regulatory agencies to adopt even lower emission levels.

MEASURING TRACE EMISSIONS

All combustion systems necessarily emit some trace materials as a direct consequence of the laws of thermodynamics. Under less than ideal mixing conditions, trace organic emissions increase. Too much air in part of the gas stream reduces the temperature and slows the reaction rate; too little air produces reducing conditions that prevent complete oxidation of the fuel. In either case, these effects prevent portions of the gas from being burned to completion. Emitted SOPCs may include:

- some of the POHCs fed to the incinerator (e.g., agent or energetics)
- PICs (i.e., organic compounds formed during the combustion process itself)
- dioxins and other substances that form downstream of the combustion zone
- inherent equilibrium products at very low concentrations
- small quantities of noncombustible materials such as ash, metal oxides, or salts, that penetrate the air pollution control system

Regardless of the source of SOPCs, properly designed, operated, and controlled combustion systems produce very low concentrations of these substances, typically well below the few parts per million level that can be reliably measured by (near real-time) continuous emissions monitors. SOPC concentrations, including concentrations of agent, are frequently below the detection limits of slower but more sensitive manual methods of monitoring. Near real-time monitors that produce an alarm if agent concentrations approach levels of concern have been developed, but even these monitors are not capable of quantifying the actual concentrations.

Incinerator gas samples are drawn through a series of traps in which the targeted materials are selectively removed and concentrated:

- Volatile organics (i.e., compounds with boiling points below 125°C [~255°F]) are sampled using volatile organics sampling trains. Most of these organics are sorbed in activated carbon and Tenex® traps, but some are separated with water vapor in a condensate trap. After sampling, the traps are desorbed, cleaned to separate co-collected interferants, and the organics are analyzed using a combination of a high-resolution gas chromatograph followed by a mass spectrometer. The method and procedures are described in SW-846, Method 0030 (EPA, 1997b).
- Semivolatile organics (i.e., compounds with boiling points between 125 and 300°C [~255 and 570°F]) include dioxins. Semivolatile organics are concentrated by means of a Modified EPA Method 5 particulate sampling train that has a sorbent trap between the filter and liquid-filled impingers

(scrubbers)(40 CFR 60, Appendix A Method 23; EPA, 1997b). In a procedure similar to the one used for volatile organic sampling, the probe, filters, and resin traps are recovered and extracted, and the extract is cleaned and analyzed using high-resolution gas chromatography coupled with high-resolution mass spectrometry to quantify the organics. The procedures are described in SW-846, Method 0010, 40 CFR 60, Appendix A, Method 23 (EPA, 1997b, 1997c) and 40 CFR 263, Appendix X, Method 23A. In Method 23, samples below the detection limit are treated as zeros for calculating total dioxins (the sum of the tetra- through octa-substituted dioxin and furan homologue totals). SW-846, Method 8290 specifies that estimated maximum possible concentration (EMPC) values (i.e., detection responses that do not meet all quality control criteria) be treated as zeros when calculating ITEQ dioxin concentrations (EPA, 1997b).

- Metals are sampled using a Method 5 train that has various liquids in the impingers following the filter. Solids deposited in the probe and caught on the filter are recovered and digested (dissolved) prior to analysis. Liquids in the impingers are also recovered and analyzed. The sampling method is described in 40 CFR 60 Appendix A, Method 29, and 40 CFR 263, Method 29. Metals are analyzed using a number of techniques described in SW-846 (EPA, 1997b). Mercury levels are usually quantified using a cold-vapor or graphite-furnace atomic absorption spectrophotometer. The balance of the metals of interest are generally analyzed using an ion-coupled plasma atomic emission spectrophotometer or mass spectrometer.

EMISSIONS CONCENTRATIONS IN EXHAUST GAS FROM JACADS AND THE TOCDF

Emissions have been tested at JACADS and the TOCDF during the incineration of agents (GB, HD, or VX), surrogate waste, and fossil fuel (oil or natural gas). All four types of incineration systems—liquid incinerator (LIC), deactivation furnace system (DFS), metal parts furnace (MPF), and dunnage incinerator (DUN)—have been tested. Table 2-1 shows the types and numbers of tests conducted through November 1998. Since 1988, all three chemical agents have been tested in the LIC at JACADS, but only agent GB has been tested in the LICs at the TOCDF, which began agent disposal operations in August 1996.

In addition to testing for particulates and hydrogen chloride—the two SOPCs regulated by the Resource Conservation and Recovery Act (RCRA) regulations for hazardous waste incinerators (40 CFR 263)—emissions at JACADS and the TOCDF have also been analyzed for the following substances:

- other halogen-containing (Cl and F) gaseous species
- 22 elements, including all 11 elemental hazardous air pollutants covered in the Clean Air Act
- 204 trace organics, including the three agents being destroyed, 54 organic compounds classified as hazardous air pollutants by the Clean Air Act, and 147 other organic chemicals
- light and total nonvolatile hydrocarbons (i.e., hydrocarbons with boiling points lower than 100°C (212°F) and higher than 300°C (572°F), respectively)

TABLE 2-1 Emissions Tests at the Two Operational Baseline Incineration Facilities, JACADS and the TOCDF

	JACADS			TOCDF		
Type of Waste	LIC	MPF	DUN	LIC	DFS	MPF
GB	2		1	2	4	2
HD	2	2			1	
VX	2				1	
Agent surrogate				1		
Fossil fuel					1	

- indicators of good combustion, such as acceptable levels of carbon monoxide and total hydrocarbons

Much of this testing has been done under trial-burn conditions designed to show emissions under simulated worst-case operating conditions. Organic emissions are maximized in some tests by reducing combustion temperature. Metals are maximized in others by spiking excess metals into the feed, maximizing combustion temperatures to volatilize as much metal as possible, and even operating the air pollution control equipment at below optimal levels.

The concentrations of emittants in the stack gas listed in Appendix B of this report for JACADS and TOCDF incinerators are among the lowest reported for all hazardous waste incinerators in the database of hazardous waste combustion emissions maintained by the EPA's Office of Solid Waste and Emergency Response (EPA, 1997d). The EPA's graphical summaries consistently show that TOCDF results either set the lower bound or are among the lowest in emissions of dioxins, mercury, semivolatile metals (cadmium and lead), and low volatile metals (arsenic, beryllium, and chromium).

Appendices IV and V of the BIF Rule (40 CFR 266) provide ambient concentration limits for risk of 1 in 100,000 (i.e., 10^{-5}) of an adverse health effect caused by breathing these ambient concentrations for 70 years (EPA, 1991). These concentration limits are called reference air concentrations (RACs) for noncarcinogenic materials and risk-specific doses (RsDs) for carcinogenic materials.

The relationship between ambient and stack concentrations is determined by a facility's design, operating profile, and site-specific dispersion characteristics. For example, based on the dispersion modeling results reported in the TOCDF HRA (Utah DSHW, 1996), an MPF stack concentration of 7,850,000 ng/dsm^3 at 7 percent O_2 produces a 100 ng/m^3 concentration at the point of maximum ground level impact. Similar values for the LIC and DFS are 36,000,000 and 22,000,000 ng/dsm^3, respectively. Comparing either the average of the detected concentrations or the lowest detection limit for all test results below detection limits, the acid gases equal 3 percent of their RACs. All measured metals are present at less than 1 percent of their RACs and less than 0.15 percent of their RsDs. The maximum ambient contribution of any trace organic is less than 4 percent of its RAC or RsD, as appropriate, with a median ambient contribution of 0.03 percent. The specific contribution for ITEQ dioxins is 0.025 percent of the RsD.

The RAC and RsD do not fully quantify risk because they are based only on inhalation, and many chemicals can translocate between media and bioaccumulate in the food chain. Quantifying the significance of these emitted concentrations would require an updated, multipathway HRA, which would include various paths of exposure.

The emission rates used in the TOCDF HRA were generally higher than the rates indicated by the data now available. A few SOPCs are emitted at rates higher than the estimated rates in the HRA; however, they contribute less to the health risk than many other SOPCs, including dioxins, that bioaccumulate and translocate and whose actual emission rates are lower than the estimated rates in the HRA. Consequently, it is logical to conclude that the actual TOCDF risk is even lower than the HRA estimate, which was below the level of regulatory concern.

Emissions Sampling and Analysis Methodology

The emissions sampling and analysis at JACADS and the TOCDF were performed following the standard sampling methodologies found in EPA documents SW-846 and 40 CFR 60, Appendix A (EPA, 1997b, 1997c). Because analytic laboratory procedures have been evolving and detection limits have improved since the original JACADS testing, detection limits for early tests were higher than they would be today—sometimes 10 to 1,000 times higher.

Moreover, in a typical analysis of flue gas, emittants are captured in several different portions of the sampling train, which are separately recovered and prepared for analysis. The extracts and digestates can frequently be combined before analysis, however, to reduce the combined detection limit for the replicate test run to the lowest practical level. The reported concentration is the sum of the results of individual analyses. The reported concentration for results below detection limits is the sum of all of the masses, assuming concentrations equal to the detection limit for each separately analyzed component of the sampling train.

This practice differs from standard stack-testing practices where individual nondetects are treated as zeroes except that the largest nondetect is used to characterize test replicates with no detected values. Adding the detection limits together results in an overall detection limit substantially higher than would have been achieved by combining them before analyzing all components of the sampling train. The value inflation of the detection limit for the overall replicate is a function of the number of sampling train components analyzed separately and the detection limit of each. For example, when the separate components of a volatile organic compound sampling train are analyzed, seven pairs of sorbent tubes and two condensate samples—16 individual samples—all produce results. For typical laboratory detection limits (10 ng for each of the 14 sorbent tubes and 80 ng for each condensate trap), the reported detection limit concentration is 300 ng or [(14)(10) + (2)(80)]. If, however, the individual sorbent tubes are desorbed, concentrated, and combined with the condensate before analysis, the detection limit becomes 10 ng, which is one-thirtieth of the value typically reported for volatile organic compounds at JACADS and the TOCDF.

Footnotes in some test reports (see, for example, Tables 5-9 and 5-19 in EG&G, 1997) state that practical quantitation limits (PQLs) were reported when results were below detection limits. When the concentration of a sample with three to five times the estimated detection limit is measured repeatedly, the replicates show some scatter, usually characterized by a bell-shaped, Gaussian distribution. When the variance is constant, the standard deviation of this distribution (S_0) is used to define the detection limit as three times S_0, and the PQL is defined as 10 times S_0 (EPA, 1997b). Based on these definitions, the PQL is 3.3 times the detection limit. For measurements at the detection limit, the analyst can be confident that the analyte is present but cannot confirm the amount. At or above the PQL, however, the analyst can be confident about the quantitation. Consequently, by reporting the PQL for results below detection limits, the maximum amount of SOPCs that might have been in the sample is overstated by at least a factor of 3.

When multiple tests are performed, there is no statistically meaningful chance that all of the actual concentrations are at the detection limit without half of them being detected. Because multiple tests are performed for all SOPCs and because many sets are all below the detection limit, the best scientific estimate of the average concentration is half the detection limit, about 15 percent of the reported PQL (Hass and Sheff, 1990). Clearly, the projections of the harmful effects and benefits of additional technological controls will necessarily be overstated for undetected SOPCs when their detection limits are used in an HRA.

The vast majority of the emissions data for JACADS and the TOCDF show a few emissions with detected values and many below the detection limit. These data sets are "left-censored" (i.e., only large values are quantified, and for the values below the detection limit, the concentration is assumed to be somewhere between zero and the detection limit). The average of the detected values is larger than the true average because a number of unknown, but by definition smaller, values are excluded from the calculations. The committee estimated the amount of positive bias for this type of data analysis by computing the ratio of the average of the detected values to estimates of maximum likelihood of the average (Cohen, 1959). The median positive bias introduced by using the average of the detected values to represent the emitted concentration or rate is 175 percent. The positive bias in JACADS and TOCDF analyses is actually higher because the highest measured value, rather than the statistically derived confidence limit,[4] was used as a bounding value for the average.

Based on the reported data characteristics at JACADS and the TOCDF, the averages are either representative (i.e., all detected values) or very conservative (117 to 660 times the most likely value, depending on whether left-censoring or the chemical analysis methodology controls the result).

Characteristics of Exhaust Gas Emissions

For JACADS and the TOCDF, the vast majority of emittants that were analyzed are below the analytic detection limit. The committee prepared box-plots of the detected concentrations showing mean, central 50 percent, and extreme values. Based on these box-plots, the characteristics of SOPC emissions at both sites for all agents and incinerator types were the same, even though JACADS uses jet fuel and the TOCDF uses natural gas as supplemental fuel. The oxygen content of the flue gas was lower and the moisture and temperature of the exhaust gas higher at the TOCDF,

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[4] The highest measured value is the nonparametric estimate of the likely mean if there are nine samples. For the 35 sample data set on dioxins now available, the upper confidence interval is the 24th highest value. Instead of a 95 percent confidence interval, the highest dioxin measurement is at the 99.99999994 percent confidence level based on the nonparametric estimating equations in Hahn and Meeker (1991).

but all other detected concentrations were similar. However, there were too few detected concentrations to verify this observation statistically. Despite emissions tests that exceed the minimum sample volume requirements given in the federal regulations (40 CFR 60, Appendix A and 40 CFR 266, Appendices IX through XIV), the data do not show detectable concentrations. Because the true concentrations are not detectable, the results are a qualitative indication of low emitted concentrations.

Upper bounds for the SOPC emission rates can be developed by combining the available information from all of the incinerators at JACADS and the TOCDF. That is, although the units and agent feeds are different, there is no reason to believe from the available information that emitted concentrations of individual chemical compounds are different. Or, stated another way, regardless of the agent being fed (GB, VX, or HD) or the incinerator being used (LIC, MPF, or DFS), the emitted concentrations of nonagent chemical compounds can reasonably be assumed to be similar. This result is in large measure attributable to the high DRE achieved and the effectiveness of the existing air pollution control systems.

Appendix B lists the tested emittants; the percentage of tests in which each emittant was found; the minimum, mean, and maximum of the detected concentrations; and the detection limit for undetected concentrations. Concentrations of gaseous emittants are expressed in conventional regulatory units, as well as parts per billion (dry volume) (ppb_{dv}) to facilitate engineering calculations. Carbon absorption systems remove trace organics in proportion to their partial pressure (see Chapter 3), which can be easily determined by multiplying ppb_{dv} by local barometric pressure. For engineering purposes, ppb_{dv} is more useful, but the standardized regulatory (mass per unit volume) concentrations are necessary for comparing emitted concentrations reported at other sources.

The emission rates actually used for risk assessments of SOPCs are usually deliberately high to yield a conservative assessment. Consequently, the concentrations that correspond to these emission rates are higher than the concentration data summarized in Appendix B.[5]

As discussed in Chapters 3 and 4 of this report, activated carbon adsorbs different amounts of individual organic vapors based on their chemical structures, their vapor pressures, and the operating temperature and pressure of the sorbent bed. The amount of any organic chemical in the bed at any time is determined by the amount introduced and the fraction adsorbed minus the amount that has degraded while adsorbed. Because the amount introduced is determined by the inlet concentration and flow rate, bounding concentration estimates are necessary to determine the bed life, benefits, and risks of activated carbon. These estimates can be derived from the existing emissions test data, including the observed below detection limit concentrations from JACADS and the TOCDF.

EMISSION RATES

The JACADS and TOCDF incineration systems have been extensively tested, and the results have consistently shown that emissions of materials regulated under Sections 111 (as criteria pollutants) and 112 (as hazardous air pollutants) of the Clean Air Act and noncriteria (trace) emittants subject to regulation are either the lowest or among the lowest in the EPA's Hazardous Waste Combustor Emissions Database (EPA, 1997a). Although emissions test results can only provide an estimate of the true mean and standard deviation for any emittant, the statistical characteristics of distributions can be used to establish bounding values likely to contain the true population parameter. For example:

- Long-term, multiyear exposures are characterized by the average emission rate. The 95 percent statistical confidence level, the upper confidence limit (*UCL*), for the mean is the bounding value:

$$UCL = \overline{X} + t_{N-1,\frac{\alpha}{2}} \frac{S}{\sqrt{N}}$$

  where $\overline{X}$ is the arithmetic average, $t_{N-1,\frac{\alpha}{2}}$ is the *t*-statistic, N is the number of replicates used to estimate the average, α is the statistical significance level (e.g., α is 0.05 for the 95 percent statistical confidence level), and S is the data standard deviation (Hahn, 1970).
- Short-duration events caused by normal fluctuations in emissions are characterized by the upper tolerance limit (*UTL*) designed to cover 99 percent of future events. The *UTL* is:

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[5] The TOCDF HRA and QRA used the highest concentrations measured at JACADS through mid-1994 (Utah DSHW, 1996; U.S. Army, 1996a). Because these values are above actual experience, they also have been used in subsequent evaluations to minimize confusion.

$$UTL = \overline{X} + S \bullet \phi^{-1}\left(\frac{1+P}{2}\right)\sqrt{\frac{N-1}{\chi^{2}_{N-1,1-\alpha}}}\left(1+\frac{1}{2N}\right)\sqrt{\frac{T}{D}}$$

where $\phi^{-1}(\ )$ is the inverse normal distribution value, P is the fraction included, and $\chi^2_{N-1,1-\alpha}$ is the chi squared statistic (Hahn, 1970). Fifteen-minute events have different maximum likely concentrations than 3, 8, or 24-hour events because the sampling distribution of the mean is different for each averaging time (Taylor, 1990). To make this correction, the square root of T/D has been added where D is the event duration, and T is the sampling time associated with the replicates used to estimate the average and standard deviation.

- Short-duration events caused by equipment failures and random high concentrations caused by, for example, combustion instability are very unlikely to occur simultaneously. Therefore, short-duration events are characterized by the average inlet concentration to the pollution control train. This average inlet concentration should be combined with the reduced control efficiency associated with the failure mode.
- Compliance test limits are described by the upper prediction limit (UPL)[6] for the number of times a facility will be tested. The UPL is:

$$UPL = \overline{X} + S \bullet t_{N-1,1-\frac{\alpha}{2k}}\sqrt{\frac{1}{N}+\frac{1}{q}}$$

where k is the number of future tests to be performed, and q is the number of replicates averaged to determine a test result (Hahn, 1970). Prediction limits are bounds that are unlikely to be exceeded by the next specified number of tests. The number of tests that should be included in the prediction limit calculation is a risk management decision. Although the number of tests has no effect on average emission rates, it produces higher and higher emissions limitations as the frequency of finding a compliant operation in violation of the standards is reduced. For a facility like the TOCDF, each incinerator may be tested annually over its seven and one-half year operating life. If the limit is for one unit, q is 7, but if no exceedance at any of the four operating TOCDF incinerators is desired, q is 28. When the number of baseline incinerator facilities in the United States is considered, q increases accordingly.

For a probabilistic HRA, Bayesian statistics can be used as an alternative treatment of the nondetects. This would eliminate the need to make assumptions about the nature of the distribution describing the likely concentrations of undetected species. Bayesian statistics could be used in refined multipathway HRAs because they provide information on the distribution of outcomes, rather than a single point estimate intended to be higher than the real risk.

Table 2-2 shows the relationship between the arithmetic average and the bounds discussed above for different coefficients of variance (i.e., the standard deviation to average ratio). The data from JACADS and the TOCDF indicate that the coefficients of variance for emittants of interest range between 0.25 and 2 for most of the measured emissions. When the coefficient of variance is larger than 1, the distribution is probably not normal, and advanced statistical techniques (e.g., normalizing transformations) are required to provide meaningful estimates. Detailing these techniques is beyond the scope of this report.

Maximum likelihood estimates of the arithmetic average and standard deviation are used when some measurements are below detection limits (Cohen, 1959). When all the measurements are nondetects, the best point estimate for the average is half the detection limit. However, there is no known estimate for the standard deviation, and there is no assurance that the detection limit is not several orders of magnitude above the true emittant concentration. Consequently, it is impossible to establish meaningful emissions limits statistically. Statistical practice is to use half the detection limit as the annual average and the detection limit for all other averaging times.[7] If the coefficient of variance is available for another analyte believed to behave like the undetected emittant, then half the detection limit for that analyte can be scaled using an appropriate value from Table 2-2 or calculated using the preceding equations.

For chemical agents (which have never been detected in any emissions test at a baseline system

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[6] The UPL is a bound below which an achievable emissions limitation cannot reside. The emissions limitation to avoid false exceedances when a facility is operating exactly as it was when the limit was set may be considerably higher.

[7] EPA Region III has published similar guidelines for the treatment of nondetects in stack tests for risk assessments used to establish permit limits.

TABLE 2-2 Effect of Data Characteristics on Emissions Characteristics for Different Averaging Times[a]

	Emissions Multiplier—Average to Likely Upper Bound					
Coefficient of Variance	25%	50%	75%	100%	150%	200%
6 runs in database						
15 minute (UTL-0.25)	5.12	9.24	13.37	17.49	25.73	33.98
1 hour (UTL-1)	3.06	5.12	7.18	9.24	13.37	17.49
3 hour (UTL-3)	2.19	3.38	4.57	5.76	8.14	10.52
8 hour (UTL-8)	1.73	2.46	3.19	3.92	5.37	6.83
24 hour (UTL-24)	1.42	1.84	2.26	2.68	3.52	4.37
annual (UCL)	1.32	1.65	1.97	2.29	2.94	3.58
3-run average (UPL-3)	1.53	2.05	2.58	3.11	4.16	5.22
18 runs in database						
15 minute (UTL-0.25)	3.62	6.24	8.86	11.48	16.73	21.97
1 hour (UTL-1)	2.31	3.62	4.93	6.24	8.86	11.48
3 hour (UTL-3)	1.76	2.51	3.27	4.03	5.54	7.05
8 hour (UTL-8)	1.46	1.93	2.39	2.85	3.78	4.71
24 hour (UTL-24)	1.27	1.54	1.80	2.07	2.61	3.14
annual (UCL)	1.14	1.29	1.43	1.58	1.87	2.16
3-run average (UPL-3)	1.30	1.61	1.91	2.22	2.82	3.43
200 runs in database						
15 minute (UTL-0.25)	2.99	4.98	6.97	8.96	12.95	16.93
1 hour (UTL-1)	2.00	2.99	3.99	4.98	6.97	8.96
3 hour (UTL-3)	1.57	2.15	2.72	3.30	4.45	5.60
8 hour (UTL-8)	1.35	1.70	2.06	2.41	3.11	3.82
24 hour (UTL-24)	1.20	1.41	1.61	1.81	2.22	2.63
annual (UCL)	1.04	1.08	1.12	1.16	1.24	1.32
3-run average (UPL-3)	1.25	1.50	1.74	1.99	2.49	2.98

[a] The upper bound will exceed the average by the factors shown.

incinerator), the average and short-term peak concentrations derived from the detection limit in ng/dsm^3 at 7 percent O_2 are:

• GB	1.8 and 3.6
• HD	115 and 230
• VX[8]	1.8 and 3.6

For dioxins and furans, expressed as ITEQs, the average loading to a carbon bed filter is 0.01 ng/dsm^3 at 7 percent O_2. The 15-minute short-term variability induced value is 0.41 ng/dsm^3 at 7 percent O_2.

SUMMARY

Trial burns have been performed at JACADS and the TOCDF to test the incinerators at each site, as well as the combustion of the various agents(although not all agents were tested with all incinerators. The reported emission concentrations are among the lowest for all hazardous waste incinerators in the EPA's Hazardous Waste Combustor Emissions Database.

Data for most of the SOPCs consisted of a few measurements at a low concentration level, with many more below the detection level. Analyses of human health risks (see Chapter 5) were based on the highest values recorded during trial burns at JACADS for each measured SOPC. A statistical evaluation of the data,

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[8] Not measured but assumed to be equal to GB.

including allowances for variances in measurement, indicates that this approach is extremely conservative. Based on the most recently developed analytical techniques, detection limits and nondetectable concentrations are now lower than when the JACADS trials were run. For example, mustard (HD) was not observed in the exhaust gases of any trial burn. Yet the concentration used in the HRA analyses for Tooele, Anniston, and Umatilla, based on the JACADS test data, was 8,700 ng/dsm^3. This can be compared to the average value derived from the trial burn detection limit of 115 ng/dsm^3.

3

Controlling Trace Organics with Passive Activated Carbon Filters

Carbon filters have been used on municipal waste combustors (MWCs) and hazardous waste incinerators in Europe since the early 1990s (see Appendix C). The NRC first recommended that the Army look into this technology in 1991, and in 1992 the Army sent a study team to Europe. Carbon filters in combination with other gas-scrubbing systems now represent a highly efficient emission-control technology. The following passage appeared in a 1994 technical paper on an MWC in Rotterdam, Holland:

> This type of retrofit designed as a five-stage gas cleaning system has become state-of-the-art technology in central Europe. Especially in Holland, Germany, Austria, and Switzerland, virtually all new MWC plants as well as most existing facilities are being equipped with these systems.
>
> The extremely high removal efficiencies obtained by these advanced flue gas cleaning systems, especially attributable to the activated char adsorbers, yield an increase in political and public acceptance of MWCs in central Europe (Hartenstein, 1994).

Activated carbon is commonly used for separating organic chemicals in process plants and recovering solvents in dry cleaning and printing press operations. Controlling emissions of flue gas with passive beds of activated carbon is a more recent application with about a decade of experience. Carbon bed filters were first used in the late 1980s in Germany as NO_x-control catalysts for large stationary sources like coal-fired steam-electric plants. An activated coke filter was commissioned in the Herten Hazardous Waste Incineration Plant (Germany) in August 1991 to "polish" reheated flue gas from the scrubber towers. Since then, the design problems listed below have been addressed:

- plugging of the bed by fine particulates that penetrated the particulate-control device preceding the filter
- rapid saturation of the leading edge of the bed with acid gases
- development of practical, zero-leakage isolation dampers
- movement of the bed and generation of fine particulates within the bed

New standards for emissions of dioxins and mercury for incinerators in several European countries in 1989 and 1990 led to the widespread use of activated carbon filters as a final stage for polishing flue gas (Hartenstein, 1993). Standards for chlorinated dioxins/furans were set at 0.1 ng ITEQ/dnm^3 at 11 percent O_2, but the reported emission levels have been substantially below this level (see Table 3-1).[1] Table 3-2 shows some reported "before" and "after" data on chlorinated dioxin/furan cleanup with a carbon filter. The gas temperatures for these operations were in the range of 100 to 150°C (212 to 302°F). Gas-flow rates and bed thicknesses were not disclosed but are believed to be close to the design conditions for the Anniston and Umatilla PFS (pollution abatement system carbon filter system) discussed in Chapter 4. These and other data demonstrate

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[1] ITEQ (international toxic equivalency) dioxin is the amount of 2,3,7,8 TCDD (2,3,7,8-tetrachlorodibenzo-p-dioxin) with toxicity equivalent to the complex mixture of 210 dioxin and furan isomers with 4 to 8 chlorine atoms found in flue gases. This equivalency is based on the International Toxic Equivalence Factor scheme adopted by the EPA and most countries to simplify the reporting of dioxin emissions.

TABLE 3-1 Emission Levels of Chlorinated Dioxins for Some European Incinerators

Incinerator Type	Dioxins/Furans (ng ITEQ/dnm^3 @ 11% O_2)
Medical waste incinerator (Germany)	0.003
Medical waste incinerator (Netherlands)	0.03
Hazardous waste incinerator (Netherlands)	0.03

Source: Adapted from Brueggendick and Pohl, 1993.

more than 95 percent removal of dioxins/furans from already low levels in the gas stream.

Early testing of these facilities showed that emissions of particulates, acid gases (HCl and SO_2), mercury, and dioxins and furans were reduced to levels near or below the detection limits for available sampling and analysis methodologies. Typical concentrations of stack gas emissions included: particulates around 1 mg/dsm^3 at 7 percent O_2; HCl and SO_2 below 3 ppm$_{dv}$ at 7 percent O_2; ITEQ dioxins and furans below 0.04 ng/dsm^3 at 7 percent O_2; and mercury below 0.003 µg/dsm^3 at 7 percent O_2 (Brueggendick and Pohl, 1993). Tests of installations in Germany and Japan have had similar results.

The available data from field tests indicate that carbon filter systems control adsorbable chemical species and act as depth (gravel bed) filters to separate particulates. (The carbon can also become a source of particulates as it erodes with use.) The proposed Army design incorporates a high-efficiency particulate air (HEPA) filter at the outlet of the filter to control dust. Unfortunately, the available information does not indicate actual performance because the outlet concentrations are frequently, but not always, below detection limits. Industrial experience with activated-carbon adsorption systems has shown that the amount of each SOPC separated is a complex function of the adsorption characteristics of individual chemical species, species concentrations, and the depth, temperature, pressure, and face velocity of the adsorption bed.

TABLE 3-2 "Before" and "After" Data on Chlorinated Dioxin/Furan Cleanup with a Carbon Filter

	Raw Gas (ng/dnm^3 @ 11% O_2)		Clean Gas (ng/dnm^3 @ 11% O_2)	
Dioxin Species	In	Out	In	Out
Tetra CDF[a] (total)	44	0.72	4.2	0.17
Penta CDF (total)	32	0.55	3.7	0.18
Hexa CDF (total)	13	0.28	2.3	0.16
Hepta CDF (total)	2.9	0.06	1.4	0.12
Octa CDF	0.9	0.02	0.6	0.1

[a] CDF = chlorinated dioxins/furans

Source: Schüller, 1994.

The Stockpile Committee's major concern in 1991, when the recommendation that the Army study carbon filters was made, was the possibility of "puffs." Although the existing PAS effectively cleans the flue gas during "normal" operations, occasional pressure pulses in furnaces, which are common in industry, could result in increases in emissions. These puffs could potentially be controlled by a carbon-bed filter.

Puffs were most likely to occur in the DFS. Whereas the other furnaces showed only minor variations in recorded pressures and possible puffs only during transients at start-up or shutdown, puffs in the DFS could be caused by small explosions from the processing of explosives and propellants. The Army has reported that puffs have been relatively infrequent, (e.g., one per week), and in any case have not been of great concern. No agent has ever been measured in the stack as a consequence, and any release from the furnace into the room air is passed with the air through carbon beds before it is released to the atmosphere.

Although the major adsorbable species of the flue gas from chemical agent incinerators have been characterized, the performance of carbon filters on this specific flue gas with its particular SOPCs has not been experimentally determined. Consequently, engineering calculations have been used to predict the performance of carbon bed filter systems applied to this novel gas stream.

FUNDAMENTALS OF ADSORPTION

The selective separation of individual components of a gas mixture by adsorption on a solid is widely practiced and has been well documented (e.g., Ruthven, 1984; Tien, 1995). Many solids can selectively separate individual materials. One common requirement for the adsorbent is that it have a large surface area; up to several hundred square meters per gram of solid is common. Pore size is also an important characteristic of the materials to be adsorbed (chlorinated dioxins and furans in this case). Because activated carbon has already been used for capturing SOPCs and other organic gases in flue-gas streams, the Army selected it as the adsorbent of choice for the scrubbed flue gas from the incineration of chemical agents.

The materials of most interest, hexavalent chromium, chlorinated dioxins and furans, mustard agent, and arsenic (because most of the health risk from the flue gas is associated with them), are at levels below the threshold of regulatory concern (U.S. Army, 1998a). Most of the chromium (solid) and arsenic will be removed by the HEPA filter that precedes the carbon filter in the proposed design. Carbon beds can also act as filters for finely divided suspended solids, therefore, as a backup for the HEPA filter.

The chlorinated dioxins and furans measured during trial burns were all at very low concentration levels, and the mustard, if present at all, was below the detection level. The Army and its contractor attempted to characterize carbon-filter adsorption, with special emphasis on these materials experimentally and theoretically (Mitretek Systems, 1997).[2]

Carbon beds on incinerators are usually designed to operate for extended periods of time before they become saturated (in the case of the PFS, for more than a year). Ultimately, a portion of the bed will become saturated, and SOPCs will start to appear in the atmospheric exhaust gas, indicating that it is time to change the carbon in the bed.

Most of the process analysis for the carbon bed presented in this chapter is based on "normal" operation of the baseline system incinerators with SOPCs present at very low levels. However, some higher concentrations (e.g., 10-fold) could occur during short-term system upsets. Because most SOPCs cannot be continuously monitored, a sudden increase could go undetected. In these circumstances, a carbon bed would have a comparative advantage over other flue gas filtration systems because it could adsorb higher-than-normal concentrations of SOPCs for extended periods of time (e.g., days).

Three properties of the flue gas/carbon adsorbent combination are considered in this chapter:

- the maximum amount of material that can be retained by the carbon adsorbent, which is important in determining the on-stream time for a given bed
- the rate of transfer of material from gas to solid phase (rate of adsorption), which dictates how close to the maximum the adsorbent capacity of the carbon can be used
- the chemical stability of the SOPCs adsorbed on the carbon, which could affect the amount of SOPCs adsorbed on the bed at any given time

Although other adsorbent properties, such as catalytic activity, hygroscopicity, and resistance to acidic attack, may also be significant, carbon was chosen because it has been used extensively in many incinerators in Europe, as well as for the adsorption and control of chemical agents in facility ventilation systems.

The performance objective is to reduce the gas-phase concentrations of SOPCs—such as dioxins and furans—by a large factor (e.g., a 90 percent or greater reduction). The performance lifetime objective of the carbon bed is one year or more. The Army has taken a twofold approach to determining whether these objectives can be met:

- a theoretical prediction (based on experimental work with other materials) of the thermodynamic equilibrium for adsorption of dioxins and furans on carbon at the very low gas-phase concentrations of interest, as well as the adsorption characteristics of more polar materials (water in particular)
- a kinetic analysis of the adsorption from the flowing gas, based on relations for mass-transfer rate and axial flow dispersion found in the literature

(Both theoretical treatments are outlined in some detail in Appendix D. For a full exposition, see Mitretek Systems, 1997.)

Although the predictions must be considered approximate, they indicate very long performance lifetimes for the suggested design—a good indication that the one-year lifetime objective will be met. The committee attempted to confirm this conclusion by comparing the predictions with results reported for

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[2] Unburned agents were not included in the Mitretek analysis, but the flue gas of the baseline system is continuously monitored for agent. No unburned agent has been detected in the JACADS or TOCDF trial-burn data. For the purposes of this report, however, they are presumed to be present in the flue gas at concentrations equal to their detection limits. VX and HD are both liquids with very low volatility and, if present, would probably be captured effectively by a carbon bed. GB is more volatile, and it is difficult to predict the length of time it would be adsorbed on the carbon.

commercial incinerators with carbon filters. Commercial data suggest that "capacity" (the amount of dioxin adsorbed at equilibrium) should not limit the "breakthrough" time. That is, the carbon in the PFS has the capacity to adsorb dioxins from the flue gas for many years before becoming saturated. The committee did not attempt to validate the kinetic analysis through an independent analysis.

MAXIMUM ADSORPTION FROM THE GAS PHASE

For any separable component in the gas phase, there is a maximum amount that can be adsorbed on the solid. The relation between the adsorbed component and its concentration in the gas phase is called the adsorption isotherm. This equilibrium relation varies with temperature and with the other adsorbed components (see Appendices D and E for details on adsorption phenomena).

Operational Modes

Two methods are commonly used for affecting contact between the effluent gas and the solid carbon adsorbent: (1) continuous relatively long-term flow through a packed bed of adsorbent, and (2) injection of a small amount of finely divided solid adsorbent into the flowing gas stream, with separation of the two after a few seconds. These two approaches can result in very different amounts of adsorption:

- In packed-bed filters, most of the solid comes to equilibrium with the gas at the *inlet* concentration of the material being adsorbed (i.e., at its maximum gas concentration). This equilibrium can be represented by an isotherm of a general shape referred to as "favorable." Adsorption of many materials on carbon yields equilibrium relations with this general shape.
- In dilute-phase (flowing) contact systems (e.g., carbon injection), the solid approaches equilibrium with the gas at the *outlet* concentration of the material being adsorbed (i.e., at its minimum gas concentration).

Packed-bed filters are capable of adsorbing more material from the gas phase than dilute-phase contact systems. Depending on the shape of the adsorption isotherm and other operating factors, the difference could be as much as 100-fold. A drawback to packed-bed filters is that they increase the system pressure drop, which results in higher power requirements. In practice, a combination of the two approaches is often used. MWCs (municipal waste combustors) typically disperse powdered activated carbon into the flue gas and separate it with a fabric filter. Thus, some separation occurs in the dilute phase, and more is adsorbed in the thin packed bed formed by the filter cake. The packed-bed design (i.e., a fixed bed of carbon) was chosen by the Army because, in addition to its higher adsorption capacity, it has two other advantages: (1) a fixed bed minimizes the amount of spent carbon adsorbent requiring disposal, and (2) a fixed bed is always present to capture accidental releases.

Application to the Incineration of Chemical Agents and Munitions

There are two basic problems in determining the adsorption isotherms for a fixed carbon bed (the PFS) with the Army's baseline incineration system:

- The SOPCs in the flue gas—possibly unburned agent and chlorinated dioxins/furans—are present at extremely low concentrations, frequently lower than the detection levels of today's best sampling and analytic methods. Because equilibrium adsorption isotherms have not been measured to such low levels, they must be predicted from experimental measurements at much higher concentrations or from related industrial experience at higher concentrations.
- Many materials in the flue gas (SOPCs, other organics, and some vapor-phase metals) compete for adsorption sites on the activated carbon. Predictions for these interactions are not well established in theory.

Adsorption Equilibrium at Low Concentrations

Several methods have been described in the literature for determining the performance of adsorption systems. Mitretek, an Army contractor, has chosen an approach developed by Dubinin and coworkers (the Dubinin-Radushkevich [D-R] relation), a summary of which appears in Ruthven (1984) (Mitretek Systems, 1997). This approach has a reasonable theoretical justification for nonpolar materials, for which the energy of adsorption is due primarily to Van der Waals forces, which are independent of temperature. In addition, this theory has been found to be useful for determining adsorption equilibria over activated carbon. A brief summary of the theory and its value for generalizing from a very few measurements is given in Appendix D.

The D-R relation has been used frequently (see for example Prakash et al., 1994) and is a useful engineering approach and a good approximation for estimating adsorption data for many materials. However, its applicability to the baseline system (equipped with the PFS) raises a serious problem :

> The expression for the characteristic curve does not reduce automatically to Henry's Law in the low concentration limit. This is a theoretical requirement for any thermodynamically consistent physical isotherm equation, although the practical consequences of this deficiency may not be important if the equation is applied only in the high concentration range (Ruthven, 1984).

Unfortunately, the concentrations of most interest in the PFS application (chlorinated dioxin/furans and chemical agents) are in a low range where the D-R relation is not accurate (it is known to overpredict the amounts that can be adsorbed, but the amount of overprediction is uncertain). This problem is discussed semiquantitatively in Appendix D.

An alternative approach, also based on the D-R relation (and described in Appendix D), underpredicts the amount that can be adsorbed. The two approaches yield a range that includes the actual adsorbed amount, although the range can be quite large. The problem at hand is limited to a few SOPCs present at very low concentrations. Most of the SOPCs reported are at concentrations that are well beyond the range of Henry's Law.

An alternative to theoretical modeling based on a small number of measurements is to use actual plant data for substances at low concentrations. Activated carbon has been used in industry to control adsorbable SOPCs in flue gas from various sources, including incinerators. If sufficient data are available, the plant data can be used to estimate dioxin loading at low gas-phase concentration. This approach has been used by the committee as a check on the theoretical analysis.

Adsorption Data

The committee examined two types of adsorption data: (1) laboratory data on individual compounds that were then used by Mitretek as a basis for estimating the adsorption of materials of direct concern, and (2) full-scale plant data on chlorinated dioxins. Mitretek measured adsorption equilibrium data for about a dozen compounds representing typical SOPCs (from a list of trace organics identified in the atmospheric exhaust gas during the JACADS trial burns). These compounds varied in type and polarity: hydrocarbons (i.e., hexane and toluene); alcohols (i.e., 1-propanol and 2-hexanol); refrigerants (mainly chlorofluorocarbons)[3] (i.e., R123, R113, R11, R318, R22, R143a); methylene chloride; acetone (a ketone); and dimethyl methylphosphonate (DMMP, a simulant for GB). The D-R relation can be checked using Mitretek's data,. Either all of the data can be matched with one "characteristic curve," or all of the adsorption data can be predicted by the measurement of the equilibrium for one compound.

Mitretek also used their data with some success to predict multicomponent adsorption. The analysis focused on water and carbon dioxide, which are present in flue gas in much higher concentrations than the other SOPCs. Mitretek determined that water had little effect on adsorption if the relative humidity of the gas was 60 percent or lower. The Mitretek analysis used ideal solution theory to predict multicomponent adsorption, including water—which obviously will not form an ideal solution with the other components. Based on experimental data, Mitretek determined that the effect of water was consistently overpredicted. Mitretek did not modify the theory but pointed out that the allowance for water led to a "conservative" result (i.e., the actual adsorption of SOPCs would be greater than the predicted adsorption). Mitretek concluded that carbon dioxide is adsorbed so weakly (despite its relatively high concentration) that it should not affect the adsorption of most SOPCs.

Plant data from the municipal waste incinerator in Camden County, New Jersey, and a small experimental medical waste incinerator were examined by the committee (NORIT Americas Inc., 1996). In these plants, powdered activated carbon was injected into the gas stream and then separated using either an electrostatic precipitator (municipal waste incinerator) or fabric filter (medical waste incinerator) prior to the cleaned gas being exhausted through the stack. Initial

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[3] The chemical names of the chlorofluorocarbons listed above by their common refrigerant designations are: R123, dichlorotrifluoroethane; R113, trichlorotrifluoroethane; R11, trichlorofluoromethane; R318, octafluorocyclobutane; R22, chlorodifluoromethane; R143a, trifluoroethane.

and final gas concentrations for the two incinerators were measured, as well as flow rates for the gas and solid-carbon adsorbent. The committee then calculated the amounts adsorbed on the carbon by material balance. The concentration of chlorinated dioxin adsorbed on the solid and the final gas concentrations for four different runs (two in each incinerator) are given in Table 3-3. The numbers represent measured values that combine all dioxin constituents.

The NORIT data show how much of the key materials can be adsorbed at a very low gas-phase concentration. (No laboratory data at this low concentration were available.) These data may represent a reasonable approach to equilibrium for the following reasons:

- The powdered carbon used for gas injection is very fine, typically passing through 325 mesh. Calculations by the committee indicated a rapid approach to equilibrium for such fine material (e.g., 90 percent in a few seconds).
- In one test, a fabric filter was used to separate the gas and solid. The solid cake built up on the filter provides a contact time of about an hour, more than enough to reach equilibrium. In the other test, electrostatic separation was used, but the level of adsorption was about the same.

The data in Table 3-3 were collected at a much higher temperature (270°F) than the Army's PFS (160°F). The lower temperature will have a substantial effect on the adsorption equilibrium. Hence, the baseline system PFS should be more efficient in reducing dioxin emissions than the carbon adsorption systems for the two incinerators in Table 3-3.

The concentration of dioxins from trial burn data (see Appendix B) is lower than the concentrations in Table 3-3. The possible loadings on the solid adsorbent have been adjusted downward by the committee by assuming they are proportional to the gas concentration. This procedure, which treats the data as though Henry's Law applies, is conservative (i.e., the prediction of a loading on the solid may be low).

Adsorption of Multicomponents

A major problem with using a theory-based approach for the PFS is the large number of materials that may be competing for adsorption sites. The "key" components in this case are the chlorinated dioxins and furans, which are present at relatively low concentrations (ng/dsm^3). Many other SOPCs are present in much larger concentrations (1,000-fold to 10,000-fold higher concentration). Industrial experience has shown that chlorinated dioxins and furans are tightly adsorbed with breakthrough times in deep beds (e.g., 6 feet) of many years. Most SOPCs, however, are much less strongly adsorbed, and breakthrough times of days or weeks should be anticipated. Determining the adsorption equilibrium of many different constituents is a daunting task because each new species affects the adsorption of the others. Attempts to predict multicomponent equilibria from single component isotherms have been reported in the literature. This strategy has been moderately successful for systems of materials with generally similar properties (e.g., all nonpolar materials of similar vapor pressures). This strategy was also used by Mitretek (Mitretek Systems, 1997).

Several theoretical approaches for predicting multicomponent equilibria have been suggested. Perhaps the simplest is the Ideal Adsorbed Solution Theory (Ruthven, 1984). As the name implies, the adsorbed materials are assumed to form an "ideal solution" in the solid adsorbent; each component then exerts a vapor pressure proportional to its mole fraction and its single

TABLE 3-3 Chlorinated Dioxins Adsorbed on Powdered Activated Carbon

Concentration of Dioxin on Solids (grams/kg carbon)	Concentration of Dioxin in Gas Phase (ng/dsm^3) Inlet	Outlet	Incinerator Type	Adsorption Temperature
0.34×10^{-3}	128	4.66	municipal waste	270°F (132°C)
1.2×10^{-3}	411	16	municipal waste	349°F (176°C)
3.5×10^{-3}	416	6	medical waste	unknown
0.32×10^{-3}	94	2	medical waste	unknown

Source: Derived from NORIT Americas Inc., 1996.

adsorption isotherm pressure. The Mitretek report uses a modification of this theory developed by Grant and Manes (1987) for computational convenience. The approach appears to be reasonable, although the predictions for equilibrium adsorption are necessarily approximate. This is particularly true for the effect of water; the Ideal Adsorbed Solution Theory consistently predicts that more material will be displaced by water than has actually been observed (see Appendix D).

Carbon Bed Breakthrough Times

Calculated equilibrium values are used to determine breakthrough times. Fortunately, approximate equilibrium values can be used for the chlorinated dioxins and furans, whose calculated breakthrough times turn out to be quite long. Consequently, even an error of a few-fold in the equilibrium saturation value can be tolerated in calculating an estimate of adsorbent lifetime.

Breakthrough times for 14 different materials calculated by Mitretek (as described above) for carbon beds using coconut-shell carbon are shown in Table 3-4. All 14 materials were detected in agent-incinerator flue gas during trial burns at JACADS, and all are considered carcinogenic. The calculations show a wide range of breakthrough times, long times for the chlorinated dioxins and furans, and much shorter times for most of the other (more volatile) materials.

Two breakthrough times for each material are shown in Table 3-4: (1) the breakthrough time if each material were present alone, based on the corresponding single adsorption isotherm; and (2) the breakthrough time based on modeling of a multicomponent mixture. The multicomponent mixture included 41 compounds detected during JACADS trial burns (i.e., the 14 compounds shown plus other trace compounds in the gas). The competition for space on the solid adsorbent has a surprisingly large effect on the breakthrough times for all materials.

For this report, the committee compared the plant data shown in Table 3-3 with the calculations in Table 3-4 as a check on whether the calculations were reasonable. The comparison was based on the following approximation and assumption:

- The dioxin/furan loadings were estimated directly from the data in Table 3-3. No attempt was made to correct them for temperature, although a much

TABLE 3-4 Estimated Carbon Filter Breakthrough Times for Substances of Potential Concern in Stack Gases from the Chemical Agent Disposal Facility Liquid Incinerator[a]

Substance	Estimated Initial Concentration ng/m^3	Estimated Breakthrough Time as Single Component[b]	Estimated Time for Multicomponent PFS Flue Gas[c]
Tetra CDD	0.13	1.5×10^7 years	> 5 years
Octa CDD	0.24	1.7×10^7 years	> 5 years
Tetra CDF	0.21	6.8×10^7 years	> 5 years
Penta CDF	0.088	2.6×10^7 years	> 5 years
Hexa CDF	0.11	2.2×10^7 years	> 5 years
Hepta CDF	0.16	1.8×10^7 years	> 5 years
Bis (2-Ethylhexyl) phthalate	19,000	650 years	> 5 years
Benzene	90,000	2.4 years	14.2 hours
Carbon tetrachloride	35,000	4.1 years	7.1 minutes
Chloroform	22,000	2.5 years	5.7 hours
Chloromethane	780,000	1.8 years	7.4 minutes
cis-1,3-dichloropropene	250,000	1.7 years	1.0 days
Methylene chloride	5,900,000	38 days	2.1 hours
Vinyl chloride	4,500	1.7 days	9.5 minutes

[a] Bed dimension = 214 square feet, 1 foot deep, 3,030 kg of carbon
[b] Calculated based on D-R equation assuming complete saturation of filter at 135°F
[c] Based on multicomponent computer model, 135°F, 67 percent relative humidity

Source: Adapted from Mitretek Systems, 1997.

larger loading on the carbon can be expected at a lower operating temperature.

- A sharp concentration "front" was assumed, so that most of the solid would be used to adsorb material before breakthrough occurred. This is a reasonable assumption (although not certain) based on the very long breakthrough times shown in Table 3-4, which in turn were based on detailed kinetic analyses. Assuming a sharp concentration front is also reasonable based on the long breakthrough times of commercial units.

Based on the flow rates and dioxin concentrations at JACADS, the breakthrough time for the PFS was estimated to be approximately two years. This is a very conservative number because it is based on observed plant operation at a much higher temperature (270°F) than is planned for the PFS (160°F). Because more can certainly be adsorbed at the lower temperature, the predicted breakthrough time at 160°F would be longer.[4] The data in Table 3-3 represent multicomponent adsorption, so the estimated breakthrough time for chlorinated dioxins and furans should be compared with the right-hand column of Table 3-4, "Estimated Breakthrough Time for Multicomponent PFS Flue Gas." Because the estimates are in roughly the same range, they lend some confidence to the calculated results in Table 3-4. Based on these analyses, the committee concludes that the carbon will be effective for reducing the emissions of dioxins and furans—and will continue to be effective for well over a year before the carbon will have to be replaced.

Similar data are not available for the adsorption of chemical agents on carbon. If any agent is present in the flue gas, it is below the level of analytical detection, so experimentally determining the vapor-to-solid equilibrium relation is very difficult. However, the committee used the theoretical analysis developed by Mitretek, based on the D-R relation, to estimate the equilibria for the three agents. The purpose was to determine whether the carbon bed would be effective in retaining agent under these conditions. In addition, the analysis would predict how much agent might be accumulated on the filter in the event of an accident that drove off the accumulated material in a short time. The range of adsorption quantities was based on the uncertainty of applying the D-R relation at very low concentration (see Appendix D).

For the analysis presented here, the committee assumed that the agents were present in the gas at the detection limit quoted by Mitretek in their analysis of the JACADS trial-burn measurements (U.S. Army, 1998a). Of course, the agents are probably present at lower concentrations or not at all. Assuming that they are present, however, and because measurements always show some fluctuation around the mean value, this method gives a conservative result. The committee made two calculations for each agent: the D-R relation as done by Mitretek, and an approximate Henry's Law calculation (see Appendix D).

The first calculation yields equilibrium adsorption levels that are too high, the second that are too low, probably bracketing the correct level. The results differ significantly, as indicated by the ranges for each agent shown in Table 3-5. GB shows the largest "spread" because it is the farthest away from the Dubinin criterion for application of the D-R relation.

For comparison, the amount of each agent that might reach the carbon was also estimated, based on Mitretek's assumed agent concentrations and a 144-week life of the plant:

GB and VX:	0.00156 g/kg carbon
HD:	0.23 g/kg carbon

The calculations show that the capacity of the carbon to adsorb agent at equilibrium levels greatly exceeds the amount that might plausibly reach it—by some orders of magnitude for VX and HD. Although the

TABLE 3-5 Calculated Range of Carbon Adsorption of Agents

Agent	Gas Concentration[a] ng/dsm^3	Range of Calculated Adsorption Capacity (g/kg carbon)
GB	60	0.478–0.0076
VX	60	19.1–0.0156
HD	8,700	27–11.25

[a]These are the "detection limit" concentrations quoted by Mitretek for trial-burn data at JACADS and are simply taken as 20 percent of the Army's acceptable stack concentrations (U.S. Army, 1998a). The trial-burn data from JACADS and the TOCDF discussed in Chapter 2 resulted in much lower values.

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[4] Various designs are under consideration for the PFS, but the actual bed temperature will be in the 160 to 190°F range.

committee did not evaluate breakthrough times, it appears unlikely that VX and HD (strongly adsorbed) would break through at all. GB might also be captured, but this is judged to be less certain. By comparison, the air from the plant, which is passed through carbon filters before being exhausted to the atmosphere, may contain measurable quantities of agent when it reaches the carbon filters, although no agent has ever been detected past the second four-inch bed of this system. These filters consist of six four-inch beds in series.

As indicated previously, chlorinated dioxins, furans, and mustard constitute a substantial fraction of the calculated risk associated with the flue gas. The other major risk contributors, chromium and arsenic, are solids and should be captured by the HEPA filters, as well as the carbon-bed filters. The analyses show that more volatile materials, such as benzene, carbon tetrachloride, and others, are retained on the carbon bed for a relatively short time before they start to break through. These materials contribute to the 5 percent of the calculated risk not associated with the major risk drivers. A carbon-filter bed will have a negligible effect on their concentrations in the flue gas.

The adsorption capacities described above are very low, less than one gram of GB per kilogram of carbon, for example. This reflects the extremely low concentrations (below the detection limit) that might exist in the gas phase. If a large amount of agent were released during a major accident, the carbon could adsorb much more (e.g., as much as 2 or 3 percent of its own weight). Because each bed contains approximately 10,000 kilograms of carbon, there would be enough capacity to adsorb an extremely large accidental release. The carbon would have to be replaced immediately, but the design of the carbon bed provides for easy replacement.

Predicting adsorptive filter performance is complex and difficult (Mitretek Systems, 1997), and the predicted breakthrough times are probably accurate only to within a factor of a few-fold. The breakthrough times in Table 3-4 are long enough, however, that operation would be considered satisfactory even if the actual times were substantially shorter (e.g., 3-fold). In addition, the plant data support the laboratory findings and, thus, reinforce the conclusion derived from theoretical modeling that the PFS carbon bed would effectively remove the compounds of greatest public concern for an extended period of time. Two beds in series would offer a safety backup; if sampling data after the first bed show a breakthrough of SOPCs, the second bed would capture them until the beds could be replaced.

Filter Upsets

Trace organics accumulate on the carbon filters as they are removed from the flue gas. In the event of a major upset (e.g., a large temperature rise), these accumulated materials could be desorbed in a short period of time, raising a question of the potential risk of desorption, particularly to workers who might be exposed to the highest concentration. The PFS is designed to prevent a rise in temperature, but the possibility cannot be ruled out.

If all of the adsorbed material is assumed to be desorbed in a short period of time (e.g., one hour) the results show that no material could exceed the "acute threshold level" (ATV).[5] Detailed results are presented in the Mitretek report, as well as in the PFS risk assessment reports for Anniston and Umatilla (Mitretek Systems, 1997; U.S. Army, 1998a, 1998b).

CHEMICAL STABILITY OF ADSORBED MATERIALS

Chemical agents can be decomposed at elevated temperatures. They are also destroyed by hydrolysis. The chemical stability of agents that might accumulate on the carbon, and the extent of decomposition during the lifetime of the PFS carbon filters, are examined below.

The thermal decomposition of agents has been tested to demonstrate that the 5X criterion for agent destruction (15 minutes at 1,000°F) will ensure "complete safety" (PMCD, 1989). These tests showed that VX is the most stable, GB less stable, and HD the least stable. Only a few of the tests were done with temperature/residence time relationships that were well enough defined to yield reaction-rate relationships. GB was the agent most extensively studied (PMCD, 1989; Baier and Weller, 1967). None of the tests involved decomposition on carbon.

More recent information has been reported on the off-gassing of agents from carbon filters (Karwacki et al., 1998), which are commonly used to treat the ventilation air flowing through agent destruction facilities, laboratories, and other facilities. Data on GB and HD equilibria (gas and solid adsorbent concentrations) and decomposition rates over a temperature range of 30°C

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[5] ATVs are draft guidelines for acute exposure established by the California state EPA in 1994; ATVs have not been formally adopted.

to 90°C (86°F to 194°F) have also been reported. The reaction rates reported were markedly faster than those of the earlier studies cited above, possibly because water was present on the carbon. (Chemical agents are susceptible to hydrolysis, so the presence of water would open another pathway for decomposition.)

Rate relations given in the 1989 PMCD (Program Manager for Chemical Demilitarization) report have been used by the committee to make the following rough estimates of the stability of the chemical agents at 71°C (160°F), the design temperature of the carbon filter. The experiments on which these rate relations are based were done in a dry atmosphere to minimize hydrolysis. The reaction data indicate first-order agent decomposition with respect to agent concentration:

$$\frac{-dn}{dt} = kn$$

The reaction-rate constants have been related to temperature in the usual way using the Arrhenius relation:

$$k = ae^{-E/RT}$$

or

$$\ln k = \ln a - E / RT$$

The rate relations chosen for the calculations presented in this report are shown below.

Rate Relations (units for k [1/sec]; T [K]):

GB Reeves and Kurtz

$$\ln k - 13.45 - \frac{11099}{T}$$

VX Dee and Berger

$$\ln k = 20.68 - \frac{13972}{T}$$

HD Cheselske

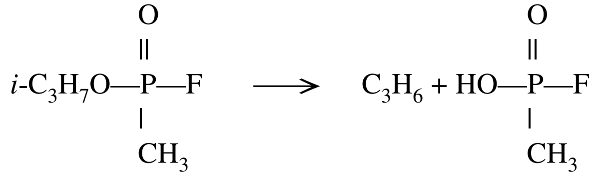
$$\ln k = 21.295 - \frac{12643}{T}$$

The half-lives $(t_{1/2})$ calculated from these equations for a carbon bed temperature of 160°F (71°C), are:

GB: 102×10^6 seconds (3.2 years)
VX: 315×10^6 seconds (10 years)
HD: 3.5×10^6 seconds (40 days)

The higher reaction rates reported by Karwacki et al. (1998) would indicate much shorter half-lives (by a factor of 10 or more). There is strong evidence that for mustard (HD) in particular, and GB to a lesser extent, a great deal of any agent adsorbed on the carbon bed would be decomposed during the period of anticipated plant operation. For example, Karwacki et al. report that about 70 percent of the mustard on carbon was decomposed after 16 weeks at 90°C (194°F).

Very little information is available on the products of decomposition. The thermal decomposition of GB at 395°C (743°F) showed propylene and methylphosphonofluoridic acid as products with little else (Baier and Weller, 1967):



$$i\text{-}C_3H_7O\text{—}\overset{\overset{\displaystyle O}{\|}}{\underset{\underset{\displaystyle CH_3}{|}}{P}}\text{—}F \longrightarrow C_3H_6 + HO\text{—}\overset{\overset{\displaystyle O}{\|}}{\underset{\underset{\displaystyle CH_3}{|}}{P}}\text{—}F$$

The data for GB on dry carbon at the much lower temperature of 50°C to 100°C (122°F to 212°F) showed isopropyl methylphosphonoic acid as the major product (Karwacki et al., 1998). Isopropanol was also present at the higher temperatures. The half-life of GB on dry carbon was reported to be about 63 days at 30°C (86°F). The products of GB decomposition noted above are not expected to show significant nerve agent activity.

For mustard, the data showed the principal volatile reaction products to be 1,4-thioxane, 1,4-dithiane, and 2-chloroethyl-ethylenesulfide. The latter would probably undergo further dechlorination with time (Ward, 1998). The 2-chloroethyl-ethylenesulfide product from HD was expected to show some vesicant properties, but at a lower level than HD; it is not known whether it retains the carcinogenic quality of HD (Ward, 1998).

Chlorinated dioxins are very stable materials, much more stable than the agents. Decomposition rates have been measured, but only at a very high temperature (i.e., 800°C [1,470°F]). Based on results from tests of oil emulsions in soils, their decomposition rate at 160°F is assumed to be negligible.

SUMMARY

Carbon filters have been added to many combustion facilities in Europe (see Appendix C) and have proven to be very effective in reducing already low concentrations of SOPCs and other troublesome components, such as mercury in flue gases. A theoretical analysis of adsorption on carbon developed by Mitretek for the Army leads to the same conclusion. Based on these studies, reasonable ranges can be predicted for the quantities of SOPCs adsorbed, and from them a prediction can be made of the useful life of the carbon beds. The calculations suggest that the carbon beds would last for the duration of the munitions destruction programs at both Anniston and Umatilla.

Chemical agents represent a special case because they are not very stable materials, and GB and mustard in particular react on carbon and decompose in a matter of days. The agents are routinely monitored in the stack gas, however, and none has been observed at JACADS or the TOCDF. The committee's analysis indicates that any agent that reaches the carbon would be completely adsorbed and that most of it would decompose. Thus, little if any agent would remain on the carbon when it was removed for disposal.

4

Facility Design with a Carbon Filter System

The addition of an activated carbon filter system, the PFS, to the baseline incineration process will impose several new design requirements. The flue gas must be "conditioned," that is, its temperature and relative humidity adjusted to ensure that the SOPCs are effectively adsorbed on the carbon. The added equipment, the carbon bed plus the gas-conditioning equipment, will increase resistance, which will increase requirements for fan or compressor power to maintain the gas flow. The carbon bed itself will introduce new safety concerns that must be addressed in the design of the PAS. Moreover, as the gas humidity is changed, the water balance in the overall facility will be significantly altered from the current baseline system design.

In response to the NRC's 1994 recommendation that the Army evaluate a fixed carbon bed as the basis for the design of the PFS, two other processes for the post-treatment of flue gas were also examined (NRC, 1994; U.S. Army, 1998c): carbon injection, with carbon collected on bag filters; and catalytic oxidation. A comparison of these processes with the fixed-bed process selected by the Army can be found in Appendix F.

Final designs for the carbon filter systems for the Umatilla or Anniston sites had not been presented to the committee at the time this report was completed. However, studies have been performed, a number of options have been examined, and some choices or directions now appear to have been chosen. The most likely choices are reviewed in this chapter.

GAS CONDITIONING

Flue gas emitted from the normal baseline system is saturated with water vapor, but high humidity can undermine the adsorption of a carbon bed by filling up the pores in the carbon particles with condensed water. The extent to which the relative humidity of the gas must be reduced in order to prevent this depends on the gas temperature (e.g., 80 percent relative humidity would be satisfactory at 170°F [77°C] and about 50 percent relative humidity at 135°F [57°C]) (Mitretek Systems, 1997).

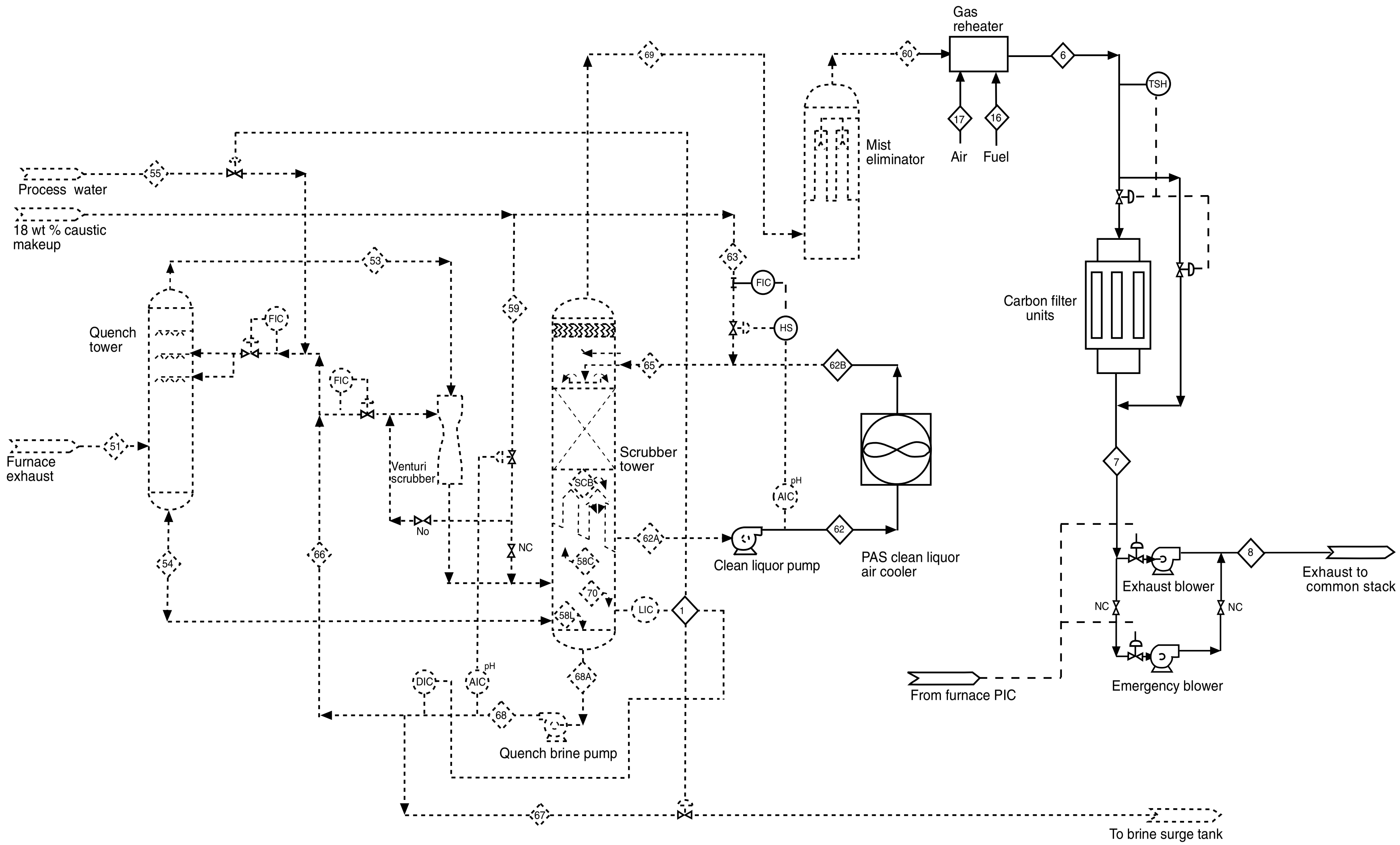
The Army evaluated three different designs for controlling humidity, all of which would provide suitably "conditioned" gas but would have major differences in cost and complexity (Parsons, 1995). The first design would use heat exchange equipment (with associated mist eliminators, etc.) to adjust gas temperature and humidity. This approach presented design difficulties (e.g., heat exchange with two-phase flow) and material requirements (e.g., stainless steel) that made its cost prohibitive. The two subsequent designs that were considered involved modifications to the existing baseline PAS, with additional process steps to adjust temperature and relative humidity. These approaches, designated Alternatives 1 and 2, proved to be much more desirable in terms of cost and simplicity. These alternatives are reviewed in this chapter.

Alternative 1

A block diagram of Alternative 1 is shown in Figure 4-1. The baseline system is shown as "dotted" lines; the added equipment is shown as solid lines. (The diagram includes instrumentation, which is not discussed in this report.)

The exhaust gases from the furnaces are treated the same way as in the baseline incineration system:

- The gas temperature is first lowered by a large



Note: Undefined acronyms are instrumentation not germane to this discussion.

FIGURE 4-1 Schematic diagram of Alternative 1 for fixed-bed PFS. Source: Parsons, 1995.

flow of alkaline water in a quench tower, which reduces the temperature from about 2,000°F (1,094°C) to about 184°F (84°C). The primary purpose of the quench tower is to reduce the temperature of the gas; its secondary purpose is to scrub most of the acid components of the gas into the quench liquid. A large amount of water is evaporated in this cooling process.

- Particulates in the flue gas are removed in a venturi scrubber; a small drop in gas temperature occurs in the venturi scrubber, to about 178°F (81°C).
- The gases are then scrubbed with sodium hydroxide solution in a counterflow packed inert bed to reduce gaseous acidic components (HCl, SO_2/SO_3, HF, P_2O_5) to a very low level. Although most of the acid gases have already been removed by the large flow of alkaline solution in the quench tower, the scrubber tower serves as a final treatment for the removal of acidic components. The neutral gases then pass to a mist eliminator (a tower with filter "candles"); in the baseline system, they are then sent to the stack for discharge.

Two process steps would be added for gas conditioning in the Alternative 1 design:

- The scrubber tower would be run at a much cooler temperature than in the baseline system. Most of the liquid feed to the tower would be withdrawn and cooled to 120°F (49°C) in an air-cooled heat exchanger. The gas (flowing countercurrent to the liquid) would leave the scrubber in contact with this 120°F liquid and would be at about 125°F. The liquid in the scrubber tower would be heated as it passes down the tower to about 149°F (65°C) as it contacts the hot gas flowing up the tower. Most of the water that was evaporated into the gas in the quench tower would be condensed at this lower temperature. These scrubber tower temperatures would be 40 to 50°F lower than in the normal baseline system. The lower temperature would drop the moisture level in the gas so that when the gas is reheated to 160°F (71°C), its *relative* humidity would be reduced. The lower operating temperature of the scrubber could also result in the removal of more acid gases from the gas stream, although the magnitude of the amount has not been evaluated.
- The gas leaving the mist eliminators would be at 100 percent relative humidity (i.e., saturated with water vapor at 125°F [52°C], approximately 13 mole percent water vapor). This gas would be heated by a direct-fired burner fueled by natural gas. The burner product gas would be mixed directly with the incinerator flue gas to raise the temperature to 160°F (71°C). Very little fuel would be required to raise the gas temperature by this modest amount (35°F), and the natural gas combustion products would add very few additional SOPCs because natural gas burns relatively cleanly. Also, very little water vapor would be added to the gas. The small flow of burner product gas would have to be mixed thoroughly into the much larger volume of flue gas. Mixing will be essential to prevent the relatively hot (albeit small) stream from causing trouble in the carbon bed (e.g., poor adsorption or even ignition of the carbon). The relative humidity calculated for the higher temperature (160°F) is 41 percent. Experience suggests that even at a higher relative humidity (50 percent) water vapor will not interfere with adsorption on carbon (Mitretek Systems, 1997).

Alternative 2

Alternative 2 is similar to Alternative 1 except that the scrubber tower liquid would not be cooled. The gas leaving the tower would be about the same temperature (178°F [81°C]) as it was when it entered. Heating the gas to 189°F (87°C) would lower the relative humidity to 80 percent, and the carbon bed adsorption would run at that temperature. Most commercial applications of carbon beds with incinerators are run at even higher temperatures (e.g., 225°F or more). The emissions of most concern from incinerators, chlorinated dioxins and mercury, are both adsorbed at the higher temperature of 189°F (87°C). Many other SOPCs of lesser concern for human health and the environment would not be adsorbed at this temperature, however.

COMPARISON OF ALTERNATIVE DESIGNS

Performance of the Carbon Bed

The Mitretek evaluations have shown that the carbon bed will be very effective for adsorbing the emission materials of greatest concern to the public—chlorinated dioxins. Any unburned VX and HD should also be retained; the retention of GB by the carbon bed is more uncertain (see Chapter 3). However, many other objectionable SOPCs would not be retained by the bed for its planned duration of operation. Many SOPCs (such as benzene) would come to equilibrium quickly and then pass through the bed with no change. The higher the operating temperature of the carbon bed, the less SOPC mass would be retained. Although this has not been quantified, it is reasonable to believe that the lower operating temperature of 160°F (71°C) in Alternative 1 would control emissions of flue gas better, even in the event of a substantial system upset.

Water Balance

The lower temperature of the gas leaving the scrubber tower of Alternative 1 would have a beneficial effect on the water balance of the plant. With Alternative 2, which has no scrubber cooling, the water balance would be essentially the same as for the baseline system. In the normal baseline system, the flue gas leaves the stack at a fairly high temperature (about 178°F) and is saturated with water vapor. In fact, it is nearly one-half water vapor. As a consequence, a lot of water is carried away. The combustion process creates water, which is introduced into the system, but the amount leaving with the flue gas is much greater. (A calculation for the incineration of GB indicated it to be about seven times as much.) The excess water, which comes from evaporation of the quench and scrubbing fluid, must be added to the system.

The lower operating temperature for the gas conditioning in Alternative 1 would have a major impact on the water balance. The humidity of the gas leaving the plant would be reduced to about 10 percent of the gas volume, little more than the water introduced by agent combustion. (A calculation for the incineration of GB, for example, showed the amount of water in the exit flue gas to be about 30 percent more.) Because of lower relative humidity, the emitted gases in Alternative 1 would also be less likely to create a visible plume from the stack.[1]

In the normal baseline system, the alkaline liquid in the scrubbing tower liquid (and the liquid in the quench tower) have to be controlled for pH and salt content. Sodium hydroxide is used up by reaction with the acidic gas components, and fresh sodium hydroxide solution must be added to maintain the pH in the desired range. Salts formed by the reaction with acid gases build up in solution and must be removed. The solution is withdrawn when it reaches a certain density (which increases as salt concentration builds up). The salts are recovered by evaporation of the water. For the Alternative 1 design, the water demand of the plant would be almost in balance, making pH and accumulated salt content easier to control.

An evaluation by Parsons (1995) suggested that the low water content of the gas in Alternative 1 would have other advantages. For example, the operation of the carbon filter is sensitive to water in the gas. A transient reduction in temperature causing gas to condense in the carbon filter would be much more damaging with Alternative 2 because of the water loading. The higher operating temperature of Alternative 2 would also increase the potential for heat loss to the environment—and consequent moisture condensation. With Alternative 2, there would be a greater likelihood of plugging of the carbon filter and more corrosion.

Design of the Scrubber Tower

Some heat and material balances have been done for the two alternative process designs, but final operating designs were not reported to the committee. It is not clear, for example, that the current design for the scrubber tower used in the baseline system will actually accomplish the heat transfer (i.e., the gas cooling and steam condensation) necessary for Alternative 1. The new design must account for the water condensation in the scrubber tower as a result of cooling. In normal baseline operation, a large amount of water is evaporated in the quench tower. As suggested earlier for Alternative 1, an almost equal amount of water would be condensed in the scrubber tower. In fact, the critical design requirement for the tower would no longer be the absorption of acid gas, but rather the heat transfer capacity necessary to condense a lot of steam. The tower would almost certainly have to be larger in diameter than the current scrubber tower to prevent flooding. It might also have to be taller and have a greater depth of packing material.

Blower Equipment

The baseline incineration system requires blowers (fans) to draw flue gas through the quench tower, venturi, and scrubber tower and to maintain the furnaces at lower pressure than the surrounding room air. Pressure drops through the process equipment have

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[1] For example, air at 70°F and 70 percent relative humidity produces no plume. Air at 70°F and 100 percent relative humidity creates some condensation around the air-to-gas concentration range of 25/75 to 10/90.

been computed (Parsons, 1995). Gas pressures upon leaving each unit and the pressure drops across these units with the LIC burning agent HD are shown in Table 4-1. The total pressure drop is 3.8 psia. The addition of a carbon filter would increase flow resistance, increasing power requirements. The committee doubts that the pressure drop through the system could be overcome by using two fans in series (the present system); a third fan might be necessary. If so, the question arises as to whether fans would be the best way to handle the pressure drop; a single compressor might be a better alternative.

The baseline system has two sets of blowers for two separate gas flows. Air is drawn through the building and exhausted through carbon filters; and air is drawn through the furnace and PAS and exhausted through the stack. The sets of blowers are independent, except that a small differential pressure must be established so that air flows into the furnace from the room. This same balance will be required for a PFS. The design of the gas conditioning process will influence the choice of blowers or a compressor. The flow rate for Alternative 1 (with gas cooling) would be one-half or less the flow rate of the normal baseline system or the flow rate for Alternative 2. The lower flow rate is attributable to two factors: (1) the removal of a very large amount of water vapor, and (2) the reduction in volume because of the lower temperature. Alternative 1 would require smaller blowers (or a smaller compressor) than either the normal baseline system or Alternative 2.

Another favorable consequence of the lower flow rate for Alternative 1 would be the lower turndown ratio (i.e., the actual flow divided by the design flow rate for normal operation). A minimum gas flow rate is required through the furnace (e.g., when the furnace is purged with ambient air after shutdown). This requirement is the same for both alternative designs. Because the maximum flow requirements for Alternative 2 and the normal baseline system are higher by a factor of more than two than for Alternative 1, the turn-down ratios will be substantially different. Parsons has estimated that the turn-down ratio for the LIC furnaces is 1:5 for the baseline system (without carbon filters) and would be 1:5 for Alternative 2; for Alternative 1 with gas cooling, the ratio would be 2:5 (Parsons, 1995). A turndown of 2:5 can probably be handled by controlling the flow rate (e.g., with guide vanes or valves). A turndown of 1:5 would require speed controls on the fans, a significant increase in cost.

TABLE 4-1 Pressure Parameters for the Incineration of HD for a PFS-Equipped Baseline System

Unit	Pressure of Gas Leaving Unit (psia)	Pressure Drop across Units (psia)
Furnace	12.1	N/A
Quench tower	10.5	1.6
Scrubber tower	10.3	0.2
Mist eliminators	9.5	0.8
Reheat furnace	9.3	0.2
Carbon filters	8.3	1.0

Source: Parsons, 1995.

Summary of Gas Conditioning

The Alternative 1 design with gas cooling in a packed bed appears to offer several advantages over Alternative 2. The principal advantage would be the lower operating temperature of the carbon bed, which would enable the bed to do a better job of meeting its design objective of reducing concentrations of SOPCs in the flue gas that would otherwise escape to the air. Alternative 1 would also have advantages in terms of system water control and flow control.

The Alternative 1 design (with gas cooling) would require some extra equipment to provide the necessary cooling capacity. The blower capacity would be substantially reduced, however, compared to the Alternative 2 design. The Parsons study indicates that the lower cost for blowers would make Alternative 1 less expensive than Alternative 2 (Parsons, 1995).

DESCRIPTION OF THE CARBON FILTER

The designs of the carbon filters for the Umatilla and Anniston sites had not been finalized at the time this report was prepared. The designs for each site will have to meet certain operating requirements:

- Sufficient carbon must be available to make replacement very infrequent. In fact, the design should probably provide for sufficient carbon to last the lifetime of the facility under “normal” operating conditions. Provisions should be made, however, for easy replacement of the carbon if it becomes necessary.
- Provisions must be made for sampling and monitoring the flow through the carbon bed to warn of possible problems and to test its operation.

- Provisions should be made for high temperature excursions that could lead to a fire in the carbon bed. Also, the flow of high humidity (near saturation) gas could decrease adsorption capacity. Therefore, provisions should be made to divert gas temporarily around the bed. Because the carbon would no longer be performing its "safety" function, diverting the flow temporarily might also require stopping all feed to the furnaces.

The Army has prepared fairly detailed specifications for the carbon bed based on existing practice. The general characteristics follow directly from American Society of Mechanical Engineers (ASME) code requirements for gas-handling systems (U.S. Army, 1997b). Important specifications include:

- two separate carbon beds
- sampling connections between beds
- testing for leaks

Proposed design information is summarized in Table 4-2 (Mitretek Systems, 1996). A proposed design philosophy is to modularize equipment and standardize equipment sizes as much as possible. The gas flow rates differ through the various incinerator systems: LIC = 9,006 actual cubic feet per minute (acfm); DFS = 26,315 acfm; MPF = 9,100 acfm. Six "standard" units have been proposed to handle these flow rates: one for each of the two LICs; two for the large flow of the DFS; one for the MPF; and a spare (see Figure 4-2).

TABLE 4-2 Design Information for the PFS Carbon Filter Unit

Parameter	Value
Flow capacity	12,000 acfm
Prefilter	80% to 85% American Society of Heating, Refrigerating, and Air Conditioning Engineers
HEPA filter	99.97% dioctyl phthalate retention
Carbon filter media	15,000 lbs. of 8 × 16 mesh coconut shell carbon
Carbon filter bed depth	12 inches
Carbon filter bed width	120 inches
Carbon filter bed height	138 inches (the lower one-third of the bed is tampered into a discharge chute)
Carbon filter face area	214 ft^2
Carbon filter superficial face velocity	56 ft/min

Source: Adapted from Mitretek Systems, 1996.

Considerable industrial experience with carbon filtration is available to guide the design for the PFS, and a number of commercially available designs were examined in the Parsons study (1995). One design that appeared to be attractive consisted of (1) an assemblage of HEPA filters at the inlet, (2) the carbon bed, (3) an outlet roughing filter, and (4) another HEPA filter. The inlet filters keep particulate matter from getting to the carbon bed and clogging it. The outlet filters prevent carbon "dust," particularly dust containing an accumulation of adsorbed SOPCs, from escaping to the atmosphere. The use of HEPA filters in the PFS design might also reduce the emissions of metals in the stack gas although the change has not been quantified.

Other features of this design that appeared to be useful are listed below:

- The design has three sets of carbon beds in parallel, with each set consisting of two 12-inch thick beds in series, separated by a small plenum. Sampling and analysis of the gas flow between beds in series should provide advanced warning if they are approaching saturation and require changing.
- The beds are filled from the top, and spent carbon can be withdrawn from the bottom. The beds would have to be mounted well above ground level to provide space below them for containers to receive the carbon discharge. Carbon replacement could be done quickly and with safeguards against releasing dust to the air.
- A mechanism is provided for preventing direct contact with spent HEPA and roughing filters when they are replaced.

Safety

Carbon filters would introduce some process hazards that must be addressed in the design. The most serious hazards, the possibility of fire and the possibility of increases in pressure pulses in the furnace (puffs), are discussed below.

The carbon in the filters is combustible, and the gas flowing through the filters contains oxygen that has leaked into the system and residual oxygen from the combustion process. In industrial use, fires have occurred when carbon filters have been used to remove high concentrations of organics from air (e.g., solvent recovery systems), but information on fires in incinerator carbon filters is sparse and mostly limited to "personal communications." The most serious incinerator fire reported was a chimney fire that did not

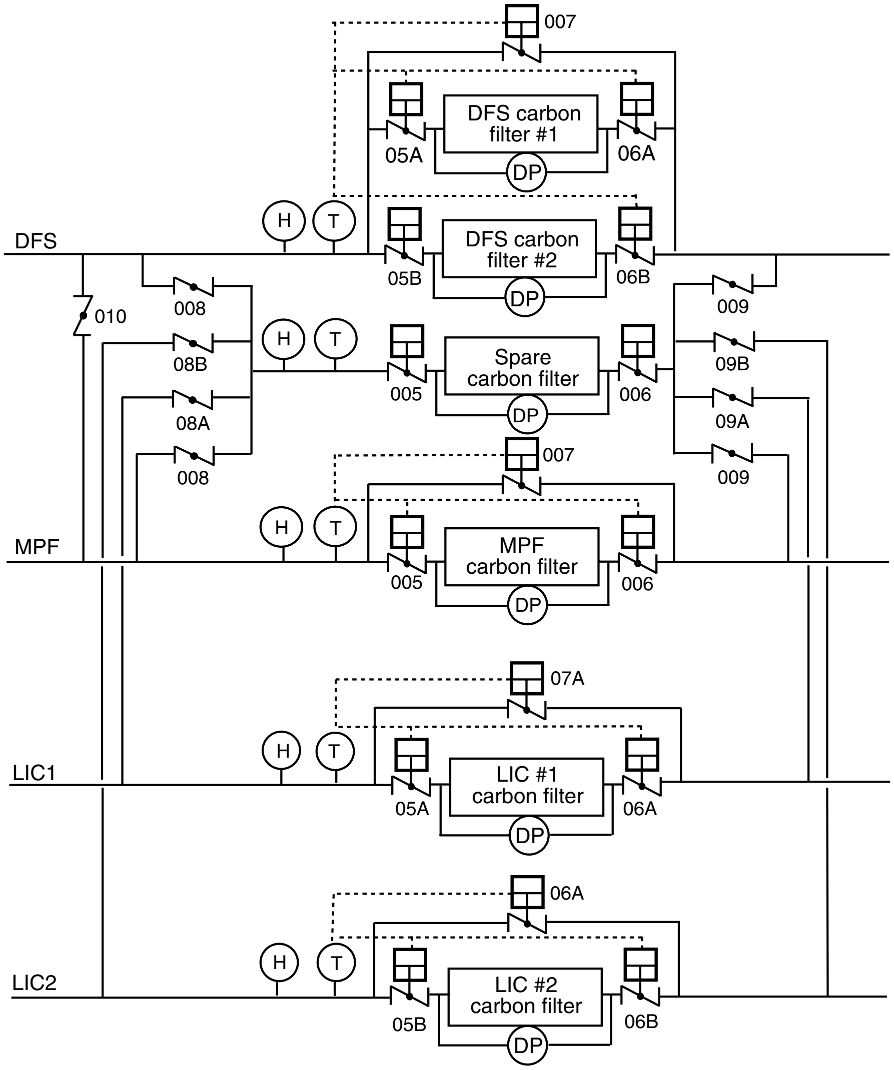

FIGURE 4-2 The six PFS filter units and dampers. Source: Mitretek Systems, 1996.

involve the carbon filter at all. Coke dust from the filter, however, was one of several possible causes (Hartenstein, 1992).

The Army should consider the possibility of a fire in the control and design of the filter. The possibility of a fire appears to be small, however, for two reasons:

- The ignition temperature for the carbon is reported by the manufacturer to be high (e.g., 475°C [887°F]). The design temperature for the PFS (Alternative 1) is about 70°C (158°F).
- The gas concentrations of species to be adsorbed are in the parts per billion range, too low to cause significant heating on adsorption, thus minimizing the likelihood of adsorption-induced combustion.

The gas flow velocity through the carbon bed is low, less than one foot per second, and the bed has a large heat capacity. Consequently, if a hot spot or fire were to develop, it would probably develop slowly, allowing ample reaction time. Once the gas flow is stopped, the temperature would rise from adiabatic combustion of the carbon with the residual air in the bed. Calculations by the committee show that this increase would be only a few degrees, much too low a temperature to ignite the rest of the bed.

In practice, several gas properties could be monitored continuously to warn of trouble: gas inlet temperature to the bed; gas temperature in the plenums after each of the beds in series; and carbon monoxide content of the gas in each plenum. Experience in

Germany has shown that "by measuring the differential carbon monoxide concentration across the bed—a function of bed temperature—one can accurately locate hot spots within the bed" (Fouhy, 1992).

The control system for the flow of flue gas in the carbon filter design involves control valves (a suggested flow-control arrangement is shown in Figure 4-2). The flue gas is bypassed around the beds during start-up, which takes place before agent is introduced to the furnaces. When the steady-state temperatures have been reached, the flow is sent through the carbon beds by closing the bypass valves and opening the isolation valves at the entrance to and exit from the filters. The gas inlet temperature is monitored. In the event of a rise in temperature of about 20°F (i.e., to 180°F for Alternative 1), the process would be reversed; gas would again bypass the carbon beds, and the beds would be isolated between the inlet and outlet valves. The time required to change valve settings should be just a few seconds. A hot spot in the bed could be quickly isolated.

The flow control valves are large (e.g., 26-inch diameter openings) and must allow very little leakage. The Army has specified zero leakage at 141 inches of water pressure differential (U.S. Army, 1997b). A number of valve types are available that could meet the performance specification (e.g., butterfly or sliding blade designs), but the Army has specified butterfly valves.

Other plant controls on all of the operating units would maintain efficient and safe operation. An example of the PFS gas reheater is shown in Figure 4-3. A signal generated by a thermocouple installed in the gas reheater outlet stream is compared to a set point maintained by a set-point controller; if actual outlet temperature varies from the set point, an error signal is sent to a current-to-pneumatic (I/P) controller, which regulates the position of the fuel throttle valve. Gas is burned in the reheater to reach a fixed temperature. In case of trouble (e.g., too much reheating and too high a gas temperature), the gas supply is shut off, and the reheater no longer functions. The drop in gas temperature could lead to a secondary problem in the carbon beds: condensing water would eventually deactivate the beds for adsorption. However, this problem would not become serious for several hours. The gas flow would be bypassed around the filters until the correct temperature was reestablished.

Furnace combustion processes frequently show small variations in pressure. The presence of a carbon filter downstream of the furnace could be expected to increase the magnitude of occasional larger changes, referred to as puffs. However, puffs have not been reported to be a problem in European waste incinerators. The carbon filters will add only a modest increment to the total drop in flow pressure (e.g., 25 percent), and puffs are not likely to be affected by this modest increase in the resistance to flow.

Sampling

A gas sampling manifold has been specified for installation in each compartment, including the prefilter and HEPA filter compartments. The sampling will serve two purposes: (1) to check on the gas (and carbon) conditions to indicate when carbon replacement may be required; and (2) to provide a mechanism for introducing test gases (e.g., dioctylphthalate [DOP]) to evaluate filter performance or test for leakage. The procedure for in-place testing for leaks with DOP or Freon is specified in ASME-N510. The requirements for the sampling manifold and connections have been specified in detail by the Army (U.S. Army, 1997b).

Maintenance

The carbon filter itself is expected to require little maintenance. The HEPA filters at the bed inlets will require replacement every 100 hours of operating time. The filter design allows for rapid replacement, with the HEPA filters dropping from the bottom and being collected in enclosed containers. The carbon beds could also require replacement, which must be included in the design. The large block valves and other control equipment will require regular checking and maintenance.

Disposal

The carbon filters recovered from the equipment at the end of their lifetime will require suitable disposal. Carbon filters are already used in the baseline system for treating ventilation air flowing through and leaving the plant. Because agent levels in remote processing areas can be relatively high, and because the air from these areas is filtered through the ventilation air carbon beds, these filters are exposed to much higher levels of agent than the flue gas carbon filters will be. The committee believes the disposal process should be the same, or very similar, for both sets of filters. Disposal of contaminated activated carbon, especially when agent is present, represents a significant issue with regard to disposal of nonprocess waste. The Army is currently

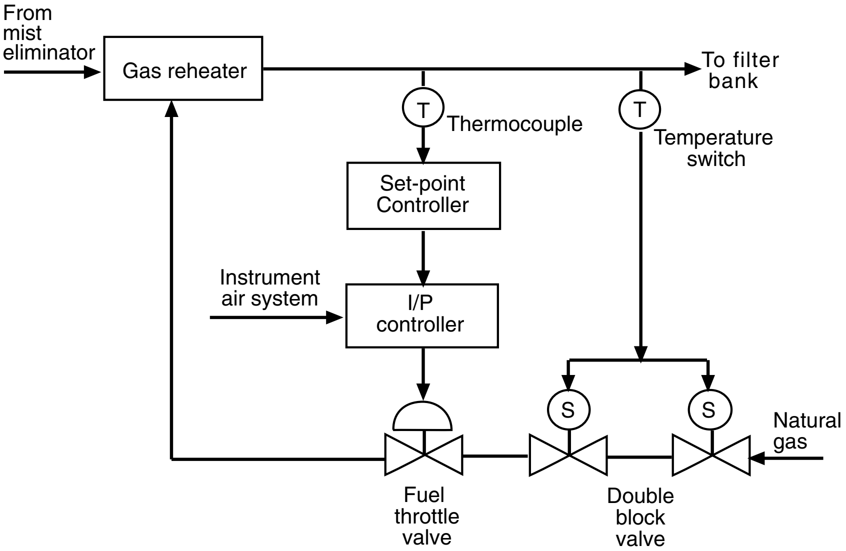

FIGURE 4-3 PFS gas reheater. Source: Adapted from Mitretek Systems, 1996.

evaluating several options for the disposal of spent activated carbon.

Summary

The requirements of the carbon bed design have been spelled out in considerable detail and examined by the Stockpile Committee. Even though no final design was available from the Army, the committee believes a safe and efficient design that incorporates early detection of "hot spots" or a fire in the carbon bed and rapid shutdown and isolation of the filter is feasible. The issue of gas conditioning for the carbon filter systems appears to have been thoroughly examined. The committee believes that extensive experience with carbon filters elsewhere can also be used for determining the efficient and safe operation of the PFS carbon filter.

5

Risk Assessments and Change Management: An Evaluation of the Army's Decision-Making Process

BACKGROUND

Carbon filters were first considered for the baseline incineration system in 1991, when the observation was made during an NRC workshop that "the use of redundant air pollution control could substantially enhance public confidence…" (NRC, 1991). In a 1992 report, the NRC recommended that "the Army should consider incorporating passive controls, such as activated carbon beds…" (NRC, 1992). In 1994, the Stockpile Committee revisited the issue of carbon filters and made the following recommendation (NRC, 1994):

> **Recommendation 13.** The application of activated charcoal filter beds to the discharge from baseline system incinerators should be evaluated in detail, including estimations of the magnitude and consequences of upsets, and site-specific estimates of benefits and risks. If warranted, in terms of site-specific advantages, such equipment should be installed.

Anticipating that carbon filters would offer a net benefit by reducing public risk or, at least, enhancing public confidence, the Army decided in 1994 to add carbon filters to the baseline incineration designs for facilities at Anniston, Alabama; Umatilla, Oregon; and Pine Bluff, Arkansas (U.S. Army, 1994d). JACADS was already built and operating in 1994, and the Army concluded that it would be extremely difficult to retrofit the facility without causing extensive delays in the destruction of the stockpile; the decision on whether to add carbon filters at the Tooele facility, which was then under construction, hinged on the results of a planned risk assessment of the Tooele PAS filter system (PFS).

In response to the NRC recommendation that the Army evaluate the effectiveness of adding the PFS, the Army issued contracts for analysis of the risks and benefits to the design and permitting of baseline incineration system facilities at Anniston, Umatilla, and Pine Bluff. Summary assessments of the risks associated with carbon filters at Anniston (U.S. Army, 1998a) and Umatilla (U.S. Army, 1998b) were provided to the Stockpile Committee; the report for the Pine Bluff facility was not available for review.

Focus of the Stockpile Committee's Review

The committee's review of the Army's risk-based decision making focused on the following issues:

- the Army's risk evaluations of the PFS at Anniston and Umatilla
- the Army's application of the CMP and public involvement in the PFS evaluation
- the Army's decision to retain the PFS in the designs for Anniston and Umatilla and to continue operating Tooele without a PFS
- what the Army should do before implementing its decision

Although no change is being proposed in the planned designs at Anniston and Umatilla, the Army decided to use its CMP to present the results of its analysis to the public (U.S. Army, 1998d). The Army's use of the CMP, as it relates to the PAS, is discussed below.

Documents Reviewed

The committee's evaluation is based on the following reports and documents:

- *Risk Assessment of the Pollution Abatement Filter System for the Anniston Chemical Agent Disposal Facility (ANCDF)* (U.S. Army, 1998a)
- *Draft Risk Assessment of the Pollution Abatement Filter System for the Umatilla Chemical Agent Disposal Facility (UMCDF)* (U.S. Army, 1998b)
- *Letter Report from the Program Manager for Chemical Demilitarization—Implementing the Change Management Process: Validation of the Anniston Chemical Agent Disposal Facility Pollution Abatement Filter System Implementation* (U.S. Army, 1998d)
- *Evaluation of the Pollution Abatement Filter System for Chemical Agent Disposal Facilities: Methodology for Evaluating Risks* (U.S. Army, 1998e)
- *PMCSD Change Management Process Plan* (U.S. Army, 1998f)
- *Letter Report from the Program Manager for Chemical Demilitarization—Umatilla Chemical Agent Disposal Facility Pollution Abatement Filter System Summary of Risk Assessment Results* (U.S. Army, 1998g)
- *The Change Management Process to Accompany the Guide to Risk Management Policy and Activities (May 1998)* (U.S. Army, 1998h)
- *Public Involvement Plan for the Chemical Stockpile Disposal Program Change Management Process* (U.S. Army, 1998i)
- *Anniston Chemical Agent Disposal Facility Phase 1 Quantitative Risk Assessment* (U.S. Army, 1997c)
- *Umatilla Chemical Agent Disposal Facility Phase 1 Quantitative Risk Assessment* (U.S. Army, 1996b)
- *Tooele Chemical Agent Disposal Facility Quantitative Risk Assessment* (U.S. Army, 1996a)
- *Review of Acute Human-Toxicity Estimates for Selected Chemical-Warfare Agents* (NRC, 1997b)
- *PAS Filter System (PFS) Analysis* (Hopkins, 1998a)
- *Bringing the PAS Filter Evaluation to Closure* (Hopkins, 1998b)

RISK ASSESSMENTS FOR ANNISTON AND UMATILLA

The PFS (carbon filter system) risk assessments carried out for Anniston and Umatilla are summary-level extrapolations of (1) the results of the site-specific HRAs performed to meet regulatory requirements and (2) the results of the Phase 1 QRAs for off-site consequences of processing accidents involving agent. The assessments include risks to on-site workers, nearby residents, and the surrounding environment for acute and chronic effects of exposure, with and without the use of the carbon filters. Effects on facility construction schedules and costs are also addressed, as well as the risks of ongoing storage. The Army's decisions about PFSs are based on this information.

The Army used the site-specific, multipathway HRAs done to meet state regulatory requirements as a starting point for its PFS analysis. The HRA evaluation performed by the Army was a "bounding" analysis of the effects of adding or removing the PFS at Anniston and Umatilla. This assessment was based on an assumption of severe conditions or minimum effectiveness of the PFS to estimate the maximum risk.

The effects of the PFS on the HRA were evaluated by comparing results for alternative designs. The only effects considered were reductions in the flow rate and temperature of the stack gas from changes in operating conditions with the PFS. These analyses did not assume the removal of SOPCs from the flue gas by the PFS but examined the effects of the PFS that exhausts gas flow rate at 160°F and 39 percent relative humidity compared to a facility without a PFS that exhausts gas at 190°F and 100 percent relative humidity. Reducing the flow rate and temperature as a consequence of adding the PFS would reduce the effective height of the stack and, therefore, reduce the atmospheric dispersion of emissions. Therefore, the Army analyzed plume dispersion to assess how the changes would affect concentrations of contaminants or health risks.

The Army considered this analysis to be a "worst case" or "bounding" calculation to ensure that the addition of the PFS would not increase public health risks. For example, the concentrations of SOPCs used in the analysis were the highest value recorded for each measured substance in the JACADS trial burns. The detailed analysis of the trial-burn data provided in Chapter 2 shows that these estimated values are much higher than the anticipated actual values. However, the Army did not conduct comparative HRAs assuming that the PFS would reduce emitted concentrations to either the analytical detection limits or to levels below analytical detection limits based on estimates of carbon filter removal efficiency. Nor did the Army quantify reductions in the emissions of acid gases or metals.

Because no SOPC removal was assumed to occur in the PFS—an assumption that is conservative but contrary to field experience and engineering calculations (see Chapters 3 and 4)—potential reductions in public risk were not evaluated in an HRA. The Army did conduct a sensitivity analysis of HRA results based on the detection limits. However, it is difficult to quantify the potential public health risk benefits without a more complete HRA evaluation for comparison.

Risks to the environment and human health could have been determined by assuming that the PFS would reduce emissions of semivolatile organics, volatile metals, particulates and their associated SOPCs, as well as acid gases, to either their detection limits as demonstrated by tests conducted at carbon filter-equipped hazardous waste incinerators (Hartenstein, 1992) or to the concentrations indicated by engineering models (Mitretek Systems, 1997). The results of the HRA evaluations were augmented by the site-specific Phase 1 QRAs, which evaluated the off-site consequences of agent-related accidents. The Phase 2 QRA, which addresses worker risk associated with agent processing at the TOCDF, was used to provide insight into possible accident scenarios at Anniston and Umatilla, which are expected to have similar designs and operating practices. The QRA analysis carried out using the Phase 2 QRA from the TOCDF identified blockage of the exhaust gas flow by the PFS, coupled with loss of the induced draft (which maintains the pressure drop for the exhaust-gas flow), as the only upset condition that would result in increased risk from a release of agent caused by the PFS.

The frequency of two types of accident scenarios would substantially increase as a consequence of potential PFS blockage and loss of induced draft: (1) an agent-vapor explosion in the MPF if agent vapors accumulated, and (2) a natural-gas explosion in the MPF if the plant was shut down but natural gas continued to flow to the burner. The magnitude of the worker risk from a natural-gas explosion leading to an agent release was much less than the risk caused by the potential agent-vapor explosion. Both scenarios had negligible impact on risk to the public ($\leq 1 \times 10^{-12}$ individual risk of fatality or cancer over the facility life). However, the potential for an agent-vapor explosion caused by PFS blockage represents 3 percent of the total worker risk. In addition, the evaluation of risk from a potential agent-vapor explosion did not consider scenarios of poorly drained munitions being processed, which could significantly increase the amount of agent in the MPF.

The Phase 1 QRAs indicate that the PFS would not be associated with any accident scenario likely to expose off-site receptors to agent. However, individual worker fatality risk from agent due to upsets in the PAS are estimated at 3.3×10^{-5} with the PFS and 1.1×10^{-5} without the PFS over the life of the facility. This is in contrast to total worker risk from agent of 4.1×10^{-4} as estimated for the TOCDF. These findings also can be compared with the worker accidental death rates of 3×10^{-5} *per year* for manufacturing industries and 1.5×10^{-4} *per year* for construction industries during 1996 (National Safety Council, 1997). The risk from the PFS is within the range of the uncertainty for worker risk analysis at the facility but significant enough to warrant further evaluation.

Although mitigation measures have not yet been identified, they will be investigated as part of the Phase 2 QRAs and HEs (job safety hazard evaluation reviews) for Anniston and Umatilla. The increased risk might be mitigated through improved maintenance procedures and heightened operator awareness. In any case, the presence of the PFS is not expected to reduce worker risk. The Phase 2 QRAs and HEs for Anniston and Umatilla are scheduled to be carried out once facility designs have been finalized and operating procedures developed.

The Army's QRA deals only with the risk of agent release caused by accidents and the consequent effects of agent on the public and on workers. It is not intended to, and does not, take into account the usual industrial risks of building, operating, maintaining, and supplying a large industrial plant. (An example of increased worker risk as a consequence of increased nonagent-related maintenance activities is the need for frequent replacement of the HEPA filters in the PFS, estimated to be required after every 100 hours of operation.) These are important management concerns, however, and they are given considerable attention in the HEs (U.S. Army, 1997a).

Based on the combined results of the HRA and QRA evaluations, the Army concluded that even a PFS with a zero removal efficiency would have off-site impacts and risks acceptable for issuing a RCRA permit. From these analyses, the Army concluded that the best course of action was to make "no change" in the current configurations (i.e., retaining the PFS at Anniston, Umatilla, and Pine Bluff but not adding a PFS to Tooele). This decision was based on the following rationale:

- Delays in processing caused by a permit change would increase public risk from continued storage.
- Delays would probably increase the overall risk to workers by increasing storage risk.
- The reduction in public risk from processing emissions (that are already below regulatory levels) by the addition of a PFS at Tooele would be more than offset by the increased risk due to delay.

The Army's decision was made in the context that the original intent of the PFS was to increase public confidence through the presence of a redundant air pollution control system. However, the Army's analyses suggested that changes to risk would be small, that these changes could represent an improvement or a degradation depending on the uncertainties in the analysis, and that risk to the public and workers might differ. The Army concluded that its bounding analyses provided sufficient information for making a reasoned management decision and that more refined analyses were unnecessary.

The Stockpile Committee agrees that properly performed screening level analyses may demonstrate that an emission is far enough below the thresholds of regulatory concern and that more refined analyses are not needed in this case. The EPA often uses the same rationale to balance environmental protection and costs. However, the committee believes that the piecemeal approach taken in the Anniston and Umatilla PFS HRAs and the use of the TOCDF QRA as a surrogate are neither the simplest nor the clearest way to support risk management conclusions. The Army did not provide the committee with an integrated analysis that clearly indicates the environmental effects, the public health benefits, or the worker safety implications of the PFS. Nor did they provide quantification (or even clear identification) of the uncertainties associated with the analyses.

THE ANNISTON PFS RISK EVALUATIONS

The following results are from the Anniston summary PFS risk assessment (U.S. Army, 1998a):

1. **For all receptors (subsistence farmer, three subsistence fishers, adult resident, and child resident), a system configuration for the ANCDF without the PFS achieves the state-approved health risk thresholds.** For example, the estimated excess cancer risk is 4E-06 for the subsistence farmer (i.e., an additional chance of about 4 in 1 million that an individual will contract cancer during his or her lifetime) and 3E06 for the adult resident. With the PFS, the estimated excess cancer risk for the subsistence farmer is 3E-06; for the adult resident it is 2E-06. For the ANCDF, the corresponding state-approved threshold for excess cancer risk is 1E-05 (an additional 10 in 1 million chance of contracting cancer).
2. **A sensitivity analysis shows that the calculated excess cancer risk values using the state-approved methodology are overly conservative.** When certain parameter values are adjusted to more accurately reflect program factors or conditions, there is insignificant difference between the risk calculated for a facility "with PFS" and one "without PFS." The difference in risk values for the 2 facilities is on the order of 3E08.
3. **The PFS is not expected to affect the potential for PAS emissions to negatively impact ecological communities.** Removal of the PFS will not change the screening level ERA [environmental risk assessment] findings that there is little potential for the SOPCs to impact vegetation, soil invertebrates, or aquatic and benthic species in the Anniston depot area.
4. **The PFS does not reduce the risk from accidents related to agent stack release.** The QRA results show that the PFS is relatively risk neutral. While the PFS could reduce the potential for agent release from the stack, the PFS has no net effect on the overall individual or societal risk from stockpile disposal activities because the risk is dominated by external events—such as aircraft crashes—which are unaffected by the PFS. Furthermore, while there is an increase in the risk for worker fatality associated with the operation and maintenance of the PFS, the magnitude of the increased risk is relatively small (i.e., 2.8E-05 risk increase over a baseline worker risk of 2.2E-04).
5. **Any delay in the disposal schedule will result in an increase in the munition storage period and therefore an increase in risk.** Facility operation with the filters is expected to result in a small delay due to additional downtime associated with filter maintenance activities. However, this is insignificant when compared to: 1) the potential delay associated with a permit change to remove the filters; or 2) the shutdown that would accompany a potential stack release on a design without filters.
6. **The hazard evaluation of solid waste generated from the PFS shows that there is some additional risk associated with solid waste disposal, but its overall impact on public and worker risk is insignificant.** The PFS increases the amount of solid waste generated for the baseline system by about 0.3 percent. Hence, removal of the PFS has no significant effect on the risk from solid waste disposal.

7. **The total cost of implementing the PFS at the ANCDF is in the range of $58 million to $68 million; however, the cost of removing the PFS from the ANCDF could range from about $52 million to $102 million.** The net effect is a cost saving of as much as $16 million ($68M–$52M) or an increase in cost of as much as $44 million ($102M–$58M). The largest uncertainty is in how long the destruction schedule could be delayed as a result of obtaining a RCRA permit modification. The increase in stockpile storage cost for destruction schedule delay is the main cost driver.

The draft Umatilla summary PFS risk assessment presents similar conclusions (U.S. Army, 1998b). Both assessments concluded that residents living near facilities with carbon filters would face essentially the same risks as residents living near facilities without carbon filters.

In neither the Anniston nor Umatilla summary PFS risk assessments has the Army made a clear presentation of the risk of adding or removing the PFS. The assessments were generated for the Army's internal use, and, therefore, the Army considered the audience for its PFS reports to be only Army management because its decision was to make "no change" (Hopkins, 1998a, 1998b). For a wider audience, the Army would have to explain the impact of the PFS on total risk at Anniston, which would require combining the results of the PFS risk assessment with information from the Anniston Phase 1 QRA, the Anniston HRA, the TOCDF Phase 2 QRA, the TOCDF QRA for the PFS, and the TOCDF HE for the PFS. The committee believes that the lack of a single document containing clear, graphical, and quantitative answers to basic questions about PFS risks is likely to interfere with effective decision making and is a crucial lapse in terms of enabling the public to follow the process or influence the results.

The Anniston Letter Report

The Army prepared a draft Anniston Letter Report (U.S. Army, 1998d) summarizing the results of the PFS risk assessment (U.S. Army, 1998a) to communicate the risks and benefits of carbon filters at Anniston to the public (U.S. Army, 1998f). The draft Anniston Letter Report shows that the Army has attempted to present the basis for its decision by explaining the difficulties in reconciling differing values, concerns, and perceptions in language more accessible to the public. The Anniston Letter Report also explains that the PMCD is ultimately responsible for the decision and outlines the process by which the PMCD intends to solicit opinions and comments from interested stakeholders.

The key findings in the Anniston summary PFS risk assessment (U.S. Army, 1998a) and the Anniston Letter Report (U.S. Army, 1998d) differ somewhat in content and presentation. The findings from the letter are reproduced verbatim in Table 5-1 (U.S. Army, 1998a, 1998d). The findings from the analogous Umatilla reports are essentially the same as those for Anniston (U.S. Army, 1998b, 1998g). The reports for the Pine Bluff facility were not available at the time this report was written.

The Anniston Letter Report cites the possibility of delays caused by permit modifications to remove the PFS and the consequent increase in storage-related risk as the main reasons for leaving the carbon filters in the current design at Anniston. However, the magnitude of the increased storage risk is dependent on the length of the delays. The increased risk from prolonged stockpile storage has been estimated on a *per year of storage* basis (U.S. Army, 1998a). For the population 2 to 5 km from the Anniston Chemical Agent Disposal Facility, the individual public fatality risk is 1.4×10^{-5} per year; the societal public fatality risk is 2.6×10^{-2} per year. By contrast, the disposal processing risks for the same population is 3.8×10^{-8} per year (individual public fatality risk) and 1.8×10^{-5} (societal public fatality risk). Thus, the *per year* risk from storage is at least three orders of magnitude greater than the risk from disposal processing. Consequently, very short delays would increase public risks more than the total public risk from disposal. A delay of approximately one year would result in increased individual public risks of the same order of magnitude as estimated increases in individual worker fatality risk over the *entire* period of disposal processing.

CHANGE MANAGEMENT PROCESS

The PFS risk assessment reports state that the evaluations were conducted in accordance with the CMP (change management process), which is the Army's recently developed and evolving process for ensuring that community views are considered in risk management decisions (U.S. Army, 1998f). According to the CMP, the Army will include a public involvement step if a proposed change meets one or more of the following criteria:

- significant physical modifications to furnaces or the PAS

TABLE 5-1 Effect of the Carbon Filter System on Risk at the Anniston Facility

	Area of Concern	Summary of Conclusions
1.	Public Health Risk from Emissions	The disposal facility emissions are low enough to meet regulatory approval even without the PFS.
2.	Public Risk from Accidental Agent Release	The total public risk of accidental agent release would be increased from any extension of stockpile storage. Delays associated with changing the current plan to operate ANCDF [Anniston Chemical Agent Disposal Facility] with carbon filters outweigh any delays caused by the presence of the filters. The public fatality risk due to accidents during disposal is unchanged by the presence of the PFS.
3.	Worker Risk	There likely would be a small increase in worker risk if the carbon filters are included, but the risk likely could be controlled to be minimal and within acceptable limits.
4.	Environmental Risk	The PFS has no impact on the screening level ecological risk assessment.
5.	Schedule Risk	Overall, it is estimated that there could be a substantial delay if there is an attempt to change the current plan to build and operate ANCDF with the filters.
6.	Cost Risk	The PFS will cost over 60 million dollars in capital and operating costs. However, the removal of the PFS at this point could cost between 50 and 100 million dollars due to changes in disposal schedule, facility design and permit modifications.

Source: U.S. Army, 1998d.

- increase in stack-emission limits specified by the permits
- significant modifications to agent and explosive material handling operations within the two most external engineering control boundaries
- significant changes in or to major process technologies, such as incineration, pollution abatement, or explosives handling
- other physical or operational modifications determined to carry significant potential for affecting the results of the QRA or HRA

Because removing or adding carbon filters would meet several of these criteria, the Army had intended the assessment of carbon filters to be the first use of the CMP to evaluate a potential major design change. The site-specific PFS risk assessments were prepared for the public-participation phase of the CMP, when the results of each risk assessment would be openly reviewed and discussed with the facility stakeholders. Because attendance at the public meetings held to discuss the results of the PFS risk assessments was extremely poor, local stakeholders and permitting authorities are likely to be under the impression that the PFS would reduce risk. In fact, neither the potential reductions in risk to the public nor the potential increases in risk to workers from the PFS have been well characterized, and the broad uncertainties associated with the estimates of risk have not been presented.

Because one of the primary reasons for adding carbon filters was "enhancing public confidence" in baseline system technology (the other being the capture of brief increases in emissions, or puffs), the committee believes the Army should quantify and verify the risk estimates and share them with affected stakeholders. The Army should include information on the change in the composition of the flue gas with the PFS in its presentation.

The committee has consistently recommended that the Army increase its efforts at obtaining meaningful public involvement in important decisions (NRC, 1994, 1996, 1997a). In addition, in the *Risk Assessment and Management* report, the committee included several recommendations for integrating public involvement and emergency management into the Army's draft *Guide* and risk management plan (NRC, 1997a; U.S. Army, 1997a). For example, the committee made the following recommendations:

> **Recommendation 5.** The Army should develop a management plan (and include it in the *Guide*) that defines the integration of management roles, responsibilities, and communications across activities by risk management functions (e.g., operations safety, environmental protection, emergency preparedness, and public outreach).
>
> **Recommendation 6.** The Army should review and expand the current draft risk management plan to include public involvement in appropriate areas beyond the management of the change [CMP] process.
>
> **Recommendation 7.** The Army should institutionalize the management of change process developed in the *Guide*. The Army should track performance of the change process and document public involvement and public responses to decisions. The Army should use the experience to improve the change process.
>
> **Recommendation 8**. The Army should expand implementation of the risk management program to ensure that workers understand the results of risk assessments and risk management decisions.

Significant portions of the PFS evaluation were completed before the CMP was fully developed. Nevertheless, the committee feels compelled to comment on the Army's progress in developing and implementing the CMP. In the *Risk Assessment and Management* report, the committee noted that the CMP was an attempt to break new ground, and the draft *Guide*, which was not yet completed, was still missing sections that were crucial to the Army's management of change, including a means of distinguishing matters of risk assessment from matters of policy (value judgments) and an approach to integrating them that would involve the public (NRC, 1997a). The committee encouraged the Army to complete the draft *Guide*, especially Chapter 7 on public involvement, so that it could become policy. The committee has continued to monitor the Army's efforts to complete the draft *Guide* and finalize the CMP as it relates to the issue of the PFS.

The first attempt to make the draft CMP operational and to obtain public input took place in July 1997 in Anniston, Tooele, and Umatilla. At the time, the proposed CMP involved only RCRA Class 2 and 3 permit changes.[1] Prior to these meetings, neither the office personnel for local public outreach nor the public was involved in the development of the CMP (Campbell, 1998). All of the public meetings on the CMP were very poorly attended. Nevertheless, in part on the basis of these meetings, the Army and its contractor, Booz, Allen, and Hamilton, began the process of reformulating the CMP; several subsequent drafts were developed, and a document labeled "Final" was published in May 1998 (U.S. Army, 1998h). After several more drafts, the *PMCSD* [Project Manager for Chemical Stockpile Disposal] *Change Management Process Plan* was approved and published in final form in November 1998 (U.S. Army, 1998f).

The Army has been ambivalent about using the PFS evaluation to exercise the public involvement portion of the CMP. According to the *PMCSD Change Management Process Plan*, the CMP was supposed to ensure that "facility or operational changes with the potential for significant risk [are] publicly reviewed *before* PMCD [the Army] decides whether the change should be made" [italic emphasis added] (U.S. Army, 1998f). The Army's ambivalence about involving the public in the PFS decision was partly a reflection of the Army's belief that keeping the PFS would not entail significant risk (Evans and Hopkins, 1998). Nevertheless, the release of the Army's Anniston and Umatilla Letter Reports summarizing the risk assessment results for the PFS took place in September and October, respectively, and was closely followed by attempts to hold "public outreach availability sessions" (Hopkins, 1998c).

The Army had already made its position clear with regard to the PFS in the letter reports, and the public hearings were held only to implement the public involvement portion of the CMP (U.S. Army, 1998d; 1998g; and 1998i). According to the CMP, if significant public opposition had been expressed, the Army would have revisited the PFS issue. Otherwise, the Army's recommendation to retain the PFS would become a matter of record (Hopkins, 1998c).

Very few, if any, members of the public attended the "public outreach availability sessions" in Anniston or Umatilla (Hopkins, 1998c). The committee considers the Army's public outreach efforts in the PFS decisions a *pro forma* exercise of the public outreach component of the CMP. The exercise did, however, reveal several shortcomings of the CMP. First, public involvement must be initiated much earlier in the process for evaluating change. For example, public involvement could have been used to help frame the questions to be answered during the PFS risk evaluation process.

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[1] RCRA Class 3 permit changes involve major physical modifications to the facility; RCRA Class 2 permit changes pertain to less significant physical changes or operational changes.

Second, the public involvement process should allow for public input prior to the Army reaching a decision on process changes, even if initial assessments indicate that the decision will be to make "no change." Once the Army had made the initial decision, significant public input during the evaluation process was no longer possible, and the Army was left in a quandary as to how public involvement and the CMP should be carried out. In effect, the CMP process was bypassed, and the decision was made by the Army, based on input from the Alabama Department of Environmental Management.

A credible public involvement process that engenders public trust requires clear guidelines for initiating the process; and the guidelines must be followed, not circumvented by executive decision. Despite the committee's recommendations and the Army's public statements acknowledging the importance of the CMP and public outreach, the Army made no meaningful attempt to use the CMP in the PFS decision.

FUTURE EVALUATIONS OF MAJOR DESIGN CHANGES

Future risk assessments of major design changes should be either probabilistic to capture the range of uncertainty associated with estimates or, if based on bounding estimates, should include both worst-case estimates and reasonable performance assumptions for reducing emissions of SOPCs. Assessments should include the incremental increase in risk to on-site workers from ordinary industrial and agent-related accidents. The following basic questions should be addressed:

1. What is the baseline risk of storing chemical agents and munitions in the community?
2. What is the risk, in terms of both probability and consequences, of incinerating chemical agents and munitions to residents and workers at the points of maximum acute and chronic exposure?
3. How does the risk change with the proposed modification (e.g., addition or removal of the PFS)?
4. How do the risks change if the proposed modification involves a change in the permitted configuration that causes a six-month delay in processing chemical agents and munitions? A year's delay?
5. How do all of these risks compare with accepted thresholds and background risks?
6. What are the risk-benefit trade-offs of the proposed modification in terms of worker risk, public risk, cost, and schedule?
7. What are the major factors contributing to risks and can they be mitigated?

Answers to many of these questions can be found in the Anniston and Umatilla PFS risk assessments and their supporting documents. However, for these assessments to be useful to anyone except the most knowledgeable participants in the Chemical Stockpile Disposal Program, the key information must be available in an integrated presentation. Neither the public nor the Stockpile Committee has sufficient resources to extract the necessary information from the raw data. Hence, the technical analyses supporting results of the risk assessments were not scrutinized for this report. Risk evaluations should also include independent peer reviews, as the Stockpile Committee has recommended (NRC, 1997a):

> **Recommendation 2.** . . . The Army should continue to obtain interactive, independent expert reviews of all site-specific risk assessments.

Given the potential risks and benefits from carbon filters, a more quantitative, peer-reviewed risk analysis should be done to support future decisions. Without a clear understanding of the nature and magnitude of the risks to human health and the environment, including a comprehensive evaluation of worker risks and how they can be controlled, no fully informed decision can be made about the overall value of the PFS. If the increased risk to on-site workers is found to be substantial, the Army should consider making design modifications, as long as they do not substantially increase overall worker risk or public risk, including the risk of storage during a prolonged delay.

The Army could consider installing the carbon filter units in accordance with current design and permitting requirements but not loading the filter elements. A PFS without the HEPA filters and activated carbon would be simply an elaborate piece of duct work that would minimize or eliminate the risks associated with operating the PFS, as well as the cost increases and schedule delays associated with removing the PFS. Leaving the PFS in place without the filter elements is one option that could be offered for consideration to the Citizens Advisory Commission at each site where permits have already been issued. The Army can still perform meaningful risk assessments and present the results to the public.

SUMMARY

The concepts outlined in the recent CMP Plan, the CMP Public Involvement Plan, and the two Letter Reports on the PFS represent positive steps in the Army's outreach and risk management programs (U.S. Army, 1998f, 1998i, 1998d, 1998g). However, the Army has not demonstrated an effective means of involving the public in its risk management process and has not successfully implemented the CMP.

A successful public outreach program requires sharing timely, accurate, useful information with affected stakeholders as a basis for informed public review and comment. Several Army technical reports have been drafted on the estimated health effects to workers and residents of installing and operating carbon filters at Anniston, Umatilla, and Pine Bluff. The Stockpile Committee is hesitant, however, about commenting on the details and conclusions of these current risk assessment reports because they are not freestanding documents and are not complete. The Army will have to provide a careful assessment of worker risk, as well as an independent technical review of the underlying PFS HRA and QRA reports to meet scientific standards and present a defensible case to the public. A complete technical review would include all risk assessments completed to date (including the Tooele HRA, which was completed under contract to the State of Utah [Utah DSHW, 1996] and other assessments done to meet regulatory requirements). The Tooele QRA has already undergone extensive independent review and does not require further assessment, although new QRA reports should reflect any updated methodologies or data that have since become available.

Conceptually, the committee agrees with the Army's decision to proceed with the current designs at Anniston and Umatilla and not to alter the operating configurations of JACADS and the TOCDF. Removing or adding carbon filters at this point would most likely cause delays that would increase the risk to workers and the public from prolonged storage of the stockpile. To mitigate the potential adverse consequences of adding carbon filters at Anniston and Umatilla, worker risk should be evaluated quickly and managed effectively.

Because of the incomplete and fragmented nature of the PFS reports and the lengthy period of evaluation prior to communicating the results to local stakeholders, it would be difficult for the Army to initiate a meaningful public involvement program on the issue now without causing delays in the processing of munitions. Proceeding without meaningful public involvement, however, would be contrary to the spirit and intent of the Army's stated public goals as expressed in the CMP (U.S. Army, 1998f) and the Anniston Letter Report (U.S. Army, 1998d).

If clear, technically adequate information can be made public quickly through the CMP or by other means, Citizens Advisory Commissions and other interested parties at each site would have an opportunity to make substantive comments while the technical data and results are undergoing review and revision. Consistent with the philosophy in the CMP, public concerns could then be formally addressed in the final PFS risk assessment reports. To further the overall goal of minimizing risk to nearby residents and workers, parallel technical and public reviews should be conducted to minimize delays that could increase the risk of continued storage. The Army can still perform meaningful risk assessments and present the results to the public.

The CMP highlights the difficult trade-offs that must be made in risk management decisions involving the disposal of chemical agents and munitions. The ongoing storage of agents and munitions poses the greatest overall risk to nearby residents and the environment; operating and maintenance requirements for the PFS, however, may add to the industrial risk to on-site workers.

Depending on the nature and extent of delays incurred by removing the carbon filters from the current designs and the resulting permit modifications, the PAS configurations for baseline incineration system facilities (with or without carbon filters) should not be changed unless (1) local stakeholders specifically request it, or worker risk is determined to be unacceptably high, and (2) the applicable regulatory agencies can expedite approval for permit modifications to minimize delays in processing the munitions. Accurate, integrated assessments of the worker and off-site risks associated with various PAS configurations would assure the public that prudent decisions are being made.

6

Findings and Recommendations

The estimated concentrations and emission rates of SOPCs from chemical agent incinerator operations developed during the permitting processes for the Anniston Chemical Agent Disposal Facility and the Umatilla Chemical Agent Disposal Facility were below the thresholds of regulatory concern, whether or not a passive carbon filtration system (like the PFS) was included in the facility design. Therefore, the committee considers PFS to be risk neutral to off-site populations.

The addition of a PFS to the PAS would probably reduce the already low emissions of some SOPCs during normal, transient, and upset operating conditions. However, a PFS would also increase worker risk by making the facility more complex and by introducing new scenarios for potential facility upsets and failures. The extent of the increase in worker risk is not clear because all of the applicable risk evaluations (e.g., Phase 2 QRAs and health, safety, and environmental evaluations) and resulting risk mitigation measures have not yet been completed. Preliminary assessments, however, indicate that the increase in worker risk would be small.

Significant changes in permitted facility designs require permit modifications, which could cause substantial delays. Because risk analyses consistently indicate that the storage risk to the public and workers is much greater than the processing risk, changing the permitted configuration at any stockpile site is likely to increase the overall risk by delaying destruction of the stockpile.

Finding 1a. The reported emitted concentrations of SOPCs measured during trial burns at the JACADS and TOCDF incinerators are among the lowest reported to the EPA. TOCDF emissions are the lowest, or at least one of the lowest, in dioxins, mercury, cadmium, lead, arsenic, beryllium, and chromium. The reported emissions of some SOPCs were based on the analytical detection limit for the constituent, which means the actual concentration could be much lower than the reported concentration. Maximum emitted concentrations from JACADS were used for the HRAs for other baseline facilities to ensure that estimates of risks would be conservative.

Finding 1b. In 1992 and 1994, the NRC recommended that the Army investigate using carbon filters for two purposes: (1) to contain transient stack emissions or accidental releases of agent and (2) to increase public confidence in incineration. Activated carbon filters in use at several large incinerators in Europe meet very stringent regulations on emissions of chlorinated dioxins/furans and are considered to be the state-of-the-art technology for this purpose. Based on preliminary design evaluations, activated carbon in the PFS of the Army's baseline incineration system is likely to have sufficient adsorption capacity to reduce emitted concentrations of dioxins, furans, HD, VX, and GB for more than a year of normal operations before the activated carbon would have to be replaced. The activated carbon would also have the capacity to adsorb a chemical agent in case of a major upset; however, a major upset would necessitate the immediate replacement of the activated carbon.

The addition of carbon filters to a baseline incineration PAS does not appear to reduce the health risk to the surrounding population substantially because the health risk is already small (see Finding 1a). Nevertheless, reinforcing public and worker confidence is an important goal.

Recommendation 1. The Army should only consider removing the carbon filtration system from the permitted designs of the Anniston, Umatilla, or Pine Bluff facilities if, after a thorough implementation of the change management process to ensure meaningful public involvement, the public supports that decision.

Finding 2. Based on the evaluation of preliminary PFS design alternatives, an effective design for the PFS is feasible. Operating facilities in several countries now have significant experience in the design and operation of activated carbon filters.

Recommendation 2. The Army should take advantage of the experience of other users of carbon filters through appropriate consultation.

Finding 3. The Army has evaluated the implications of adding or removing passive carbon filter systems to the baseline incineration systems at the Tooele, Anniston, and Umatilla disposal facilities. Some of the impacts on risk to public health from stack emissions were evaluated by comparing the HRAs for the existing baseline facilities to estimates of the upper bound of public health risk posed by the addition of the PFS. However, the potential reductions in public health risk were not estimated, and the evaluations of impacts to off-site populations were incomplete.

An estimate of the impact on risk of accidents leading to agent-related public fatalities was made by expanding the Anniston and Umatilla Phase 1 QRAs to consider the addition of the PFS. The impact of the PFS on worker risk, which is not evaluated in the Anniston and Umatilla Phase 1 QRAs, was estimated by extrapolating the Tooele Phase 2 QRA results (which does include worker risk) to these other facilities. The Phase 1 QRAs for the Anniston and Umatilla facilities were also used to estimate increases in risk to the public from extended storage of the stockpile due to the PFS. Thus, the QRA evaluations completed to date are initial estimates of the magnitude of increased risk to the public from accidental releases of agent resulting from the addition of the PFS, but they are not complete evaluations of worker risk. Moreover, the range of potential delays to stockpile destruction caused by permit modifications and physical changes to the current site-specific baseline incineration configurations has not been defined.

Based on these estimates, the Army concluded that "[the] current plan to install and operate the PFS at the ANCDF [Anniston] and the UMCDF [Umatilla] remains the best course of action for maximizing human health and environmental protection," and that the TOCDF should continue to operate without a PFS. The decision to continue with the current configurations at permitted facilities eliminates increases in risks to the public and workers from potential delays in stockpile destruction caused by facility modifications or permit changes. Although worker risk from current PFS configurations is uncertain, based on the available risk estimates and projected schedules, the committee concurs with the Army's conclusion.

Recommendation 3. To minimize increased risks to off-site populations and on-site workers from delays in stockpile destruction, the Army should proceed with the current configurations, which include carbon filtration systems at Anniston and Umatilla, and should continue operations at Tooele, which does not have a carbon filtration system.

Finding 4. Only the Phase 1 Anniston and Umatilla QRAs have been completed. The risk of acute hazards to workers, probably the receptors at greatest risk from a mishap involving the PFS, has not been adequately characterized. Early initiation of the Phase 2 QRAs could identify these risks while facility design and construction are in progress and give the Army greater flexibility to modify facility designs and operating procedures, if necessary.

Recommendation 4a. The site-specific Phase 2 QRAs for Anniston, Umatilla, and Pine Bluff, which would identify and analyze specific failure modes, should include a complete evaluation of worker risk associated with the addition of the pollution abatement system filter system. The Phase 2 QRAs for each site should be initiated as soon as possible and should be completed and reviewed by independent technical experts before systemization of the facilities at Anniston, Umatilla, and Pine Bluff is completed.

Recommendation 4b. A risk management plan should be developed to minimize worker risk during the operation and maintenance of the pollution abatement system filter systems. The evaluation of operating and maintenance risks should include the operational experience of similar systems. If the increased risk to on-site workers is found to be substantial, the Army should consider making modifications, as long as they do not substantially increase overall worker or public risk from prolonged storage.

Finding 5. If increased worker risks and hazards are identified, it is not clear what steps the Army would take to mitigate them. Nor does the Army have a clear decision basis for balancing reductions in public risk and increases in worker risk.

Recommendation 5. The Army should clarify to the public and facility workers the risk management actions that would be taken if increased worker risks are identified. The Army should also clarify the decision basis for balancing reductions in public risk against increases in worker risk while fulfilling its mandate to protect both workers and the public.

Finding 6. The PFS was assumed to have no effect on concentrations of SOPCs in the HRA calculations for Anniston and Umatilla. The effects of SOPCs emitted from the stacks at these facilities have been estimated to be below the thresholds of regulatory concern without the benefit of the PFS. However, changes from installing a PFS have not been determined in a way that facilitates quantitative comparisons.

Recommendation 6. Future health risk assessments should include estimates of emitted and ambient concentrations of SOPCs, with and without the PFS, for all substances that contribute significantly to the overall risk. Because PFS performance cannot be based on actual measurements, the analysis should consider the implications of reducing emissions to both the method detection limit and the levels indicated by engineering calculations, including quantitative evaluations of the uncertainties associated with each risk estimate. The results, including the acute and latent risks, should be reviewed by independent technical experts. The results should then be presented in a way that facilitates public input to decision making.

Finding 7. Because of the length of time required to complete the preliminary PFS risk assessment, the fact that this evaluation is still incomplete, and the status of construction activities at Anniston and Umatilla, meaningful public involvement in the decision to include the PFS at these sites is no longer possible. The CMP Plan and the CMP Public Involvement Outreach Plan were not effectively implemented during the Army's analysis of the PFS. The lack of public involvement in this process represents a lost opportunity for the Army to develop its CMP and to implement the CMP public outreach process.

Recommendation 7a. The health risk assessment and quantitative risk assessment for Pine Bluff should be completed as quickly as possible and communicated to the public in a timely manner so that there can be meaningful public involvement in the decision process to retain or remove the carbon filter system. The risk assessments should be subject to independent expert review and the findings incorporated into the decision-making process.

Recommendation 7b. The Army should continue to refine its change management process and the change management process public involvement plan. Public involvement should be an integral part of future evaluations of the pollution abatement system filter system, especially at Pine Bluff. The committee repeats its recommendation that the Army involve the public meaningfully in the Chemical Stockpile Disposal Program as a whole.

References

Aslander, O. 1987. The Swedish Dioxin Moratorium. Pp. 41–50 in Proceedings of the ASCE Dioxin Symposium. Reston, Va.: American Society of Civil Engineering.

Baier, R.W., and S.W. Weller. 1967. Catalytic and thermal decomposition of isopropyl methyl fluorophosphonate. Industrial Engineering and Chemical Process Design and Development 6(3): 380–385.

Brueggendick, H., and F.G. Pohl. 1993. Operating Experience with STEAGS Activated Carbon Processes -a/c/t®- in European Waste Incineration Plants. Pp. 787–794 in Proceedings of the Annual International Pittsburgh Coal Conference. Pittsburgh, Pa.: University of Pittsburgh, School of Engineering, Center for Energy Research.

Campbell, C. 1998. Interview of Craig Campbell, Tooele Outreach Office, by Alvin Mushkatel, member of the Committee on Review and Evaluation of the Army Chemical Stockpile Disposal Program, April 18, 1998.

Clarke, M.J. 1991. A review of activated carbon technologies for reducing MSW [municipal solid waste] incinerator emissions. Pp. 975–994 in Proceedings of the International Conference on Municipal Waste Combustion. Pittsburgh, Pa.: Air and Waste Management Association.

Cohen, A.C., Jr. 1959. Simplified estimators for the normal distribution when samples are singly censored or truncated. Technometrics 1(3): 217–237.

EG&G (EG&G Defense Materials, Inc.). 1997. Tooele Chemical Agent Disposal Facility (TOCDF), RCRA Agent Trial Burn Report for the Liquid Incinerator System #2 [LIC/GB]. Prepared for Southern Research Institute, October 27, 1997. Tooele, Utah: EG&G Defense Materials, Inc.

EPA (Environmental Protection Agency). 1989. Interim Procedures for Estimating Risks Associated with Exposures to Mixtures of Chlorinated Dibenzo-p-Dioxins and –Dibenzofurans (CDDs and CDFs): 1989 Update. EPA/625/3-89/016. Washington, D.C.: Environmental Protection Agency, Risk Assessment Forum.

EPA. 1991. Hazardous Waste Burned in Boilers and Industrial Furnaces. 40 CFR 266, Subpart H. Effective August 21, 1991. Washington, D.C.: Government Printing Office.

EPA. 1994. Standards of Performance for New Stationary Sources: Municipal Waste Combustors. Federal Register 49: 49198 (September 20, 1994). Washington, D.C.: Government Printing Office.

EPA. 1996. Revised Standards for Hazardous Waste Combustors: Hazardous Waste Combustors Maximum Achievable Emissions Control Technology Proposal. (Proposed Rule) EPA Office of Solid Waste. Federal Register 61: 17358–17536, April 19, 1996. Washington, D.C.: Government Printing Office.

EPA. 1997a. Draft Report of Revisions to Hazardous Waste Combustor Database Based on Public Comments Submitted in Response to the January 7, 1997, Notice of Data Availability. Federal Register 62: 24213 (May 2, 1997). Washington, D.C.: Government Printing Office.

EPA. 1997b. Test Methods for Evaluating Solid Waste (SW-846). Final Updates I, II, IIA, IIB, and III. November 1986; revised May 1997. Washington, D.C.: U. S. Environmental Protection Agency, EPA Office of Solid Waste.

EPA. 1997c. Revised Technical Standards for Hazardous Waste Combustion Facilities (Proposed Rule: May 2, 1997: Federal Register 62: 5818-5819; per 40 CFR 60, et al. (Appendix A). Washington, D.C.: U.S. Government Printing Office, Office of Solid Waste.

EPA. 1997d. Draft Technical Support Document for the Hazardous Waste Combustors Maximum Achievable Emissions Control Technology (MACT) Standards (Notice of Data Availability, Volume 1: MACT Evaluation Based on Revised Database) April 1997. Washington, D.C.: U. S. Environmental Protection Agency, Office of Solid Waste and Emergency Response.

Evans, M., and M. Hopkins. 1998. Pollution abatement system filter system. Briefing to the Committee on Review and Evaluation of the Army Chemical Stockpile Disposal Program, Washington, D.C., National Research Council, June 24, 1998.

Fouhy, K. 1992. Legislation scrubs fluegas emissions. Chemical Engineering 99(6): 31–35.

Grant, R., and M. Manes. 1987. Adsorption of binary hydrocarbon gas mixtures on activated carbon. Industrial Engineering Chemistry Fundamentals 5: 490–497.

Hahn, G.J. 1970. Statistical intervals for a normal population. Part II: formulas, assumptions, some derivations. Journal of Quality Technology 2(4): 195–206.

Hahn, G.J., and W.Q. Meeker. 1991. Statistical Intervals: A Guide for Practitioners. New York: John Wiley and Sons.

Hartenstein, H.-U. 1992. A fixed bed activated coke/carbon filter as a final gas cleaning stage retrofitted for a hazardous waste incinerator plant—the first 6 months of operating experience. Paper 92-48.C4. Pittsburgh, Pa.: Air and Waste Management Association.

Hartenstein, H.-U. 1993. Activated carbon for flue-gas polishing of MWIs (municipal waste incinerators). Pp. 87–105 in Proceedings of an International Specialty Conference, VIP-32.

Hartenstein, H.-U. 1994. The retrofit of the MWC ROTEB in Rotterdam, Holland, with a modern flue gas cleaning system including an activated char adsorption unit. Pp. 1–10 in National Waste Processing Conference Proceedings, Boston, Massachusetts, June 5–8, 1994. New York: American Society of Mechanical Engineers. Pittsburgh, Pa.: Air and Waste Management Association.

Hass, C.N., and P.A. Sheff. 1990. Estimation of averages in truncated samples. Environmental Science and Technology 24: 912–929.

Hopkins, M. 1998a. PAS filter system (PFS) analysis. Briefing by Martin Hopkins, Operations Team, Project Manager for Chemical Stockpile Disposal, to the Committee on Review and Evaluation of the Army Chemical Stockpile Disposal Program, September 23, 1998, Woods Hole, Massachusetts.

Hopkins, M. 1998b. Bringing the PAS filter evaluation to closure. Briefing by Martin Hopkins, Operations Team, Project Manager for Chemical Stockpile Disposal, to the Committee on Review and Evaluation of the Army Chemical Stockpile Disposal Program, September 23, 1998, Woods Hole, Massachusetts.

Hopkins, M. 1998c. Teleconference between Martin Hopkins, Operations Team, Project Manager for Chemical Stockpile Disposal, with the Committee on Review and Evaluation of the Army Chemical Stockpile Disposal Program carbon filter working group, November 2, 1998.

Karwacki, C.J., J.J. Mahle, J.H. Buchanan, T.E. Rosso, and L.C. Buettner. 1998. Summary report on agent offgassing from activated carbon filters. Aberdeen Proving Ground, Md.: U.S. Army Edgewood Research, Development and Engineering Center, Chemical Biological Filtration Team.

Mitretek Systems. 1996. Evaluation of the Pollution Abatement Filter System for Chemical Agent Disposal Facilities. Methodology for Evaluating Risks. MTR-1996-3. December 1996. Aberdeen Proving Ground, Md.: U.S. Army Program Manager for Chemical Demilitarization.

Mitretek Systems. 1997. Pollution Abatement System Carbon Filter Simulation Model Development. January 1997. Aberdeen Proving Ground, Md.: U.S. Army Program Manager for Chemical Demilitarization.

National Safety Council. 1997. Accident Facts, 1997 Edition. Itasca, Ill.: National Safety Council.

New York State Legislative Commission on Solid Waste Management. 1986. New York Moratorium. Albany, N.Y.: New York State.

NORIT. 1996. NORIT Americas Inc., Activated Carbons for the Removal of Mercury and Dioxin from Flue Gas. Paper obtained at Norit booth at ASME SWPD, 4/1/96. Norit Americas Inc., 1050 Crown Pointe Parkway, Suite 1500, Atlanta, Georgia 30338. (800) 641-9245.

NRC (National Research Council). 1984. Disposal of Chemical Munitions and Agents. Committee on Demilitarizing Chemical Munitions and Agents, Board on Army Science and Technology. Washington, D.C.: National Academy Press.

NRC. 1991. Summary of Workshop on the Pollution Abatement System of the Chemical Agent Demilitarization System. May 15–17, 1991. Committee on Review and Evaluation of the Army Chemical Stockpile Disposal Program, Board on Army Science and Technology. Washington, D.C.: National Research Council Board on Army Science and Technology.

NRC. 1992. Letter report on review of the choice and status of incineration for destruction of the chemical stockpile. June 15, 1992. Committee on Review and Evaluation of the Army Chemical Stockpile Disposal Program, Board on Army Science and Technology. Washington, D.C.: National Research Council Board on Army Science and Technology.

NRC. 1993. Alternative Technologies for the Destruction of Chemical Agents and Munitions. Committee on Alternative Chemical Demilitarization Technologies, Board on Army Science and Technology. Washington, D.C.: National Academy Press.

NRC. 1994. Recommendations for the Disposal of Chemical Agents and Munitions. Committee on Review and Evaluation of the Army Chemical Stockpile Disposal Program, Board on Army Science and Technology. Washington, D.C.: National Academy Press.

NRC. 1996. Public Involvement and the Army Chemical Stockpile Disposal Program (Letter Report, October 1996). Committee on Review and Evaluation of the Army Chemical Stockpile Disposal Program, Board on Army Science and Technology. Washington, D.C.: National Research Council Board on Army Science and Technology.

NRC. 1997a. Risk Assessment and Management at Deseret Chemical Depot and the Tooele Chemical Agent Disposal Facility. Committee on Review and Evaluation of the Army Chemical Stockpile Disposal Program, Board on Army Science and Technology. Washington, D.C.: National Academy Press.

NRC. 1997b. Review of Acute Human-Toxicity Estimates for Selected Chemical-Warfare Agents. Committee on Toxicology, Board on Environmental Studies and Toxicology. Washington, D.C.: National Academy Press.

Parsons. 1995. Value Engineering Report. PFS Alternative Configuration Study. Prepared by the Ralph M. Parsons Company (Task B-11G1) for the U.S. Army Program Manager for Chemical Demilitarization, September 1995. Aberdeen Proving Ground, Md.: U.S. Army Program Manager for Chemical Demilitarization.

Prakash, J., N. Nirmalakhandan, and R.E. Speece. 1994. Prediction of activated carbon adsorption isotherms for organic vapors. Environmental Science and Technology 28: 1403–1409.

PMCD (Program Manager for Chemical Demilitarization). 1989. 5X Demonstration Review and Decontamination. Briefings by Barbara A. Kuryk, chief, Process Development Branch, to Vernon N. Houk, assistant surgeon general and director, Center for Environmental Health and Injury Control, March 27, 1989.

Ruthven, D.M. 1984. Principles of Adsorption and Adsorption Processes. New York: John Wiley and Sons.

Schüller, H.-P. 1994. Nachrüstung eines Gegenstromadsorbers. Pp. 536–543 in Thermische Abfallbehandlung by Karl Joachim Thomé-Kozmiensky. Berlin: EF-Verlag Für Energie- und Umwelttechnik GMBH**.**

Taylor, J.K. 1990. Statistical Techniques for Data Analysis. Chelsea, Mich.: Lewis Publishing.

Tien, Chi. 1995. Adsorption Calculations and Modeling. Boston: Butterworth Heinemann.

U.S. Army. 1994a. Evaluation of National Research Council Furnace Pollution Abatement System, Subtask No.1 (June 24, 1994). Aberdeen Proving Ground, Md.: U.S. Army Program Manager for Chemical Demilitarization.

U.S. Army. 1994b. Evaluation of Potential Applications of Pollution Abatement Systems for Chemical Demilitarization Facilities (June 24, 1994). Aberdeen Proving Ground, Md.: U.S. Army Program Manager for Chemical Demilitarization.

U.S. Army. 1994c. Comparison of Alternative Pollution Abatement Systems for New and Existing Chemical Demilitarization Facilities (June 24, 1994). Aberdeen Proving Ground, Md.: U.S. Army Program Manager for Chemical Demilitarization.

U.S. Army. 1994d. U.S. Army's Alternative Demilitarization Technology Report to Congress, April 11, 1994. Aberdeen Proving Ground, Md.: U.S. Army Program Manager for Chemical Demilitarization.

U.S. Army. 1996a. Tooele Chemical Agent Disposal Facility Quantitative Risk Assessment. SAIC-96/2600. Aberdeen Proving Ground, Md.: U.S. Army Program Manager for Chemical Demilitarization.

U.S. Army. 1996b. Umatilla Chemical Agent Disposal Facility Phase 1 Quantitative Risk Assessment. Aberdeen Proving Ground, Md.: U.S. Army Program Manager for Chemical Demilitarization.

U.S. Army. 1997a. A Guide to Risk Management Policy and Activities. January 1997. 176-009. Aberdeen Proving Ground, Md.: U.S. Army Program Manager for Chemical Demilitarization.

U.S. Army. 1997b. Specification for Pollution Abatement System (PAS) Filter Units, CSDP/Specs/F2B/UMrDF. (In accordance with ECP UM-193). Aberdeen Proving Ground, Md.: U.S. Army Program Manager for Chemical Demilitarization.

U.S. Army. 1997c. Anniston Chemical Agent Disposal Facility Phase 1 Quantitative Risk Assessment. Aberdeen Proving Ground, Md.: U.S. Army Program Manager for Chemical Demilitarization.

U.S. Army. 1998a. Risk Assessment of the Pollution Abatement Filter System for the Anniston Chemical Agent Disposal Facility (ANCDF). Prepared by Mitretek Systems. August 1998. Aberdeen Proving Ground, Md.: U.S. Army Program Manager for Chemical Demilitarization.

U.S. Army. 1998b. Draft Risk Assessment of the Pollution Abatement Filter System for the Umatilla Chemical Agent Disposal Facility (UMCDF). Prepared by Mitretek Systems. May 1998. Aberdeen Proving Ground, Md.: U.S. Army Program Manager for Chemical Demilitarization.

U.S. Army. 1998c. Chemical Stockpile Disposal Program, UMCDF Alternative DFS Concepts. Contract DACA 87-66-C-0084. Prepared by Parsons Company. Aberdeen Proving Ground, Md.: U.S. Army Program Manager for Chemical Demilitarization.

U.S. Army. 1998d. Letter Report from the Program Manager for Chemical Demilitarization—Implementing the Change Management Process: Validation of the Anniston Chemical Agent Disposal Facility Pollution Abatement Filter System Implementation, September 1998. Aberdeen Proving Ground, Md.: U.S. Army Program Manager for Chemical Demilitarization.

U.S. Army. 1998e. Evaluation of the Pollution Abatement Filter System for Chemical Agent Disposal Facilities. Methodology for Evaluating Risks. January 1998. MTR-1996-3. Aberdeen Proving Ground, Md.: U.S. Army Program Manager for Chemical Demilitarization.

U.S. Army. 1998f. PMCSD Change Management Process Plan. November 1998 Final; July 1998 Draft. Prepared by the U.S. Army Program Manager for Chemical Demilitarization. Aberdeen Proving Ground, Md.: U.S. Army Program Manager for Chemical Demilitarization.

U.S. Army. 1998g. Letter Report from the Program Manager for Chemical Demilitarization—Umatilla Chemical Agent Disposal Facility Pollution Abatement Filter System Summary of Risk Assessment Results, October 1998. Aberdeen Proving Ground, Md.: U.S. Army Program Manager for Chemical Demilitarization.

U.S. Army. 1998h. The Change Management Process to Accompany the Guide to Risk Management Policy and Activities, May 1998. Aberdeen Proving Ground, Md.: U.S. Army Program Manager for Chemical Demilitarization.

U.S. Army. 1998i. Public Involvement Plan for the Chemical Stockpile Disposal Program Change Management Process. (Undated). Aberdeen Proving Ground, Md.: U.S. Army Program Manager for Chemical Demilitarization.

Utah DSHW (Division of Solid and Hazardous Waste). 1996. Tooele Chemical Demilitarization Facility Screening Risk Assessment. No. UT5210090002. Salt Lake City, Utah: Department of Environmental Quality.

Ward, R. 1998. Personal communication from J. Richard Ward, Chief Scientist, Product Manager for Alternative Technologies and Approaches, to Walter May, member of the Committee on Review and Evaluation of the Army Chemical Stockpile Disposal Program, November 9, 1998.

Appendices

Appendix A

Reports of the Committee on Review and Evaluation of the Army Chemical Stockpile Disposal Program (Stockpile Committee)

Comments on Operational Verification Test and Evaluation Master Plan for the Johnston Atoll Chemical Agent Disposal System (JACADS). 1989.

Demilitarization of Chemical Weapons: On-Site Handling of Munitions. 1989.

Demilitarization of Chemical Weapons: Cryofracture. 1989.

Letter report on workshop on the pollution abatement system of the chemical agent demilitarization system. May 1991.

Letter report on siting of a cryofracture chemical stockpile facility. August 1991.

Letter report commenting on proposed cryofracture program testing. August 1991.

Letter report on review of the MITRE report: Evaluation of the GB Rocket Campaign: Johnston Atoll Chemical Agent Disposal System Operational Verification Testing, dated May 1991. September 1991.

Letter report on review of the choice and status of incineration for destruction of the chemical stockpile. June 1992.

Letter report to recommend specific actions to further enhance the CSDP [Chemical Stockpile Disposal Program] risk management process. January 1993.

Recommendations for the Disposal of Chemical Agents and Munitions. 1994.

Review of Monitoring Activities within the Army Chemical Stockpile Disposal Program. 1994.

Evaluation of the Johnston Atoll Chemical Agent Disposal System Operational Verification Testing: Part I, July 1993. Part II, April 1994.

Evaluation of the Army's Draft Assessment Criteria to Aid in the Selection of Alternative Technologies for Chemical Demilitarization. December 1995.

Review of Systemization of the Tooele Chemical Agent Disposal Facility. 1996.

Public Involvement and the Army Chemical Stockpile Disposal Program (Letter Report). October 1996.

Risk Assessment and Management at Deseret Chemical Depot and the Tooele Chemical Agent Disposal Facility. 1997.

Using Supercritical Water Oxidation to Treat Hydrolysate from VX Neutralization. 1998.

Appendix B

Consolidated Exhaust Gas Characteristics for the JACADS and TOCDF Baseline Incineration Systems

Emissions test results were originally reported in the units required by the cognizant agencies at the time. Over time, the reporting units have changed and are now different for each facility. Consequently, direct comparisons and meaningful summaries require converting results into common units. The information in this appendix is standardized to Environmental Protection Agency (EPA) reference conditions (68°F for temperature; 760 mm Hg for pressure; 0 percent for moisture; and 7 percent for residual oxygen content) and conventional EPA regulatory units (ppm_{dv} for gaseous criteria pollutants and acid gases; mg/dsm^3 for particulates; $\mu g/dsm^3$ for individual elements; and ng/dsm^3 at 7 percent O_2 for trace organics). In developing this appendix, the committee reviewed the underlying laboratory and field reports to verify the overall accuracy of data reduction and quality assurance warnings. Reported results were compared to database values prior to standardization to eliminate transcription errors and identify errors in data reduction.

TABLE B-1 Exhaust Gas Characteristics for the JACADS and TOCDF Baseline Incineration Systems

Values are at 7% O_2 Unless Otherwise Specified	Risk-Specific Dose or Reference Air Concentration (RsD or RAC)[a] µg/m^3	Total Runs N	Nondetects Lower than Lowest Detected Values[b] N	Nondetects Lower than Lowest Detected Values[b] Detection Limit	Detected Values Only N	Detected Values Only Minimum	Detected Values Only Average	Detected Values Only Maximum	Detected Values	Average or DL ppb$_{dv}$
Exhaust Gas Characteristics										
Temperature (°F)		155			155	180	208.23	280	100%	
Flow rate (dsft^3/min)		149			149	2,275	6,043	11,493	100%	
Oxygen (%)		162			162	1.2	12.955	15.1	100%	
Moisture (%)		158			158	31.3	40.543	56.2	100%	
Combustion Quality Indicators (ppm$_{dv}$)										
Carbon monoxide		35	0		35	2	39	62	100%	
Total hydrocarbons as carbon		20	0		20	2.6	6.6	9.0	100%	
Chemical Agents (ng/dsm^3)										
GB (Sarin)		28	28	3.6	0				0%	0.0006
HD (mustard gas)		12	12	230	0				0%	0.035
VX		0	0		0					
Particulates										
PM (gr/dsm^3)		103	0		103	0.9	14.7	50	100%	
PM (gr/dscf)		103	103		103	0.0004	0.006	0.022	100%	
CAA Acid Gas HAPs (ppm$_{dv}$)										
Hydrogen chloride		60	44		16	0.01	11	44.16	27%	11,172
Chlorine gas		6	3	(0.03)	0				0%	(30.00)
CAA Trace Element HAPs (µg/dsm^3)										
Arsenic	(2.3)	49	37	(0.02)	12	1	10	42	24%	
Beryllium	(4.2)	35	0		2	0.008	0.008	0.008	6%	
Cadmium	(5.6)	35	7	(0.20)	28	0	6	50	80%	
Cobalt		9	0		9	0.08	0.23	0.8	100%	
Chromium (total)	1,000,000	46	0		41	0.22	7.4	56	89%	
Chromium (hexavalent)	(0.83)	20	13	(0.3)	7	0.34	1.8	4.2	35%	
Mercury	300	43	0		26	0.25	7.1	25	60%	0.9

TABLE B-1 Continued

Values are at 7% O_2 Unless Otherwise Specified	Risk-Specific Dose or Reference Air Concentration (RsD or RAC)[a] µg/m^3	Total Runs N	Nondetects Lower than Lowest Detected Values[b] N	Nondetects Lower than Lowest Detected Values[b] Detection Limit	Detected Values Only N	Detected Values Only Minimum	Detected Values Only Average	Detected Values Only Maximum	Detected Values	Average or DL ppb$_{dv}$
CAA Trace Element HAPs (µg/dsm^3)										
Manganese		30	0		30	0.43	233	2,105	100%	
Phosphorus		12	0		12	84	1,508	5,934	100%	
Antimony	300	35	28	(0.11)	7	0.16	1.9	5.4	20%	
Selenium		24	0		6	0.16	6.2	15	25%	
Other Trace Elements (µg/dsm^3)										
Aluminum		9	0		9	82	98	125	100%	
Barium	50,000	42	0		34	1	14	86	81%	
Boron		12	0		12	0.41	36	257	100%	
Copper		24	0		19	0.20	49	294	79%	
Potassium		20	0		14	19	1,253	5,940	70%	
Nickel	(42)	19	0		17	0.16	33	216	89%	
Lead	90	49	0		34	0.16	122	1,704	69%	
Tin		24	0	(14)	18	2.0	122	692	75%	
Thallium		35	35	(0.1)	0				0%	
Vanadium		9	9	(0.81)	0				0%	
Zinc		39	0		35	7.5	119	488	90%	
CAA Trace Organic HAPs (ng/dsm^3)										
4-aminobiphenyl		12	12	(6,074)	0				0%	(0.9)
Aniline	(14,000)	12	12	(6,074)	0				0%	(2)
Benzene	(12,000)	39	0		23	0.10	17,401	99,286	59%	5
Benzidene	(0.15)	12	12	(9,994)	0	0%				(1)
Bromoform		39	0		26	0.0002	6,234	18,230	67%	1
Bromomethane	800	21	14	(2,904)	7	3,690	5,320	6,775	33%	1
Butadiene		18	18	(11,564)	0				0%	(5)

CAA Trace Organic HAPs (ng/dsm^3)										
Carbon tetrachloride	(670)	26	18	(2,219)	8	2,823	26,655	86,623	31%	4
Chloroform	(430)	33	0		21	0.0001	8,069	42,304	64%	2
Carbon disulfide	200,000	29	23	(812)	6	14,020	25,127	47,170	21%	8
Dibenzofuran		12	12	(6,074)	0				0%	(0.9)
1,3-dichlorobenzene	10,000	12	12	(6,074)	0				0%	(1)
1,4-dichlorobenzene	10,000	12	12	(6,074)	0				0%	(1)
3,3-dichlorobenzidine		12	12	(10,974)	0				0%	(1)
Trans-1,3-dichloropropene	(0.029)	15	15	(2,219)	0				0%	(0.5)
3,3-dimethylbenzidene		12	12	(6,074)	0				0%	(0.7)
2,4-dinitrotoluene	(110)	12	12	(6,074)	0				0%	(0.8)
Ethlylene dibromide	(0.45)	12	12	(2,336)	0				0%	(0.3)
Ethylbenzene		26	19	(403)	7	521	2,016	4,250	27%	0.5
Ethyl chloride		18	18	(1,958)	0				0%	(0.7)
Bis(2-ethylhexyl)phthalate	(42,000)	15	10	(6,178)	5	10,723	94,214	272,641	33%	6
N-hexane		21	17	(1,958)	4	2,336	2,523	2,682	19%	0.7
Hexachlorobenzene (total)		12	12	(6,074)	0				0%	(0.5)
Hexachlorobutadiene		12	12	(6,074)	0				0%	(0.5)
Hexachlorocyclopentadiene	5,000	12	12	(6,074)	0				0%	(0.5)
Hexachloroethane		12	12	(6,074)	0				0%	(0.6)
Isophorone		12	12	(6,074)	0				0%	(1)
Methyl ethyl ketone	80,000	24	20	(10,572)	4	69,856	78,682	92,667	17%	26
Methylene chloride	(2,400)	39	15	(0.00006)	18	0.0004	205,026	3,088,889	55%	58
2-methylphenol [o-cresol]	50,000	15	12	(6,074)	3	77,222	164,605	264,762	20%	37
Naphthalene		12	12	(6,074)	0				0%	(1)
Nitrobenzene	800	12	12	(6,074)	0				0%	(1)
4-nitrophenol		12	12	(7,722)	0				0%	(1)
Styrene		35	19	(1,283)	16	3,947	42,283	514,734	46%	17
1,1,2,2-tetrachloroethane	(170)	27	25	(1,283)	2	2,206	2,206	2,206	7%	0.3
1,1,2-trichloroethane	(630)	18	18	(1,958)	0				0%	(0.4)
Tetrachloroethylene	(21,000)	6	3	(3,349)	3	4,277	16,135	26,476	50%	2
Toluene	300,000	36	0		24	0.00	5,960	28,234	67%	0.8
Vinyl bromide		9	9	(9,789)	0				0%	(2)
Vinylidene chloride		3	3	(2,219)	0				0%	(0.6)

TABLE B-1 Continued

	Risk-Specific Dose or Reference Air Concentration (RsD or RAC)[a]	Total Runs	Nondetects Lower than Lowest Detected Values[b]		Detected Values Only				Detected Values	Average or DL ppb_{dv}
Values are at 7% O_2 Unless Otherwise Specified	µg/m^3	N	N	Detection Limit	N	Minimum	Average	Maximum		
Caa Trace Organic HAPs (ng/dsm^3)										
Methyl chloride		12	9	(3,527)	3	29,938	1,135,218	3,088,889	25%	541
Vinyl chloride	(1,400)	26	18	(415)	8	996	5,325	21,502	31%	2
Vinyl acetate		24	22	(1,324)	2	1,497	1,497	1,497	8%	0.4
Xylene(m & p)	80,000	22	17	(434)	5	456	2,910	5,169	23%	0.7
Xylene(o)	80,000	22	0		6	934	2,066	3,676	27%	0.5
Pentachlorophenol (total)	30,000	12	12	(30,370)	0				0%	(3)
Phenol	30,000	12	7	(6,765)	5	7,125	9,632	13,440	42%	2
1,4-benzenediamine		12	12	(6,074)	0				0%	(1)
1,2,4-trichlorobenzene	20,000	12	12	(6,074)	0				0%	(0.8)
4-methylphenol [p-cresol]	50,000	3	1	(6,178)	2	51,323	943,503	1,835,683	67%	210
3-methylphenol [m-cresol]	50,000	3	0		2	2,780	12,422	22,063	67%	3
Dimethylphthalate		9	0		8	9,953	30,987	99,942	89%	4
Di-n-butylphthalate	100,000	3	0		3	10,811	31,013	66,190	100%	3
Cis-1,3-dichloropropene	(0.029)	3	3	(2,336)	0				0%	(0.5)
Other Trace Organics (ng/dsm^3)										
Acenaphthene		12	12	(6,074)	0				0%	(0.9)
Acenaphthylene		12	0		1	1,000	1,000	1,000	8%	0.05
Acetone		39			28	0.001	32,851	110,317	72%	14
Acetophenone	100,000	12	11	(6,074)	1	6,828	6,828	6,828	8%	1
2-acetylaminofluorene		12	12	(60,739)	0				0%	(7)
3-amino-9-ethycarbazole		12	12	(60,739)	0				0%	(7)
Anthracene		12	12	(6,074)	0				0%	(0.8)
Aramite		12	12	(6,074)	0				0%	(0.4)
Benzoic acid		12	12	(60,739)	0				0%	(12)
Benz(a)anthracene	(11)	12	12	(6,074)	0				0%	(0.6)
Bromodichloromethane		21	12	(2,937)	9	3,271	6,968	13,440	43%	1
Benzo(b)fluoranthene		12	12	(6,074)	0				0%	(0.6)
Benzo(j)fluoranthene		12	12	(6,074)	0				0%	(0.6)
Benzo(k)fluoranthene		12	12	(6,074)	0				0%	(0.6)
Benzo(g,h,i)perylene		12	12	(6,074)	0				0%	(0.5)
Benzo(a)pyrene	(3)	12	12	(6,074)	0				0%	(0.6)
Bromodichloromethane		12	12	(6,074)	0				0%	(0.7)

Other Trace Organics (ng/dsm^3)										
Benzyl alcohol		12	12	(6,074)	0				0%	(1)
Benzaldehyde		12	10	(6,074)	2	9,438	19,791	30,145	17%	4
Benzenethiol		12	12	(60,739)	0				0%	(13)
Biphenyl		12	12	(6,074)	0				0%	(0.9)
Bromophenyl-phenylether(4)		12	12	(6,074)	0				0%	(0.5)
Butylbenzylphthalate		12	12	(6,074)	0				0%	(0.5)
Cis-1,4-dichloro-2-butene		21	21	(1,958)	0				0%	(0.4)
Trans-1,4-dichloro-2-butene		12	12	(2,336)	0				0%	(0.4)
Cis-1,3-dichloropropene	(2.2)	31	18	(403)	13	478	140,561	898,154	42%	30
4-chloroaniline		9	9	(6,074)	0				0%	(1)
Bis(2-chloroethoxy)methane		12	12	(6,074)	0				0%	(2)
Bis(2-chloroethyl)ether	(0.16)	12	12	(6,074)	0				0%	(1)
2,2-oxybis(1-chloropropane)		12	12	(6,074)	0				0%	(2)
Chlorobenzilate		12	12	(6,074)	0				0%	(0.4)
4-chloro-3-methylphenol		12	12	(6,074)	0				0%	(1)
1-chloronaphthalene		12	12	(6,074)	0				0%	(0.9)
2-chloronaphthalene		12	12	(6,074)	0				0%	(0.9)
2-chlorophenol		12	12	(6,074)	0				0%	(1)
4-chlorophenyl-phenylether		12	12	(6,074)	0				0%	(0.7)
Chrysene		12	12	(6,074)	0				0%	(0.6)
2-chloropropane		12	12	(2,336)	0				0%	(0.7)
Chlorobenzenes (total)		29	22	(434)	7	539	2,519	3,942	24%	(0.09)
4,4-DDE		12	12	(60,739)	0				0%	(5)
Diallate		12	12	(11,681)	0				0%	(1)
Dibenz(a,h)anthracene	(0.71)	12	12	(6,074)	0				0%	(0.52)
Dibromochloropropane		12	12	(60,739)	0				0%	(6)
di-n-butyl phthalate	100,000	12	12	(6,074)	0				0%	(0.5)
1,2-dichlorobenzene	10,000	12	12	(6,074)	0				0%	(1)
2,4-dichlorophenol	3,000	12	12	(6,074)	0				0%	(0.9)
2,6-dichlorophenol		12	12	(6,074)	0				0%	(0.9)
Dichloromethane		9	3	(1,958)	6	7,201	9,353	11,797	67%	3
Dibromomethane		18	18	(2,219)	0				0%	(0.3)

TABLE B-1 Continued

Values are at 7% O_2 Unless Otherwise Specified	Risk-Specific Dose or Reference Air Concentration (RsD or RAC)[a]	Total Runs	Nondetects Lower than Lowest Detected Values[b]		Detected Values Only				Detected Values	Average or DL ppb_{dv}
	μg/m³	N	N	Detection Limit	N	Minimum	Average	Maximum		
Other Trace Organics (ng/dsm³)										
1,1-dichloroethene		25	25	(415)	0				0%	(0.1)
1,2-dichloroethene		12	12	(1,958)	0				0%	(0.5)
1,2-dichloropropane		27	25	(1,103)	2	1,047,846	1,047,846	1,047,846	7%	223
1,1-dichloroethane	(380)	18	18	(1,958)	0				0%	(0.5)
1,2-dichloroethane	(200)	15	15	(2,219)	0				0%	(0.5)
Dihydrosafrole		12	12	(7,722)	0				0%	(1)
Diethylphthalate	800,000	15	12	(6,074)	3	66,190	400,164	933,286	20%	43
P-dimethylaminoazobenzene		12	12	(6,074)	0				0%	(0.6)
7,12-dimethylbenzo(a)anthracene		12	12	(6,074)	0				0%	(0.6)
a,a-dimethylphenethyl-amine		12	12	(6,074)	0				0%	(1)
2,4-dimethylphenol		12	12	(6,074)	0				0%	(1)
Dimethylphthalate		12	11	(5,840)	1	41,456	41,456	41,456	8%	5
1,3-dinitrobenzene (m,o,p)		12	12	(6,074)	0				0%	(0.9)
4,6-dinitro-2-methylphenol		12	12	(6,074)	0				0%	(1)
2,4-dinitrophenol		12	12	(30,370)	0				0%	(4)
2,6-dinitrotoluene		12	9	(6,074)	3				25%	(0.8)
Dioxathion		12	12	(60,739)	0				0%	(3)
Di-n-octylphthalate		15	14	(5,988)	1	48,540	48,540	48,540	7%	4
1,2-diphenylhydrazine	(4.5)	12	12	(6,074)	0				0%	(0.6)
Diphenylamine		12	12	(6,074)	0				0%	(0.9)
Ethylmethanosulfonate		12	12	(6,074)	0				0%	(1)
Ethylparathion		12	12	(60,739)	0				0%	(12)
Fluoranthene		12	12	(6,074)	0				0%	(0.7)
Fluorene		12	12	(6,074)	0				0%	(0.7)
Freon 12		12	12	(2,336)	0				0%	(0.5)
Freon 113		18	18	(1,958)	0				0%	(0.3)
2-hexanone		27	25	(600)	2	3,500	3,500	3,500	7%	0.8
Heptachlor	(7.7)	12	12	(44,800)	0				0%	(3)
Hexachlorophene	300	12	12	(6,074)	0				0%	(0.4)
Hexachloropropene		12	12	(7,095)	0				0%	(0.7)
Indeno(1,2,3-cd)pyrene		12	12	(6,074)	0				0%	(0.5)
Isosafrole		12	12	(6,074)	0				0%	(0.9)
Methapyrilene		12	12	(6,074)	0				0%	(0.6)

Other Trace Organics (ng/dsm^3)										
4-methyl-2-pentanone		24	23	(1,283)	1	10,370	10,370	10,370	4%	2
Methoxyclor	50,000	12	12	(60,739)	0				0%	(4)
3-methylcholanthrene	(3.7)	12	12	(6,074)	0				0%	(0.5)
Methylmethanesulfonate		12	12	(6,074)	0				0%	(1)
3,4-methylphenanthrene		12	12	(6,074)	0				0%	(0.8)
2-methylnaphthalene		12	12	(6,074)	0				0%	(1)
2-methyl-5-nitroaniline		12	12	(60,739)	0				0%	(11)
1-naphthylamine		12	12	(6,074)	0				0%	(1)
2-naphthylamine		12	12	(6,074)	0				0%	(1)
2-nitrophenol		12	12	(6,074)	0				0%	(1)
4-nitroquinoline-1-oxide		12	12	(6,074)	0				0%	(0.6)
N-nitrozo-di-n-butylamine ng/dsm ^{3}		12	12	(6,074)	0				0%	(1)
N-nitroso-di-n-propylamine		12	12	(6,074)	0				0%	(1)
N-nitrosodiethylamine	(0.23)	12	12	(6,074)	0				0%	(1)
N-nitrosodimethylamine		12	12	(6,074)	0				0%	(2)
N-nitrophenylamine		12	12	(6,074)	0				0%	(1)
1,4-naphthoquinone		12	12	(6,074)	0				0%	(1)
5-nitroacenaphthene		12	12	(60,739)	0				0%	(7)
2-nitroaniline		12	12	(35,474)	0				0%	(6)
3-nitroaniline		12	12	(35,474)	0				0%	(6)
4-nitroaniline		12	12	(35,474)	0				0%	(6)
2-propanol		12	12	(230,226)	0				0%	(92)
1,1,1,2-tetrachloroethane		12	12	(2,336)	0				0%	(0.5)
Trans-1,2-dichloroethane	(38)	15	15	(1,958)	0				0%	(0.5)
Trichloroethane		3	3	(2,219)	0				0%	(0.4)
1,1,1-trichloroethane		31	26	(403)	5	479	9,131	20,416	16%	2
Tetrachloroethene		31	22	(403)	9	428	2,814	8,541	29%	0.4
Trichlorofluoromethane	300,000	18	18	(1,958)	0				0%	(0.3)
1,1,2-trichloroethene		7	6	(0)	1	0.0003	0.0003	0.0003	14%	0.00000005
Trichloroethylene	(7,700)	15	15	(1,958)	0				0%	(0.4)
1,2,3-chloropropane		3	3	(3,349)	0				0%	(1)
Trans-1,3-dichloropropene	(0.029)	15	15	(2,219)	0				0%	(0.5)

TABLE B-1 Continued

	Risk-Specific Dose or Reference Air Concentration (RsD or RAC)[a]	Total Runs	Nondetects Lower than Lowest Detected Values[b]		Detected Values Only				Detected Values	Average or DL ppb_{dv}
Values are at 7% O_2 Unless Otherwise Specified	µg/m³	N	N	Detection Limit	N	Minimum	Average	Maximum		
Other Trace Organics (ng/dsm³)										
Bromoethane		9	9	(11,564)	0				0%	(3)
N-nitrosomethylethylamine		12	12	(6,074)	0				0%	(2)
N-nitrosomorpholine		12	12	(6,074)	0				0%	(1)
N-nitrosopiperidine		12	12	(6,074)	0				0%	(1)
N-nitrosopyrrolidine	(16)	12	12	(6,074)	0				0%	(2)
5-nitro-o-toluidine		12	12	(6,074)	0				0%	(1)
Pentachlorobenzene (total)	800	12	12	(7,095)	0				0%	(0.7)
Penthachloroethane		12	12	(6,074)	0				0%	(0.7)
Pentachloronitrobenzene	(140)	12	12	(30,370)	0				0%	(3)
Phenacetin		12	12	(6,074)	0				0%	(0.8)
Phenanthrene		12	11	(6,074)	1	8,752	8,752	8,752	8%	1
2-picoline		12	12	(6,074)	0				0%	(2)
Pronamide	(2,200)	12	12	(6,074)	0				0%	(0.6)
Pyrene		12	12	(6,074)	0				0%	(0.7)
Pyridine	1,000	12	12	(11,681)	0				0%	(4)
Quinoline		12	12	(60,739)	0				0%	(11)
Safrole		12	12	(6,074)	0				0%	(0.9)
1,2,4,5-tetrachlorobenzene	300	12	12	(6,074)	0				0%	(0.7)
2,3,4,6-tetrachlorophenol	30,000	12	12	(30,370)	0				0%	(3)
P-toludine		12	12	(60,739)	0				0%	(14)
2-toluidine		12	12	(6,074)	0				0%	(1)
Tributylamine		12	12	(60,739)	0				0%	(8)
2,4,5-trichlorophenol	100,000	12	12	(6,074)	0				0%	(0.7)
2,4,6-trichlorophenol	(1,800)	12	12	(6,074)	0				0%	(0.7)
0,0,0-triethylphosphorothioate		12	12	(60,739)	0				0%	(10)
1,3,5-trinitrobenzene		12	12	(6,074)	0				0%	(0.7)
Chloromethane	28,000	12	9	(3,349)	3	705,692	786,818	904,603	25%	375
Total xylene	80,000	3	2	(1,283)	1	1,986	1,986	1,986	33%	0.4
Trans-1,2-dichloroethylene		3	3	(2,336)	0				0%	(0.6)
N,n'-diisopropylcarbodiimide		6	6	(52,000)	0				0%	(10)
Diisopropylmethylphosphonate		6	6	(60,739)	0				0%	(10)
1,2,3-trichlorophenol		6	6	(2,000)	0				0%	(0.2)

Polychlorinated Dibenzo-P-Dioxins and Dibenzo-Furans (ng/dsm^3)										
2,3,7,8-tetrachlorodibenzo-p-dioxin	(0.00022)	32	31	(0.0002)	1	0.002	0.002	0.002	3%	0.0000002
Tetrachlorodibenzo-p-dioxins (total)		47	13	(0.0004)	36	0.001	0.110	0.968	72%	0.000008
2,3,7,8-tetrachlorodibenzofuran		32	9	(0.002)	26	0.003	0.015	0.066	74%	0.000001
Tetrachlorodibenzofurans (total)		50	0		51	0.004	0.208	1.244	96%	0.00002
1,2,3,7,8-pentachlorodibenzo-p-dioxin		32	32	(0.001)	0				0%	(0.0000001)
Pentachlorodibenzo-p-dioxins (total)		43	28	(0.001)	15	0.005	0.181	0.877	33%	0.00001
1,2,3,7,8-pentachlorodibenzofuran		32	30	(0.001)	2	0.054	0.064	0.074	6%	0.000005
2,3,4,7,8-pentachlorodibenzofuran		32	29	(0.0005)	3	0.041	0.086	0.159	9%	0.000006
Pentachlorodibenzofurans (total)		47	17	(0.001)	30	0.004	0.357	1.815	60%	0.00003
1,2,3,4,7,8-hexachlorodibenzo-p-dioxin (0.00000001)	(0.0077)	32	32	(0.0002)	0				0%	
1,2,3,6,7,8-hexachlorodibenzo-p-dioxin (0.00000001)	(0.0077)	32	32	(0.0001)	0				0%	
1,2,3,7,8,9-hexachlorodibenzo-p-dioxin	(0.0077)	32	31	(0.0002)	6	0	0.0211	0.1269	17%	0.000001
Hexachlorodibenzo-p-dioxins (total)		47	28	(0.0002)	19	0.006	0.528	2.860	38%	0.00003
1,2,3,4,7,8-hexachlorodibenzofuran		32	27	(0.0002)	5	0.12	0.20	0.31	14%	0.00001
1,2,3,6,7,8-hexachlorodibenzofuran		32	28	(0.0001)	9	0	0.0283	0.0861	26%	0.000002
1,2,3,7,8,9-hexachlorodibenzofuran (0.00000001)		32	32	(0.0002)	0				0%	
2,3,4,6,7,8-hexachlorodibenzofuran		32	27	(0.0002)	10	0	0.0212	0.1776	29%	0.000001
Hexachlorodibenzofurans (total)		47	20	(0.0003)	27	0.0059	0.3394	1.1381	54%	0.00002
1,2,3,4,6,7,8-heptachlorodibenzo-p-dioxin		32	23	(0.0004)	9	0.0051	0.0777	0.2982	26%	0.000004
Heptachlorodibenzo-p-dioxins (total)		47	28	(0.0004)	19	0.005	0.281	1.047	38%	0.00002
1,2,3,4,6,7,8-heptachlorodibenzofuran		32	25	(0.0003)	7	0.0051	0.0887	0.1822	20%	0.000005
1,2,3,4,7,8,9-heptachlorodibenzofuran		32	28	(0.0001)	9	0	0.0576	0.2157	26%	0.000003
Heptachlorodibenzofurans (total)		44	17	(0.0003)	27	0.007	0.204	1.138	57%	0.00001
Octachlorodibenzo-p-dioxin		47	27	(0.002)	20	0.015	0.183	0.634	40%	0.00001
Octachlorodibenzofuran		50	42	(0.001)	8	0.018	0.152	0.426	15%	0.000008
Total dioxins & furans		40	0		40	0.010	1.372	8.645	100%	0.00009
International toxic equivalency (1989		36	36		39	0.001	0.037	0.206	100%	0.000003
ITEQ calculated setting all BDL values to 0		35	0		35	0.0	0.010	0.131	100%	0.000001

[a] Average annual reference air concentrations (RAC) and risk specific dose (RsD) values in μg/m^3 are taken from 40 CFR 266, Appendices IV and V. RsD values are shown in parentheses. The RAC is 0.1 μg/m^3 for SOPCs without a pollutant-specific RAC or RsD. Since the emitted concentration ranges are between 642,000 (MPF), 919,000 (LIC), and 1,350,000 (DFS) times greater than the annual average concentration represented by the RAC and RsD, to compare these inhalation pathway-based concentrations with measured concentrations and detection limits, multiply the RAC or RsD by 1,000,000 for particulates and metals. The multiplier for trace organic emissions is 1,000,000,000 to account for the difference in reported units.

[b] Nondetected concentrations with detection limits above detected values for other sampling intervals have been excluded from the table to facilitate summary presentation of the data. To determine the number of these runs, subtract the number of detects and nondetects less than the lowest detected value from the total number of runs.

TABLE B-1 Continued

Source: Compiled from data in sources listed below.

JACADS Data Sources:

Metco Environmental. 1992a. Source Emissions Survey of Johnston Atoll Chemical Agent Disposal System Liquid Incinerator Stack [LIC/GB]. Prepared for Southern Research Institute, August 1992. Addison, Texas: Metco Environmental.

Metco Environmental. 1992b. Source Emissions Survey of Johnston Atoll Chemical Agent Disposal System Liquid Incinerator Stack [LIC/VX], February and March 1992. Prepared for Southern Research Institute, February 1992. Addison, Texas: Metco Environmental.

Raytheon Engineers & Constructors, Inc. 1995. RCRA Trial Burn Report for Agent GB/Dunnage, in the Dunnage Incinerator at the Johnston Atoll Chemical Agent Disposal System [DUN/GB]. Prepared for Program Manager for Chemical Demilitarization, March 1995. Philadelphia, Pa.: Raytheon Engineers & Constructors, Inc.

SRI. 1991. Results of the RCRA Trial Burn with GB Feed for the Liquid Incinerator at the Johnston Atoll Chemical Agent Disposal System [LIC/GB]. Prepared for Program Manager for Chemical Demilitarization, June 17, 1991. Birmingham, Ala.: Southern Research Institute.

SRI (Southern Research Institute). 1992a. Results of the RCRA Trial Burn with VX Feed for the Liquid Incinerator at the Johnston Atoll Chemical Agent Disposal System, Volume IV (SRI-APC-92-384-7530.11.1-I) [LIC/VX]. Prepared for Program Manager for Chemical Demilitarization. Birmingham, Ala.: Southern Research Institute.

SRI. 1992b. Results of the RCRA Trial Burn of the Metal Parts Furnace System with HD at the Johnston Atoll Chemical Agent Disposal System, Volume II (SRI-APC-92-834-7530.9.1-I) [MPF/HD]. Prepared for Program Manager for Chemical Demilitarization. Birmingham, Ala.: Southern Research Institute.

SRI. 1992c. Results of the RCRA Demonstration Burn with HD Feed for the Liquid Incinerator at the Johnson Atoll Chemical Agent Disposal System, Volume IV, Appendix F (SRI-APC-92-7530.10.1-I) [LIC/HD]. Prepared for Program Manager for Chemical Demilitarization. Birmingham, Ala.: Southern Research Institute.

United Engineers (United Engineers & Constructors, Inc.). 1992. RCRA Trial Burn Report for HD-Mustard Ton Containers-Metal Parts Furnace at the Johnston Atoll Chemical Agent Disposal System [MPF/HD]. Prepared for Program Manager for Chemical Demilitarization, December 16, 1992. Philadelphia, Pa.: United Engineers & Constructors, Inc.

United Engineers. 1993. Results of the Demonstration Test Burn for Thermal Destruction of Agent HD in the Johnston Atoll Chemical Agent Disposal System Liquid Incinerator, [LIC/HD]. Prepared for Program Manager for Chemical Demilitarization, February 1993. Philadelphia, Pa.: United Engineers & Constructors, Inc.

TOCDF Data Sources:

Alliance Technologies Corporation. 1992. RCRA Compliance Test Results with Mixed Agent HD/Munitions for the Cryofracture Program on the Deactivation Furnace System, Chemical Agent Munitions Disposal System [DSF/HD]. Prepared for Program Manager for Chemical Demilitarization. Windsor, Conn.: TRC Environmental Corp.

EG&G. 1995. Tooele Chemical Disposal Facility (TOCDF), Surrogate Trial Burn Report for Liquid Incinerator Number 1 [LIC/STB]. Prepared for Program Manager for Chemical Demilitarization, November 29, 1995. Tooele, Utah: EG&G Defense Materials, Inc.

EG&G. 1997a. MPF GB ATB Report, Rev. 2 (partial report), [MPF/GB]. Prepared for Southern Research Institute, December 31, 1997a. Tooele, Utah: EG&G Defense Materials, Inc.

EG&G. 1997b. Tooele Chemical Agent Disposal Facility (TOCDF), RCRA Agent Trial Burn Report for the Liquid Incinerator System #2 [LIC/GB]. Prepared for Southern Research Institute, October 27, 1997. Tooele, Utah: EG&G Defense Materials, Inc.

EG&G. 1997c. Tooele Chemical Agent Disposal Facility (TOCDF), RCRA Agent Trial Burn Report for the Metal Parts Furnace, Appendices A–K [MPF/GB]. Prepared for Program Manager for Chemical Demilitarization, August 15, 1997. Tooele, Utah: EG&G Defense Materials, Inc.

EG&G. 1997d. Tooele Chemical Agent Disposal Facility (TOCDF), RCRA Agent Trial Burn Report for the Liquid Incinerator System #1, Appendices A–K, [LIC/GB]. Prepared for Program Manager for Chemical Demilitarization, July 7, 1997. Tooele, Utah: EG&G Defense Materials, Inc.

EG&G. 1997e. Tooele Chemical Agent Disposal Facility (TOCDF), DFS TSCA Demonstration Test Burn Report for the Deactivation Furnace System [DFS/GB]. Prepared for Program Manager for Chemical Demilitarization, April 24, 1997. Tooele, Utah: EG&G Defense Materials, Inc.

EG&G. 1997f. Tooele Chemical Agent Disposal Facility (TOCDF), RCRA Agent GB Trial Burn Report for the Deactivation Furnace System [DFS/GB], Appendices A–J. Prepared for Program Manager for Chemical Demilitarization, April 9, 1997. Tooele, Utah: EG&G Defense Materials, Inc.

EG&G (EG&G Defense Materials, Inc.). 1998. Tooele Chemical Agent Disposal Facility (TOCDF), RCRA Agent Trial Burn Report for the Deactivation Furnace System [DSF/GB]. Prepared for Southern Research Institute, January 14, 1998. Tooele, Utah: EG&G Defense Materials, Inc.

TRC (TRC Environmental Corporation). 1993a. Results of the Chromium Emissions Test Program on the Deactivation Furnace System Baseline Test Conditions, Chemical Agent Munitions Disposal System (CAMDS), Tooele, Utah [DFS/Propane]. Prepared for Program Manager for Chemical Demilitarization, May 1993. Aberdeen Proving Ground, Md.: U.S. Army Program Manager for Chemical Demilitarization.

TRC. 1993. RCRA Compliance Test Results with Mixed Agent VX/Munitions for the Cryofracture Program on the Deactivation Furnace System, Chemical Agent Munitions Disposal System [DFS/VX]. Prepared for Program Manager for Chemical Demilitarization, October 1993. Aberdeen Proving Ground, Md.: U.S. Army Program Manager for Chemical Demilitarization.

Appendix C

Commercial Application of Carbon Bed Filters to Combustion Sources

Carbon bed filters are widely used in the chemical processing industry to recover low-concentration chemicals from dilute gas streams. They are also used to control volatile organic emissions from production processes, like rotogravure printing and fiberglass and plastics forming. In the mid-1980s, carbon bed filters were first used in large combustion sources, like coal-fired utility boilers, hazardous waste incinerators, and municipal waste combustors, to polish effluent-gas streams. They are used to remove residual sulfur dioxide and hydrogen chloride, mercury, organic solvents, and semivolatile organics like dioxins and furans from exhaust-gas streams. Testing indicates that the depth-filter function of the activated carbon fill separates metals and organics associated with solid particulates.

Table C-1 is a partial listing of commercial activated

TABLE C-1 Partial List of Activated Carbon Bed Filter Installations

Location	Type of Facility/ Incinerator	Number and Capacity of Filters	Start-up Year
Lausward, Dusseldorf, FRG	coal power plant	8 × 250,000 nm^3/h	1989
Flingern, Dusseldorf, FRG	coal power plant	2 × 250,000 nm^3/h	1989
Garth, Dusseldorf, FRG	coal power plant	1 × 65,000 nm^3/h	1988
Energiever Sorgung Oberfranken, Arzberg, FRG	coal power plant	1 × 650,000 nm^3/h 1 × 45,000 nm^3/h	1990 1989
Hoechst, Hoescht, FRG	coal power plant	1 × 1, 330,000 nm^3/h	1990
Zavin-Dordrecht, NL	medical waste	1 × 13,750 sm^3/h	1991
Universitatsheizwerk, Heidelberg, FRG	medical waste	2 × 6,500 sm^3/h	1991
AVR Chemi, NL	chemical waste	1 × 77,000 sm^3/h	1992
AVT-Rotterdam, NL	municipal waste	6 × 155,000 sm^3/h	1992/93[a]
RWE-Energle, Essen, FRG	municipal waste	4 × 168,000 sm^3/h	1995
WAV, Wels, Austria	municipal waste	1 × 55,000 sm^3/h	1995
RHE, Mannheim, FRG	municipal waste	2 × 206,000 sm^3/h	1995
RZR Herten, AGR Essen, FRG	industrial waste	2 × 70,000 sm^3/h	1991/96[a]
AVI ROTEB, Rotterdam, NL	municipal waste	4 × 75,000 sm^3/h	1993
Rozenburg, DTO-8, AVR Chemi Rotterdam, NL	hazardous waste	1 × 70,000 sm^3/h	1994
MVA Neu-Ulm, FRG	municipal waste	2 × 57,000 sm^3/h	1996
MVA Stapelfeld, Hamburg, FRG	municipal waste	2 × 120,000 sm^3/h	1996
MHKW Kassel, FRG	municipal waste	2 × 70,000 sm^3/h	1996
AEZ Kreis Wesel, FRG	municipal waste	2 × 70,000 sm^3/h	1996
HKW Nord MK4, Mannheim, FRG	municipal waste	1 × 195,000 sm^3/h	1997
RVA Bohlen, FRG	hazardous waste	1 × 40,000 sm^3/h	1998
MVA Koln, FRG	municipal waste	4 × 95,000 sm^3/h	1998

[a] Multiple start-up years indicate plant expansions.

TABLE C-2 Performance of Activated Carbon Bed Filters

SOPC	Control Efficiency (%)	Detection Limit
Mercury	90–99.9	
Particulates	~100	< 1 mg/dnm^3 @ 11% O_2
Metals	~100	< 2-200 $\mu g/dnm^3$ @ 11% O_2
SO_2/HCl	~100	< 2-6 mg/dnm^3 @ 11% O_2
Dioxins/furans	99–99.9$^+$	
Polychlorinated phenols	94.7–99.9	
Polycyclic aromatic hydrocarbons	61.7–97.9	
Total hydrocarbons	41.7–96.2	
Polychlorinated chlorobenzenes	97.5–9$^+$	

carbon bed filters. The list includes 22 facilities and 52 carbon bed filters. Capacities range from about a quarter of the size needed for individual baseline system incineration units to more than 50 times the required capacity.

The published emissions control performance for activated carbon bed filters is summarized in Table C-2. Removal efficiencies are reported as greater than a specified percentage because the outlet concentrations are below the detection limits for existing measurement techniques.

Appendix D

Theoretical Modeling of Adsorption

Mitretek used a theoretical analysis to predict the adsorption on carbon of many materials present at very low concentrations in the incinerator flue gas of the baseline system (Mitretek Systems, 1997). The theoretical treatment of adsorption based on work by Polanyi and Dubinin and coworkers is described briefly below. A fuller explanation can be found in Ruthven (1984). The problem encountered at very low gas concentrations is also explained.

Adsorption potential (ε) is defined in terms of the equilibrium pressure of adsorbate in the gas phase *(p)* and its saturation vapor pressure *(p_{sat})*:

$$\varepsilon = -RT\ln\left(\frac{p}{p_{sat}}\right)$$

For a given adsorbate and solid adsorbent, the relation between the volume of adsorbed contaminant and the adsorption potential can be determined experimentally for a particular adsorbent/adsorbate combination at a specified temperature. The characteristic curve defined by this relation can then be used to predict the behavior of other adsorbates on the same adsorbent at the same or other temperatures.

The form of the characteristic curve observed with activated carbon as the adsorbent can usually be expressed in a Gaussian form:

$$W = W_0 e^{-k\varepsilon^2}$$

where W = volume adsorbed and W_o = volume absorbed at saturation (taken to be the total micropore volume of the solid adsorbent). If this relationship holds, then it becomes possible to predict the characteristic curve for a second adsorbent, based on a single data point. Dubinin and coworkers rewrote this relationship with an added factor (β) characteristic of the adsorbed materials:

$$W = W_0 e^{-k(\varepsilon/\beta)^2}$$

The constant k is a characteristic of the solid adsorbent. From the two relations:

$$\ln(W) = \ln(W_0) - \left(\frac{k}{\beta^2}\right)\left(RT\ln\left(\frac{p}{p_{sat}}\right)\right)^2$$

Mitretek measured adsorption equilibrium data for several compounds and found a useful correlation with the following substitutions: β was set equal to the critical temperature, T_c; T/β = reduced temperature, T_r; and $W = V_m q$, where V_m = liquid molar volume and q = adsorbed phase, mols/kg of carbon. The final empirical relation used by Mitretek was:

$$\ln(q) = \ln\left(\frac{321}{V_m}\right) - \left(\frac{1}{4.7}\right)^2\left(T_r\ln\left(\frac{p}{p_{sat}}\right)\right)^2$$

Unfortunately, some of the data of most interest for the baseline incineration system pollution abatement system filter system are in a low concentration range where the Dubinin-Radushkevich (D-R) relation cannot be applied because it will overpredict the adsorbed amount, as indicated in Figure D-1.

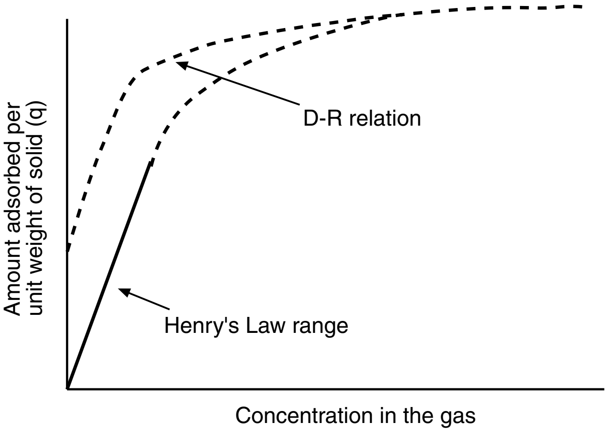

FIGURE D-1 Sketch of adsorption equilibrium.

Once this problem was recognized, suggestions were made for handling it. The D-R relation should hold for "relative pressure" values above 10^{-6}. That is, for

$$\frac{partial\ pressure}{vapor\ pressure}, \frac{p}{p_{sat}} > 10^{-6}$$

(This criterion is given by Mitretek, attributed to Dubinin.)

Therefore, the D-R relation should be applied for values above this criterion. For values below 10^{-6} to zero, a linear relationship (i.e., Henry's Law) could be applied. The correct equilibrium adsorption *(q)* will fall between the two relations at values below 10^{-6}. This appears to be a reasonably conservative approach to solving the problem. A more direct approach would be to use data obtained at the very low concentration of interest to define a Henry's Law relation.

The materials of most interest for adsorption in this case are unburned agent (although none was observed in trial burns at JACADS or the TOCDF) and chlorinated dioxins and furans. The latter are responsible for a substantial amount of the health risk in the HRA (health risk assessment) analyses for the baseline incineration system. For the most part, the concentrations of both unburned agent and dioxins and furans are below the criterion suggested by Dubinin, (p/p_{sat} is *less* than 10^{-6}) for most of these materials. The alternative analysis suggested above could be applied for these materials.

TABLE D-1 Vapor Pressures for Various Chlorinated Dioxins

Dioxin	Vapor Pressure 71°C (Pa)
Dibenzo dioxin (DD)	10
2-chloro DD	1.8
2, 3-dichloro DD	0.1
1, 2, 3, 4-tetrachloro DD	0.012
1, 2, 3, 4, 5-pentachloro DD	0.001 (est.)
Perchloro DD	~ 10^{-7}

Source: Adapted from Rordorf, 1985.

Vapor pressures for various chlorinated dioxins are shown in Table D-1. Trial-burn data showed individual dioxins to be present at concentrations of less than 1 ng/m^3. Assuming a concentration of 1 ng/m^3, partial pressures can be calculated and compared with the vapor pressures in Table D-1. Results are shown in Table D-2.

Only the most highly chlorinated dioxins have p/p_{sat} > 10^{-6}, the Dubinin criterion. A similar estimate suggests that the criterion will not apply to chemical agents. Although no agent was detected in the trial-burn flue gas, they are assumed to be present at the detection limits suggested by Mitretek (see Table D-3).

TABLE D-2 Calculated Partial Pressures for Chlorinated Dioxins Based on 1 ng/m^3

Dioxin	Molecular Weight	p (Pa)	p/p_{sat} (71°C)
Dibenzo dioxin (DD)	184	1.6×10^{-8}	1.6×10^{-9}
2-chloro DD	218.5	1.33×10^{-8}	7.4×10^{-9}
2, 3-dichloro DD	253	1.15×10^{-8}	1.15×10^{-7}
1, 2, 3, 4-tetrachloro DD	322	0.90×10^{-8}	7.5×10^{-7}
1, 2, 3, 4, 5-pentachloro DD	356.5	0.81×10^{-8}	8.1×10^{-6}
Perchloro DD	460	0.63×10^{-8}	0.063

TABLE D-3 Agent Detection Limits

Agent	Detection Limit
GB	6×10^{-2} (g/m^3)
VX	6×10^{-2} (g/m^3)
HD	8.7 (μg/m^3)

Source: U.S. Army, 1998.

Assuming that agents are present at these values and using estimated vapor pressure values, the p/p_{sat} values would be those given in Table D-4. All are less than the Dubinin criterion of 10^{-6}.

It should be clear that modeling adsorption for the levels of principal organic hazardous constituents (POHCs) and substances of potential concern (SOPCs) concentrations in baseline-system flue gas is very difficult and is subject to considerable uncertainty. The carbon bed will initially adsorb most organic SOPCs leaving extremely low levels in the flue gas. The uncertainty arises in the duration of the bed life (i.e., how long the bed will remain on stream before materials saturate the carbon and start to appear in the outlet gas). For dioxins and furans, the predicted bed life is based on a theoretical analysis as well as commercial operating experience. The bed life is sufficiently long that, with proper monitoring, adequate notice will be provided for replacement of the bed, which should be infrequent.

The theoretical analysis was not extended to possible agent breakthroughs because agent is routinely monitored in the stack gas, and the facility would automatically shut down if any were detected. Trial burns have shown that agent in the flue gas is below the detection limit (see Appendix B).

ADSORPTION FROM A FLOWING GAS STREAM TO A PACKED BED

The adsorption process in a packed bed has been described in the literature at many different levels of sophistication (e.g., simple to complex equilibrium relations, simultaneous mass and heat transfers, combinations of mass transfer resistance in series, etc). The Mitretek approach is explained in the following excerpt from the Mitretek report (Mitretek Systems, 1997).

TABLE D-4 Agent Vapor Pressures and p/p_{sat} Ratios Based on Agent Detection Limits

Agent	Vapor Pressure 71°C est. (Pa)	p/p_{sat}
GB	3,750	3.3×10^{-10}
VX	4.17	1.6×10^{-7}
HD	206.6	7.7×10^{-7}

Carbon Filter Simulation Model Development

The computer simulation model is a mathematical representation of the carbon adsorption process. It is based on current theories about the adsorption process. Existing engineering relationships and data were used to the maximum extent possible in developing the model. Where necessary, new relationships were developed and laboratory scale experiments were run to obtain needed data. A major challenge to the modeling effort is the widely different adsorption characteristics of the chemical substances present in the PAS exhaust gases, which are present at very low concentration levels.

The model consists of differential energy and material balance equations which are solved to calculate the changes in the temperature and contaminant concentration in the carbon and in the flowing gas stream with time. The set of equations consists of one material balance equation for each contaminant, and an energy balance equation for the system.

The material balance equation is developed by considering that, at any position in the carbon bed, contaminants are either adsorbed by the carbon or are transported by dispersion and the bulk fluid flow. The governing material balance equation for the fixed-bed adsorption process, excluding fluid phase accumulation, addresses adsorption equilibrium, rate processes for mass transfer and fixed bed dynamics is:

$$\rho_b \frac{\partial q}{\partial t} = k_f \alpha \left(c_i - c_i^*\right) = D_l \frac{\partial^2 \xi ci}{\partial z^2} - \frac{\partial \xi v c_i}{\partial z} \tag{E1}$$

where

ρ_b = density of the bulk carbon, g/m^3

q = moles of contaminant on carbon per unit mass of carbon, moles/kg

t = time, seconds

D_l = dispersion coefficient, cm^2/sec

z = axial position in carbon filter, cm

ξ = fractional void space of the carbon bed, unitless

v = interstitial fluid velocity, cm/sec

$k_f\alpha$ = rate constant for mass transfer to the adsorbent surface, sec^{-1}

c_i = bulk vapor phase concentration of the *i*th contaminant, moles/cm^3

c_i^* = vapor-phase concentration of the *i*th contaminant in equilibrium with the adsorbed phase concentration of that contaminant, moles/cm^3

The energy balance is solved considering only the effects of water adsorption/desorption and temperature changes in the inlet stream. It accounts for the thermal mass of the adsorbent, the thermal mass of the bulk fluid and the enthalpy transfer due to adsorption and desorption of water vapor. The energy balance is as follows:

$$\left(c_s + q_w c_w\right)\frac{\partial T}{\partial t} - \lambda_w \frac{\partial q_w}{\partial t} + \frac{\partial \xi v c c_p T}{\partial z} = 0 \qquad \text{(E2)}$$

where

c_s = heat capacity of the adsorbent (J/kg K), (assumed to be constant in model)

q_w = adsorbed-phase concentration of water, moles/kg

c_w = adsorbed-phase heat capacity of water (assumed to be constant in model)

T = adsorption temperature (K)

λ_w = enthalpy of adsorption of water (assumed to be constant in model), J/mole K

ξ_v = superficial velocity, cm/sec

c = total molar density of the fluid phase, moles/cm^3

c_p = constant pressure heat capacity of the fluid-phase air-water mixture, J/mole K

z = axial distance, cm

The fluid-phase accumulation and the effective thermal dispersion are neglected. Also, the rate of heat transfer to the adsorbent is assumed to be instantaneous and heat losses to or through the column wall are assumed to be negligible. This simplification of the energy balance was made to permit the simulation of a feed temperature upset and to predict the change in filter temperature due to a change in relative humidity without unduly increasing computation time. It requires the use of accurate estimates of physical and adsorption properties.

The rate at which contaminant mass moves from the bulk gas onto the particle is affected by the resistance to mass transfer both inside and outside of the adsorbent particle. On the basis of empirical data for dimethyl methyl phosphonate (DMMP) (Croft and Friday et al., 1995), the model considers only the resistance external to the particle as defined by the rate constant for adsorption which is equal to the product of the external film mass transfer coefficient, k_f, and the area per unit volume of carbon, “a.” Intraparticle (solid phase) mass transfer resistance is assumed to be negligible.

The model uses the correlation of Wakao and Funazkri (1978), which is recommended by Yang (1987) for use in modeling fixed bed adsorbers when axial dispersion is included, to calculate values of the external mass transfer film coefficient:

$$\frac{k_f d_p}{D_{AB}} = 2.0 + 1.1\left[\frac{\xi v \rho d_p}{\mu}\right]^{0.6}\left[\frac{\mu}{D_{AB}\rho}\right]^{0.333} \qquad \text{(E3)}$$

where

d_p = particle diameter assuming spherical particles, cm

D_{AB} = diffusion coefficient of the chemical in the mixture, cm^2/sec

ρ = density of the vapor-phase, gm/cm^3

μ = viscosity of the vapor-phase, gram seconds/cm

ξv = superficial velocity, cm/sec

For non-spherical particles the particle diameter may be multiplied by a shape factor , ϕ_s to obtain an equivalent diameter. The area per unit volume was defined as

$$a = \frac{6(1-\xi)}{d_p \phi_s} \qquad \text{(E4)}$$

Axial dispersion of adsorbate within the carbon bed is another factor that influences the bulk gas concentration gradient within the carbon bed. On the basis of empirical data for DMMP (Croft and Friday et al., 1995) the following modified version of the Langer et al. (1978) correlation was determined to be the appropriate equation to use in the model to calculate the effective dispersion coefficient:

$$\frac{D_1}{\xi v d_p} = \gamma \frac{D_{AB}}{\xi v d_p} + \left(\frac{1}{R_1}\right)\frac{0.45}{\left(1 - \beta\gamma \dfrac{D_{AB}}{\xi v d_p}\right)} \qquad \text{(E5)}$$

where

γ = tortuosity factor and is set equal to 0.73

β = constant set equal to 10

$$R_1 = \left.\frac{cdq}{qdc}\right|_{c=cfeed}$$

[This equation does not apply at $c = c_{sat}$]

The first term on the right accounts for molecular diffusion in the axial direction. The second term on the right accounts for dispersion due to non-uniform flow and the decreased dispersion due to radial diffusion and mixing. The modification involves the addition of the ($1/R_1$) factor where R_1 represents the separation factor defined as the ratio of the concentration of contaminants in the bulk gas phase to the concentration of contaminants in the solid phase.

The equilibrium relation for the organic species chosen by Mitretek (and required in this analysis) is the D-R relation described previously. Other equilibrium relations were considered for other species, (described by Mitretek below).

Mercury Isotherm. The available experimental data for mercury adsorption equilibrium does not fit the potential theory-based correlation presented in Figure E-1. An alternative set of parameters for the potential theory based D-R correlation for mercury was obtained by a least squares fit of equilibrium data reported in the open literature for mercury adsorption on non-impregnated activated carbons that are similar to the coconut shell carbon.

The isotherm equation used for mercury in the model is:

$$\ln q = \ln\left(1.8 \times 10^{-3}\right) - \left(\frac{1}{2300}\right)^2 \left(T \ln\left(\frac{p}{p_{sat}}\right)\right)^2 \qquad \text{(E14)}$$

Acid Gas Isotherm. Hydrogen chloride is another substance in the chemical demilitarization incinerator stack gases that is expected to have a different equilibrium isotherm than the organic compounds. Experimental data for HCl adsorption suggests that, under humid conditions, nearly twice as much HCl is adsorbed as would be expected from water solubility considerations. Thus, an assumption that HCl loading on the carbon is limited by its solubility in the water adsorbed onto the carbon provides a conservative estimate of the capacity of the carbon for HCl. Additional studies are under way to verify the findings of these experiments.

The solubility of HCl in water as a function of its partial pressure in the gas stream can be represented by the following potential type equation:

$$\ln(q) = \ln(21.65) - \left[\left(\frac{3217}{T}\right)\left(\ln\left(\frac{p}{p_{sat}}\right)\right)\right]^2 \qquad \text{(E15)}$$

where q is the solubility of HCl in water when the partial pressure of HCl in the gas stream is p and p_{sat} is the saturation vapor pressure of HCl. If the amount of water adsorbed on the carbon is known, then the above equation can be used to calculate the amount of HCl that would dissolve in the adsorbed water.

Water Isotherm. Water does not interact with activated carbon based adsorbents in the same way as most other compounds. The amount of water adsorbed on activated carbon depends markedly on operating conditions prior to the introduction of the water vapor into the gas stream. Therefore for water, alternative isotherm correlations were evaluated from the literature. The best correlation of water isotherm data on coconut shell carbon was obtained from the following equation:

$$\frac{p}{p_{sat}} = \left[\left(1 - \gamma_2 - \gamma_{1/2} - \gamma_3\right)\theta + \gamma_2\theta^2 + \gamma_{1/2}\theta^{1/2} + \gamma_3\theta^3\right]^{T_{ref}/T} \qquad \text{(E16)}$$

where

$\theta = q/q_{sat}$ for water

q = carbon capacity for water at the relative humidity of the bulk gas, moles of water per unit mass of carbon at the partial pressure, p, of water vapor in the bulk gas phase, moles/kg

q_{sat} = carbon capacity for water at 100 percent humidity, moles of water per unit mass of carbon at the saturation vapor pressure p_{sat} of water (100 percent humidity), moles/kg

T_{ref} = 298 K

$\gamma_2 = -4.01$

$\gamma_{1/2} = 0.35$

$\gamma_3 = 2.91$

Multi-component adsorption. When more than one adsorbate is present in the bulk gas phase, each adsorbate fills only a fraction of the pore space that it would have filled as a pure adsorbate. For carbon adsorption, an extension of the potential theory to multi-component adsorption and the ideal adsorbed solution theory (IAST) approaches are commonly used to predict multi-component equilibrium. The IAST assumes that fundamental thermodynamic equations used for liquid-phase equilibrium calculations apply to the adsorbed phase.

The potential theory for multi-component adsorption assumes that the adsorption potential of each component is equal to the adsorption potential of the mixture. If Raoult's law is valid for the relationship between the partial pressure of each adsorbate and its mole fraction in the adsorbed mixture and the adsorbates form an ideal solution (the adsorbate volumes are additive), the amount and composition of adsorbed mixture corresponding to a given gas phase composition can be calculated from the known single-gas isotherms. This is represented by the following equations:

$$p_i = x_i p_i^0\left(\theta^0, T\right) \tag{E17}$$

where

x_i = mole fraction of the *i*th component in the absorbed phase

p_i^0 = single component bulk gas phase equilibrium partial pressure, in Pascals, that would be exerted if the loading of the *i*th component was the same as the total loading of the mixture, i.e., θ^0.

$\theta^0 = \Sigma\theta_i$, the effective fractional loading of the mixture

θ_i = fractional loading of the *i*th component in the mixture, i.e., $\theta_i = q_i / q_{sat}$. It is equal to 1 at the saturation vapor pressure of the liquid.

The assumption is made that the partial pressure of each adsorbate in the vapor phase is equal to the product of its mole fraction in the adsorbed phase mixture times the vapor pressure it would exert if it were a pure adsorbate and filled the carbon pores to the same extent as the mixture (like Roault's law).

For the model developed in this study, the extension of the potential theory, suggested by Grant and Manes (1966) was used. This method is explicit and requires no iterative root finding. Therefore it is ideal for use in a numerical model. The evaluation by the model starts with known q_i's and T. The mole fractions are determined by:

$$x_i = \frac{q_i}{\sum q_j} \tag{E18}$$

where q_j represents all the adsorbates including q_i. The fractional loading for the *i*th adsorbate, θ_i, is then determined by dividing the loading of the *i*th adsorbate, q_i, by its pure component loading, q_{sat}, at the saturation vapor pressure. This is the value at which the pore is considered filled. The fractional loadings are summed to determine the total or effective fractional loading. This result is then used in equation (E10) with the value of the parameters of the D-R equation for coconut shell carbon, the bulk gas phase temperature, and the critical temperature of the adsorbate to determine the adsorbate partial pressure.

Effects of Water. Extension of the multi-component model to include water requires the assumption that water forms an ideal mixture with the organics and Raoult's law for adsorption holds. A water isotherm in the form of equation (E16) can then be used to calculate the water partial pressure. It is recognized, however, that Raoult's law may not be appropriate for non-ideal mixtures such as water and non-water-soluble substances. Because the mechanism of adsorption of water is different than it is for organics and the effect of water varies for different adsorbates, e.g., water soluble, volatile adsorbates are affected by water vapor to a greater extent than others, and with different humidity levels, methods to adequately model the effect of water on adsorption are limited. The current model, using a Raoult's law approach for the prediction of water/organic equilibrium, was shown to provide conservative predictions in that it tends to predict earlier breakthrough of the organic adsorbates than is observed experimentally. In an experiment with hexane, this approach was found to over-predict the effect that water has on the adsorption of hexane. Although agreement between experimental data and the predictions was good at low relative humidity (< 50 percent), it aü ôme increasingly poorer as the relative humidity increased. This indicates that water coadsorption with organics represents an extreme case of adsorbed phase non-idealities.

Recently reported experimental results of adsorption experiments with several non-ideal two-component mixtures of various compounds with water on activated carbon suggest that the carbon loading can be dramatically reduced, especially above 70 percent relative humidity for the less strongly adsorbed (light), water-insoluble, organic species vapors. Conversely, for a water-soluble chemical, such as acetone, the presence of adsorbed water actually results in an increase in the carbon loading above the loading observed in the absence of adsorbed water. (Rudisill, Hacskaylo et al., 1992; Eissmann and LeVan, 1993). Further refinement of the model to better account for the effect of humidity could involve a major research effort that may not be warranted at this time.

Effect of inert gases on adsorption. The effect of the presence of inert gases, such as carbon dioxide (CO_2), on the capacity of the carbon for the contaminants of concern was also considered. CO_2 is of particular interest because it is present in the stack gases at higher concentrations than in air, being on the order of 6 percent by volume. Based on adsorption data for CO_2 on BPL carbon, carbon filter loading under the stack conditions is estimated to be 5.8×10^{-5} mole/kg. The CO_2 adsorption capacity is orders of magnitude lower than that of all compounds of potential concern with regard to risk to public health except vinyl chloride. Based on this, it is expected that CO_2 would only affect breakthrough of vinyl chloride, i.e., it may cause vinyl chloride to breakthrough earlier than it might have in the absence of CO_2.

Solution of model equations. The differential material balances for each component and the energy balance constitute a set of non-linear partial differential equations. The computer simulation model calculates the temperature and contaminant concentrations in the bulk fluid and in the carbon over the length of the carbon bed after specified increments of time. It does this by solving material balances for each contaminant in the feed stream to the carbon bed. The energy balance is solved considering only the effects of water adsorption/desorption and temperature changes in the inlet stream.

Among the significant assumptions made in order to solve the equations of the model are:

- The potential theory explains adsorption onto activated carbon.
- The adsorption potential of each pure adsorbed component in a mixture is determined by the total adsorbate volume of the mixture.
- Raoult's law is valid as the relationship between the partial pressure of each component and its mole fraction in the mixture.
- The adsorbate mixture forms an ideal solution.
- Multi-component equilibrium can be predicted from single component equilibrium relationships.
- The equilibrium relationship between the bulk gas phase concentration of the organic components and the amount of those components that are adsorbed on the carbon can be represented by a "universal" D-R type equilibrium equation applicable to all organic compounds.
- Water and other inorganic compounds, such as mercury, form an ideal mixture with the organic compounds, and Raoult's law for adsorption holds.
- Water soluble compounds, such as HCl, will be adsorbed to the extent of their solubility in adsorbed water.

The computer model works by solving the partial differential equations to calculate the temperatures, bulk gas phase contaminant concentrations, and carbon bed loading along the length of the bed at a discrete time interval by the method of lines. In this method, the carbon column is divided into a series of stages along its length. A series of sets of ordinary differential equations results (one set of equations for each stage) that can be solved using a standard initial value ordinary differential equation solver.

The model is capable of running on a Pentium™ processor equipped PC with a minimum of 8 megabytes of memory. Computer requirements vary depending on the number of contaminants in the feed stream to the carbon bed.

The model requires initial input data from two input files created in a specified format. The first input data file contains information on the filter characteristics, and feed stream characteristics. It also allows specification of whether 25 or 50 stages should be used and whether an energy balance should be performed. Filter characteristics that need to be specified include the cross sectional area, the filter length, the adsorbent shape factor, carbon particle diameter in millimeters, and bulk density of the carbon in kilograms per cubic meter. Feed stream characteristics that need to be specified include the feed temperature in degrees Fahrenheit, the system pressure in Pascals, the relative humidity, the flow rate in standard cubic feet per minute at 80°F, and the filter operating time in days. The number of adsorbates that are in the stream need to be specified. Each adsorbate needs to be named and physical properties provided (e.g., molecular weight, vapor pressure, and concentration).

The second input file specifies the initial filter loading, q, for each adsorbate in each stage of the filter. If this file does not exist, the model creates it with a loading of zero. As the model runs, the loading data is updated at each time increment during the run.

The model creates three output files. One output file contains data on the concentration of each contaminant in the outlet stream from the filter at each time increment during the run. Software can be used to plot the data. A second output file contains the adsorbed phase loading and the bulk gas phase concentration in each stage of the filter at the end of the run. A third file contains information to assist in verifying that the model performed properly, e.g., a material balance.

The Mitretek model was tested against laboratory breakthrough data with modestly successful results. The reader is referred to the Mitretek report for details. Finally, Mitretek made the following assessment of the approach.

Observations and Conclusions

The prediction of adsorptive filter performance is a complex and difficult task. It is necessary to include all substances in the feed stream to model filter performance because even though some substances may be innocuous from a risk standpoint, they may affect the adsorption capacity of the filter for the substances that are of concern.

Overall, the current form of the model appears to be appropriate for an order of magnitude prediction of carbon performance which is adequate to support the PFS risk assessment. Comparison of the model with multi-component experimental data indicated that breakthrough time predictions were accurate to within a factor of 3 with the model tending to give conservative results with regard to breakthrough times. Additionally, there was no apparent effect on model predictions due to an increase in the number of compounds in the feed to the filter.

Most of this error is attributable to the use of a universal isotherm (in lieu of measured data for all components) due to the limited availability of isotherm data for many of the contaminants in the CDF incinerator stack gases. This universal correlation appears to provide a satisfactory estimate of adsorption equilibrium for the organic compounds against which it was tested. For adsorbates where no isotherm data are available, the estimated adsorption isotherms provided by this correlation may be in error by two orders of magnitude, especially at low concentrations where information is sparse.

Overall, however, the demonstrated model accuracy is adequate for assessing the fundamental performance issues of dioxin and furan breakthrough times and emission levels relative to detection limits. For a test case based on preliminary ANCDF information, the model has been used to make predictions regarding the capability of the PFS to capture and retain the major chronic risk drivers, i.e., dioxins and furans, for a reasonable time period and also to determine whether the presence of the PFS could contribute to acute health effects during operational upsets in which the filter would be exposed to high temperatures and/or humidity. Results indicated that further improvements in model accuracy would not change the fundamental assessment conclusions.

Improvements in the accuracy of the model would require further research. Confidence in and accuracy of the single-component isotherm estimations could be increased, for example, by obtaining isotherm data for additional adsorbates on coconut shell carbon. Also, alternative multi-component isotherm models could be evaluated. Some models proposed in the literature (Okazaki et al., 1970) for predicting the effects of water on adsorption also appear to provide improved accuracy. Additional resources and time are required to provide a more accurate multi-component carbon filter simulation model that includes the effects of humidity. Given the capability of the current model to support the requirements of the PFS risk assessments, this additional effort is not warranted.

The committee concurs with Mitretek's conclusion. Mitretek performed an excellent study of a very difficult problem, and the results were accurate enough to show very long breakthrough times. The results also appear to be consistent with operating experience from commercial incinerators.

Some factors may not have been adequately considered, however, and surprises are always possible. Operability problems could arise (e.g., dust formation, uneven flow, etc.). Because these are all "first of a kind" plants, these problems will warrant close attention during start-up and early operation.

REFERENCES

Mitretek Systems. 1997. Pollution Abatement System Carbon Filter Simulation Model Development. January 1997. Aberdeen Proving Ground, Md.: U.S. Army Program Manager for Chemical Demilitarization.

Rordorf, B.F. 1985. Thermodynamic and thermal properties of polychlorinated compounds: the vapor pressures and flow tube kinetics of ten dibenzo-para-dioxins. Chemosphere 14(6/7): 885–892.

Ruthven, D.M. 1984. Principles of Adsorption and Adsorption Processes. New York: John Wiley and Sons.

U.S. Army. 1998. Risk Assessment of the Pollution Abatement Filter System for the Anniston Chemical Agent Disposal Facility (ANCDF). Prepared by Mitretek Systems, August 1998. Aberdeen Proving Ground, Md.: U.S. Army Program Manager for Chemical Demilitarization.

Appendix E

Adsorption Separations: Alternative Modes of Operation

Two different methods of contacting gas with carbon adsorbent have been used in industry both of which were considered by the Chemical Stockpile Disposal Program (CSDP). These methods can result in quite different amounts of adsorbed material. The difference in adsorptive capability is explained in this appendix and the chosen methods described (the method not chosen is described in Appendix F).

In the chosen mode of operation, the gas flows through a bed (or series of beds) of solid adsorbent. Sufficient adsorbent is provided so that the operation can continue for a "long" time, from several hours to a year or more, before the bed becomes saturated. In this mode, the leading part of the bed comes to equilibrium with the inlet concentration of the compound being adsorbed. A typical concentration profile of adsorbed material is shown in Figure E-1. (The shape actually depends on the nature of the adsorption isotherm; the shape shown in Figure E-1 applies to a common type of isotherm—a "favorable" isotherm, shown in Figure E-2.)

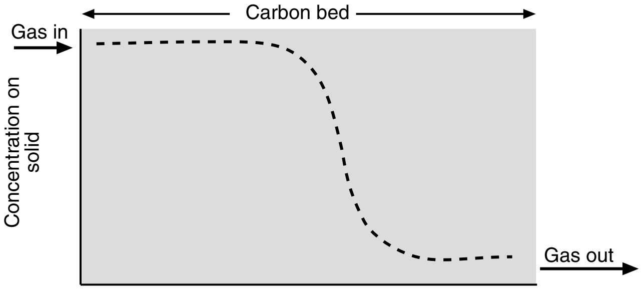

FIGURE E-1 Typical concentration profile of a material strongly adsorbed on a solid.

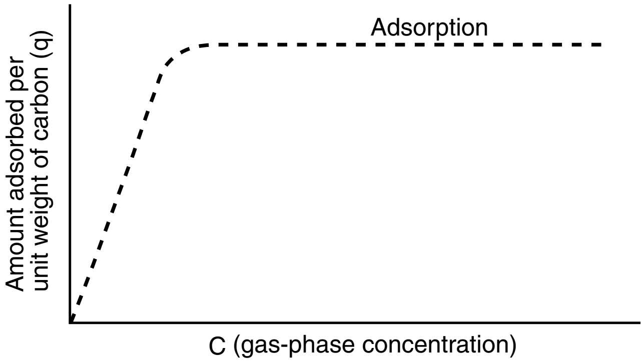

FIGURE E-2 "Favorable" adsorption isotherm for strongly adsorbed species.

The concentration "front" shown in Figure E-1 applies to material on the solid. A similar profile applies to the gas-phase concentration; the concentration of material to be adsorbed drops almost to zero in the gas leaving the bed. The "front" will gradually move through the bed and finally break through at the end (i.e., adsorbable material will start to show in the exit gas). At that point the operation is stopped. In this type of operation, most of the solid in the bed becomes saturated (i.e., comes to equilibrium) at the *inlet* concentration.

The second mode of operation, which is commonly used for cleanup of flue gas, involves injecting a small amount of solid adsorbent into the flowing gas, providing sufficient contact time for the efficient use of the carbon and then separating the solid adsorbent before discharging the gas up the stack. This process has the advantage of causing less pressure drop than the "bed" operation, but the use of the adsorbent is less efficient.

This is illustrated by the following analysis based on the "favorable" isotherm shown in Figure E-2.

Let the gas flow rate be *F* and the solids injection rate be *r*. Then, as the two flow downstream together, a material balance shows: $r\,dq = -Fdc$. Since *r* and *F* change little in the process, this equation is a straight line, as shown on Figure E-3, with slope ; it goes through the initial conditions (q_i assumed to be zero, and $dq / dc = \frac{-F}{r}$ gas concentration C_i). The maximum that can be adsorbed corresponds to the intersection of this material balance line with the equilibrium adsorption isotherm. The maximum amount that can be adsorbed is thus shown to be much less than with the fixed bed method.

In operation, the flow-through process may assume some of the fixed-bed properties when the solids are separated from the gas using a bag filter. The solid is allowed to build up on the filter until the pressure drop becomes excessive, when the solids are blown off. While the solids are building up on the filter bag, they act as a solid bed (i.e., the first mode of operation), enabling an increased amount to be adsorbed on the solid. An alternative means for solids separation is an electrostatic precipitator. Electrostatic precipitators do not provide the short flow time through a bed, and therefore, have lower adsorption capacity.

Both methods of implementing activated carbon pollution control systems significantly reduce the gas concentrations of adsorbed species. Data presented in Chapter 3 for the direct-injection method showed that activated carbon could reduce dioxins by 96 to 98 percent. Similar reductions have been reported for fixed-bed carbon systems (Brueggendick and Pohl, 1993; Schüller, 1994; Hartenstein, 1993, 1994). In principle, fixed-bed adsorbers can be more effective than injection systems. Prior to the time of breakthrough, the gas leaving a fixed bed comes in contact with some portion of the carbon that has little or no material adsorbed on it.

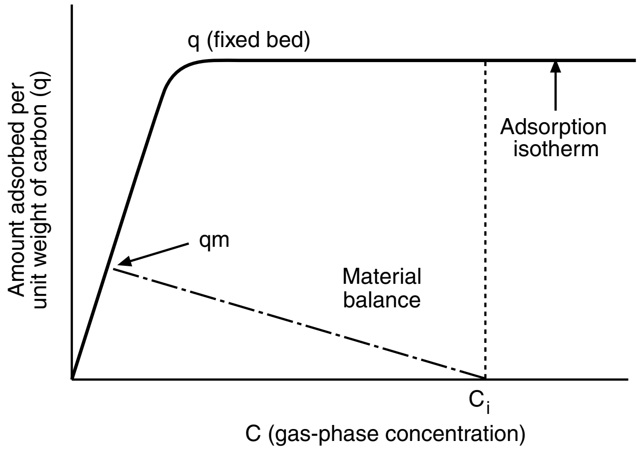

FIGURE E-3 Comparison of maximum adsorption for fixed bed (*q*) and solids injection (*qm*) adsorption separation modes.

REFERENCES

Brueggendick, H., and F.G. Pohl. 1993. Operating Experience with STEAGS Activated Carbon Processes -a/c/t®- in European Waste Incineration Plants. Pp. 787–794 in Proceedings of the Annual International Pittsburgh Coal Conference. Pittsburgh, Pa.: University of Pittsburgh, School of Engineering, Center for Energy Research.

Hartenstein, H.-U. 1993. Activated carbon for flue-gas polishing of MWIs (municipal waste incinerators). Pp. 87–105 in Proceedings of an International Specialty Conference. Pittsburgh, Pa.: Air and Waste Management Association.

Hartenstein, H.-U. 1994. The retrofit of the MWC ROTEB in Rotterdam, Holland, with a modern flue gas cleaning system including an activated char adsorption unit. Pp. 1–10 in National Waste Processing Conference Proceedings, Boston, Massachusetts, June 5–8, 1994. New York: American Society of Mechanical Engineers.

Schüller, H.-P. 1994. Nachrüstung eines Gegenstromadsorbers. Pp. 536–543 in Thermische Abfallbehandlung by Karl Joachim Thomé-Kozmiensky. Berlin: EF-Verlag Für Energie- und Umwelttechnik GMBH.

Appendix F

Alternative Flue Gas Cleaning Systems for Substances of Potential Concern

The carbon filter system chosen by the Army for the pollution abatement system filter system (PFS) is a fixed-bed design. The Army also briefly considered two alternative filter processes: a carbon-injection system; and a catalytic oxidation system. Following a discussion of available types of adsorbents; these alternative processes are briefly described.

TYPES OF ADSORBENT MATERIAL

The activated carbon chosen for evaluation in the experimental work performed by Mitretek was a coconut-shell carbon—the same material used by the Army for ventilation air filters at chemical disposal facilities. The Army has indicated a preference for this type of carbon simply to avoid the need to stock various types. Other types of carbon are made principally from coal. The Army's choice for the PFS was not known at the time this report was prepared, but the committee suspects that it will probably be coconut-shell carbon. Based on the Mitretek analysis and the Army's experience with air filtration, coconut-shell carbon will probably perform satisfactorily. Whether other types of activated carbon might perform better (e.g., with less dust formation or better adsorption) could only be determined on the basis of operating experience.

A number of synthetic adsorbents have been developed over the last 30 years (e.g., several zeolites), and remarkable selectivities have been observed for specific separations that are otherwise difficult. However, carbon has remained the universal choice for treating flue-gas. This is probably because of economics, particularly when the material will be used only once (i.e., with no regeneration). The Army prefers not to attempt to regenerate carbon that is significantly contaminated with agent.

CARBON INJECTION

The fixed-bed system uses carbon particles of 8 to 16 mesh (1.2 to 2.4 mm)—particulates large enough to limit the pressure drop through the beds to a reasonable level. An alternative is to grind the carbon to a much finer size (e.g., passing 200 mesh [0.074 mm]) and injecting this "micronized" carbon directly into the gas flow to provide a few seconds of contact time. The system approaches equilibrium in a matter of seconds because of the small particle size. That is, mass transfer rates increase rapidly as particle size is reduced.

The solids are then separated from the gas using either an electrostatic precipitator or a bag filter. In practice, carbon-injection systems are frequently retrofited systems to existing facilities, and the separation device is the one that was installed originally. If bag filters are used, the micronized carbon may thinly coat the surfaces, increasing gas/solid contact as gas flows through this layer. This process works basically the same way as the fixed-bed design chosen by the Army (i.e., with uniform flow of gas through a carbon bed). Adequate contact can be obtained even with very thin beds of fine particles.

The carbon-injection process evaluated by the Army contractor involved a thin layer of carbon coating on a bag filter. The coating was assumed to be 0.2 inches thick, which is comparable to the filter cake maintained on pulse-jet filters. The process was considered to have the following drawbacks compared with a "conventional" carbon bed:

- Handling the micronized carbon introduces problems associated with housekeeping and potential respiratory problems in the event of a failure in a filter element. This problem would be compounded because the carbon dust would be contaminated with substances of potential concern (SOPCs). In addition, finely divided activated carbon dust presents a fire and explosion hazard.
- The process requires that a layer of uniform thickness be built up on the bag filter to provide uniform treatment for all of the gas. If the thickness varies, gas will pass preferentially through the thinner sections. It was not clear how uniform thickness would be achieved.
- More carbon consumption is required in the dry sorbent-injection design than the fixed-bed design (see Appendix E). Thin layers on bag filters would have to be replaced frequently, during which breakthroughs would have to be avoided while acceptable flow and pressure were maintained.

CATALYTIC OXIDATION

Catalytic oxidation is conceptually a simple process. The output from the mist eliminator of the baseline system would be preheated and passed through a fixed bed of a platinum catalyst chosen for its resistance to poisoning by chlorine, phosphorus, and sulfur. SOPCs and any residual agent would be oxidized in the catalyst bed. The process would operate at 700°F (371°C) or higher, so substantial amounts of natural gas would be required to heat the flue gas to reaction temperature. The flow rates to the blowers would also be much higher because of the higher temperature and the addition of more combustion products from the natural gas; therefore, the blowers would have to be much larger, which would increase energy consumption. All of these factors would add to the cost of the facility, making the system more expensive than the fixed-bed carbon filter system.

The catalytic oxidation system's demonstrated very high levels of destruction (e.g., 5 nines) was also questioned by the Army contractor. This destruction level would be extremely difficult to demonstrate during normal operations, when the materials of most concern in the flue gas—dioxins and furans—would already be down to parts per trillion, or nondetectable levels. Measuring outlet concentrations of one-millionth of the already difficult-to-measure values would require sampling times longer than the facility operating life. In the event of an incinerator upset that induced higher flue gas concentrations, a fixed activated carbon bed would be able to handle the problem. The ability of the catalytic oxidation unit to do so was judged to be less certain, although foreseeable upsets should produce inconsequential increases in SOPCs. Another concern about the catalytic oxidation system was the potential for poisoning the catalyst, thus reducing its effectiveness.

Catalytic oxidation has one potential advantage over the fixed carbon bed—it would oxidize a lot of the SOPCs that would not be captured by the carbon because they are not strongly adsorbed. Health risk assessments, however, indicate that most of the risk is associated with chlorinated dioxins and furans, which *are* strongly adsorbed. The volatile materials that might escape a carbon bed would be at such low concentrations that they would contribute very little to the health risk.

Based on differences in operating experience and costs, the Army's decision to choose carbon bed filtration over catalytic oxidation appears to be sound.

Appendix G

Biographical Sketches of Committee Members

David S. Kosson *(chair)* has a B.S. in chemical engineering, an M.S. in chemical and biochemical engineering, and a Ph.D. in chemical and biochemical engineering from Rutgers, The State University of New Jersey. He joined the faculty at Rutgers in 1986 and was made an associate professor with tenure in 1990 and a full professor in 1996. He teaches graduate and undergraduate courses in chemical and environmental engineering and conducts research for the Department of Chemical and Biochemical Engineering on the development of microbial, chemical, and physical treatment methods for hazardous waste. He is responsible for project planning and coordination, from basic research through full-scale design and implementation. He has published extensively in the fields of chemical engineering, waste management and treatment, and contaminant fate and transport in soils and groundwater. Dr. Kosson has served on several Environmental Protection Agency advisory panels involved in waste research and is the director of the Physical Treatment Division of the Hazardous Substances Management Research Center in New Jersey. He is a member of the American Institute of Chemical Engineers and recently served as a member of the National Research Council Committee on Alternative Chemical Demilitarization Technologies.

Charles E. Kolb *(vice chair)* is president and chief executive officer of Aerodyne Research, Inc. Since 1971, his principal research interests at Aerodyne have included atmospheric and environmental chemistry, combustion chemistry, materials chemistry, and the chemical physics of rocket and aircraft exhaust plumes. He has served on several National Aeronautics and Space Administration panels dealing with atmospheric chemistry and global change, as well as on five National Research Council committees and boards dealing with environmental issues. From 1996 to 1999, he was atmospheric sciences editor for *Geophysical Research Letters.* In 1997, he received the Award for Creative Advances in Environmental Science and Technology from the American Chemical Society.

David H. Archer, a member of the National Academy of Engineering, has a Ph.D. in chemical engineering and mathematics from the University of Delaware. He is a retired consulting engineer with the Westinghouse Electric Company and is currently adjunct professor at Carnegie Mellon University. Dr. Archer has worked in both industry (at Westinghouse as an engineer, supervising engineer, department manager, and consulting engineer) and academia (at the University of Delaware and Carnegie Mellon University) for almost 10 years. He has considerable experience in research and management related to chemical engineering, as well as experience with combustion and plant management.

Piero M. Armenante has a Ph.D. in chemical engineering from the University of Virginia and is currently professor of chemical engineering at the New Jersey Institute of Technology. Dr. Armenante's research interests include multiphase mixing in agitated systems, the biological treatment of hazardous waste, industrial sterilization processes, and biomedical engineering. He has an extensive list of peer-reviewed and other publications and has administered numerous grants, studies, and projects.

Dennis C. Bley is president of Buttonwood Consulting, Inc., and a principal of The WreathWood Group, a joint venture company that supports multidisciplinary research in human reliability. He has more than 25 years of experience in nuclear and electrical engineering, reliability and availability analysis, plant and human modeling for risk assessment, diagnostic system development, and technical management. Dr. Bley has a Ph.D. in nuclear engineering from the Massachusetts Institute of Technology and is a registered professional engineer in the state of California. He has served on a number of technical review panels for U.S. Nuclear Regulatory Commission and U.S. Department of Energy programs and is a frequent lecturer in short courses for universities, industries, and government agencies. He is active in many professional organizations and is on the Board of Directors of the International Association for Probabilistic Safety Assessment and Management. Dr. Bley has published extensively on subjects related to risk assessment. His current research interests include applying risk analysis to diverse technological systems, modeling uncertainties in risk analysis and risk management, technical risk communication, and human reliability analysis.

Frank P. Crimi is a part-time consultant and retired vice president of Lockheed Martin Advanced Environmental Systems Company. He has a B.S. in mechanical engineering from Ohio University and has done graduate work in mechanical engineering at Union College in Schenectady, New York. In addition to his appointment to the National Research Council Committee on Decontamination and Decommissioning of Uranium Enrichment Facilities, Mr. Crimi has firsthand knowledge and experience with radioactive and hazardous-waste treatment and disposal technologies.

Elisabeth M. Drake, a member of the National Academy of Engineering, is the associate director of the Massachusetts Institute of Technology Energy Laboratory. A chemical engineer with experience in risk management and technology associated with the transport, processing, storage, and disposal of hazardous materials, as well as chemical engineering process design and control systems, Dr. Drake has a special interest in the interactions between technology and the environment. She has often been a consultant to government and industry and has been active in the American Institute of Chemical Engineers, especially the Center for Chemical Process Safety. She belongs to a number of environmental organizations, including the Audubon Society, the Sierra Club, and Greenpeace.

J. Robert Gibson is the assistant director of the Haskell Laboratory, E.I. du Pont de Nemours and Company, and an adjunct associate professor of marine studies at the University of Delaware. Since receiving his Ph.D. in physiology from Mississippi State University, Dr. Gibson has specialized in toxicology. He has been certified by the American Board of Toxicology and is the author of numerous publications.

Michael R. Greenberg is a professor in the Department of Urban Studies and Community Health at Rutgers, The State University of New Jersey, and an adjunct professor of environmental and community medicine at the Robert Wood Johnson Medical School. His principal research and teaching interests include urbanization, industrialization, and environmental health policy. Dr. Greenberg holds a B.A. in mathematics and history, an M.A. in urban geography, and a Ph.D. in environmental and medical geography.

Kathryn E. Kelly received her Ph.D. in public health from Columbia University, with a concentration in environmental toxicology. She is the founder and president of Delta Toxicology, Inc., in Crystal Bay, Nevada. Dr. Kelly has broad experience in toxicology, waste combustion, environmental policy, and risk communication.

Richard S. Magee (chair from 7/94 to7/98) is a professor in the Department of Mechanical Engineering and the Department of Chemical Engineering, Chemistry, and Environmental Science and the associate provost for research and development at the New Jersey Institute of Technology (NJIT). He also directs the Environmental Protection Agency's Northeast Hazardous Substance Research Center. He is a fellow of the American Society of Mechanical Engineers (ASME) and a diplomate of the American Academy of Environmental Engineers. Dr. Magee's research expertise is in combustion, with a focus on the incineration of municipal and industrial wastes. He has served as vice chairman of the ASME Research Committee on Industrial and Municipal Wastes and as a member of the United Nations Special Commission (under Security Council Resolution 687) Advisory Panel on Destruction of Iraq's Chemical Weapons Capabilities. He was recently a member of the North Atlantic Treaty Organization (NATO) Science Committee's Priority Area Panel on disarmament technologies and is presently a member of the NATO Science Committee's

Security-Related Civil Science and Technology Panel. He recently chaired the National Research Council Panel on Review and Evaluation of Alternative Chemical Disposal Technologies.

James F. Mathis, a member of the National Academy of Engineering, graduated from the University of Wisconsin with a Ph.D. in chemical engineering. Dr. Mathis was vice president of science and technology for Exxon Corporation, where he was responsible for worldwide research and development programs, and chair of the New Jersey Commission on Science and Technology until his retirement in 1997. Dr. Mathis' expertise is in research and development and chemical engineering.

Walter G. May has a B.S. in chemical engineering and an M.S. in chemistry from the University of Saskatchewan and a D.Sc. in chemical engineering from the Massachusetts Institute of Technology. He joined the faculty of the University of Saskatchewan as a professor of chemical engineering in 1943. In 1948, he began a distinguished career with Exxon Research and Engineering Company, where he was a senior science advisor from 1976 to 1983. From 1983 until his retirement in 1991, he was professor of chemical engineering at the University of Illinois, where he taught process design, thermodynamics, chemical reactor design, separation processes, and industrial chemistry and stoichiometry. Dr. May has published extensively, served on the editorial boards of *Chemical Engineering Reviews* and *Chemical Engineering Progress*, and has obtained numerous patents in his field. He is a member of the National Academy of Engineering, a fellow of the American Institute of Chemical Engineers, and the recipient of special awards from the American Institute of Chemical Engineers and the American Society of Mechanical Engineers. He is also a registered professional engineer in the state of Illinois. Dr. May was a member of the National Research Council Committee on Alternative Chemical Demilitarization Technologies and the Committee on Decontamination and Decommissioning of the Uranium Diffusion Plants.

Alvin H. Mushkatel, professor in the School of Planning and Landscape Architecture, Arizona State University, is an expert in emergency management risk perceptions. His research interests include emergency management, natural and technological hazards policy, and environmental policy. He has been a member of the National Research Council Committee on Earthquake Engineering, the Committee on Decontamination and Decommissioning of Uranium Enrichment Facilities, and the Panel on Review and Evaluation of Alternative Chemical Disposal Technologies. His most recent research has been focused on intergovernmental policy conflicts involving high-level nuclear-waste disposal and the role of citizens in decision-making processes. He has published extensively on issues related to the siting of hazardous waste facilities.

H. Gregor Rigo attended Ohio University and earned his Ph.D. in mechanical and environmental engineering from the University of Illinois. He is currently president of Rigo & Rigo Associates, Inc., in Berea, Ohio. He has extensive experience in plant start-up, process and environmental engineering, and applied statistics focused on the use and control of emissions from nontraditional fuels; technical, environmental, and economic evaluations; and multipathway health risk assessments.

Kozo Saito has a Ph.D. in mechanical engineering from Seikei University in Tokyo and is currently professor of mechanical engineering in the Department of Mechanical Engineering at the University of Kentucky. Dr. Saito's expertise and experience are in experimental combustion studies, thermal sensing and control, and lean manufacturing and control. He is a member of the Combustion Institute, the American Society for Engineering Education, and the American Society of Mechanical Engineers.

Arnold F. Stancell, a member of the National Academy of Engineering, graduated from the Massachusetts Institute of Technology with a Sc.D. in chemical engineering. Dr. Stancell is currently a professor of chemical engineering at Georgia Institute of Technology and recently was visiting professor of chemical engineering at the Massachusetts Institute of Technology. For many years he worked for Mobil Oil, where he started in research and eventually became vice president of Mobil Chemical and then vice president in the crude oil and natural gas business, both domestic and international. He was responsible for a $5 billion per year business with 5,000 employees. Dr. Stancell's expertise is in the management of large businesses, including chemical operations.

Chadwick A. Tolman received his Ph.D. in physical chemistry from the University of California at Berkeley and is currently a program officer in organic and macromolecular chemistry in the Division of Chemistry at the National Science Foundation. He has extensive experience and expertise in chemistry and chemical process development. Dr. Tolman spent 31 years in Central Research at the DuPont Experimental Station. His work has spanned a broad range of subject areas, including hydrocarbon oxidation, organometallic chemistry, and the destruction of toxic organic compounds in wastewater.

William Tumas is currently the group leader for the Waste Treatment and Minimization Science and Technology Group at Los Alamos National Laboratory. He is a senior chemist known primarily for his work in science and engineering research on waste treatment and minimization. His work has included research and technology development for industrial-waste applications and environmental restoration for the U.S. Department of Energy. At Los Alamos, he has studied supercritical fluids, oxidation, and organic transformations. He has written numerous papers and is a member of several professional organizations. In addition, Dr. Tumas was recently a member of the National Research Council Panel on Review and Evaluation of Alternative Chemical Disposal Technologies.