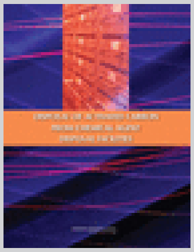

The Disposal of Activated Carbon from Chemical Agent Disposal Facilities

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DISPOSAL OF ACTIVATED CARBON FROM CHEMICAL AGENT DISPOSAL FACILITIES

Committee to Examine the Disposal of Activated Carbon from the Heating, Ventilation, and
Air Conditioning Systems at Chemical Agent Disposal Facilities

Board on Army Science and Technology

Division on Engineering and Physical Sciences

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NOTICE: The project that is the subject of this report was approved by the Governing Board of the National Research Council, whose members are drawn from the councils of the National Academy of Sciences, the National Academy of Engineering, and the Institute of Medicine. The members of the committee responsible for the report were chosen for their special competences and with regard for appropriate balance.

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Cover: The photograph on the cover shows part of a bank of activated carbon filter trays used for the HVAC systems at chemical agent disposal facilities. A detailed view of the structure and airflow through a filter tray can be seen in Figure 2-4. Courtesy of the U.S. Army Anniston Chemical Agent Disposal Facility, Anniston, Alabama.

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Preface

For more than two decades, the United States has been in the process of destroying its chemical agent and munitions stockpile. At this time, except for the nerve agent stored at a site where Congress has forbidden incineration and a few containers of legacy nerve agent GA (also known as tabun) at another site where they will soon be destroyed, the nation's entire stockpile of nerve agents has been destroyed. The operating chemical agent disposal sites are in the process of destroying the remaining mustard agent munitions. The Army is now turning its attention to preparing for the closure of these facilities and the disposal of all the secondary wastes that have been stored on-site. One of the secondary wastes is an estimated total of more than 1,300 tons of activated carbon that has been used as an adsorptive medium to protect site personnel and adjacent communities from potential exposure to the agents. Some of this carbon (about 20 percent) has been exposed to chemical agents, although over time the adsorbed agents have reacted with the water also adsorbed on the carbon and formed hydrolysis products. In most cases, only trace amounts of agent remain on this carbon. The remaining carbon (about 80 percent) has not been exposed to agent but continues to be available for this purpose as one of the safety measures designed into the facilities.

The U.S. Army's Chemical Materials Agency (CMA) asked the National Research Council to convene a committee to study the disposal of all the carbon used at chemical agent disposal facilities. While this project seemed simple at first, it turned out to be complex. For one thing, the carbon is used in different kinds of filter units throughout the facility. Which of them are actually contaminated with agent? Most of the carbon is not contaminated and could be disposed of as ordinary hazardous waste. Another complication is that some of the mustard munitions contain high levels of mercury, a challenge for disposal. To address the mercury contamination requires changing the carbon in some filter units to sulfur-impregnated carbon, which will adsorb the mercury. Fortunately, the mercury-contaminated carbon is not expected to be exposed to agent unless there is a severe operational upset.

Still another issue, already noted, is that the agents on the carbon degrade by reacting with the water adsorbed on the carbon and forming the usual hydrolysis products. But how much agent remains on the filters? Is this level below the waste control limits established by regulatory authorities? How can one measure the amounts of residual agent on the carbon given the very low parts-per-billion (ppb) level? How can one minimize or altogether prevent the re-formation of nerve agent GB (also known as sarin) during analysis? These are some of the issues that concerned the committee during this study, and they all have implications for how and where the activated carbon used in the course of destroying chemical agents can be disposed of. Fortunately, I believe the committee has "gotten its arms around this gorilla." As its chair, I thank the members, who have worked as volunteers, for their contributions to this report. They included traveling and attending meetings at various sites, followed by a series of virtual meetings to write the report.

The committee is grateful to Timothy Garrett, who was the committee's point of contact at CMA for the study. It was he who organized the presentations and hosted the meeting in Anniston, Alabama. Also, we thank all the Army participants, who gave up their time, traveled to meetings, and openly discussed their problems with us. Finally, we thank the staff of the Board on Army Science and Technology (BAST) for its support and logistical help. In particular we thank Margaret Novack, the program director for this project; Harrison Pannella, who reviewed the report for us in detail and provided sound advice; and Nia Johnson, who provided project research support.

The BAST members, listed on page vi, were not asked to endorse the committee's conclusions or recommendations, nor did they review the final draft of this report before its release, although board members with appropriate expertise may be nominated to serve as formal members of study committees or as report reviewers. The BAST was established in 1982 by the National Academy of Sciences at the request of the Army. It brings broad military, industrial, and academic experience and scientific, engineering, and management expertise to bear on Army technical challenges and other issues of importance to senior Army leaders. BAST also discusses potential studies of interest; develops and frames study tasks; ensures proper project planning; suggests potential committee members and reviewers for reports produced by fully independent, ad hoc study committees; and convenes meetings to examine strategic issues.

Robert A. Beaudet, *Chair*
Committee to Examine the Disposal
of Activated Carbon from the Heating,
Ventilation, and Air Conditioning
Systems at Chemical Agent Disposal
Facilities

Acknowledgment of Reviewers

This report has been reviewed in draft form by individuals chosen for their diverse perspectives and technical expertise, in accordance with procedures approved by the National Research Council's (NRC's) Report Review Committee. The purpose of this independent review is to provide candid and critical comments that will assist the institution in making its 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 review comments and draft manuscript remain confidential to protect the integrity of the deliberative process. We wish to thank the following individuals for their review of this report:

Madan M. Bhasin, NAE, Dow Chemical Company (retired),
Richard A. Conway, NAE, Union Carbide Corporation (retired),
Gary S. Groenewold, Idaho National Laboratory,
George W. Parshall, NAS, DuPont (retired),
Danny Reible, NAE, University of Texas,
William R. Rhyne, Consultant,
William J. Walsh, Pepper Hamilton, LLP, and
Calvin Willhite, State of California Environmental Protection Agency.

Although the reviewers listed above have provided many constructive comments and suggestions, they were not asked to endorse the conclusions or recommendations, nor did they see the final draft of the report before its release. The review of this report was overseen by John R. Howell, NAE. Appointed by the National Research Council, he was responsible for making certain that an independent examination of this report was carried out in accordance with institutional procedures and that all review comments were carefully considered. Responsibility for the final content of this report rests entirely with the authoring committee and the institution.

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Abbreviations and Acronyms

ABCDF	Aberdeen Chemical Agent Disposal Facility
ACAMS	automatic continuous air monitoring system
ACS	agent collection system
ADEM	Alabama Department of Environmental Management
ADEQ	Arkansas Department of Environmental Quality
AEGL	acute exposure guideline level
ANCDF	Anniston Chemical Agent Disposal Facility
BGCAPP	Blue Grass Chemical Agent Destruction Pilot Plant
BTRA	boundary transportation risk assessment
CERCLA	Comprehensive Environmental Response, Compensation, and Liability Act
CH	mustard chlorohydrin
CH-TG	sulfonium ion
CMA	Chemical Materials Agency
CMS	carbon micronization system
CWC	Chemical Weapons Convention
DAAMS	depot area air monitoring system
DFS	deactivation furnace system
DOT	Department of Transportation
DPE	demilitarization protective ensemble
ECBC	U.S. Army Edgewood Chemical and Biological Center
EMPA	ethyl methylphosphonic acid
EONCs	enhanced on-site containers
EPA	U.S. Environmental Protection Agency
GA	nerve agent
GAC	granulated activated carbon
GB	nerve agent (sarin)
GC	gas chromatography
GPL	general population limit
H	mustard agent
HCl	hydrochloric acid
HD	distilled mustard agent
HF	hydrofluoric acid
Hg	mercury
HT	distilled mustard mixed with bis(2-chloroethylthioethyl) ether
HVAC	heating, ventilation, and air conditioning
IMPA	isopropyl methylphosphonic acid
JACADS	Johnston Atoll Chemical Agent Disposal System
LDR	land disposal restrictions
LIC	liquid incinerator

MAS	magic angle spinning
MDB	munitions demilitarization building
MDL	method detection limit
MPF	metal parts furnace
MS	mass spectrometry
MWI	municipal waste incinerator
NaOH	sodium hydroxide
NECDF	Newport Chemical Agent Disposal Facility
NMR	nuclear magnetic resonance
NRC	National Resource Council
ODEQ	Oregon Department of Environmental Quality
ONCs	on-site containers
OTS	off-gas treatment system
PAC	powdered activated carbon
PAS	pollution abatement system
PBCDF	Pine Bluff Chemical Agent Disposal Facility
PCAPP	Pueblo Chemical Agent Destruction Pilot Plant
PCC	permit compliance concentration
PFS	PAS filtration system
ppb	parts per billion
ppm	parts per million
ppm_w	parts per million by weight
RCRA	Resource Conservation and Recovery Act
STEL	short-term exposure limit
STL	short-term limit (no time component specified)
SwRI	Southwest Research Institute
TCLP	toxic chemical leaching procedure
TG	thiodiglycol
TOCDF	Tooele Chemical Agent Disposal Facility
TRA	transportation risk assessment
TSDF	treatment, storage, and disposal facility
UDEQ	Utah Department of Environmental Quality
UMCDF	Umatilla Chemical Agent Disposal Facility
VSL	vapor screening level
VX	nerve agent
VX-pyro	diethyl dimethylpyrophosphonate
WAP	waste analysis plan
WCL	waste control limit

Summary

For the past two decades, the United States has been destroying its entire stockpile of chemical agents. At the facilities where these agents are being destroyed, effluent gas streams pass through large activated carbon filters before venting to ensure that any residual trace vapors of chemical agents and other pollutants do not escape into the atmosphere in exceedance of regulatory limits.[1] All the carbon will have to be disposed of for final closure of these facilities to take place.

In March 2008, the Chemical Materials Agency (CMA) asked the National Research Council (NRC) to convene a committee to study, evaluate, and recommend the best methods for proper and safe disposal of the used carbon from the operational disposal facilities. The statement of work reads as follows:

STATEMENT OF TASK

The National Research Council will establish an ad hoc committee to:

- examine the current heating, ventilation, and air conditioning (HVAC) systems of the U.S. Army's Chemical Materials Agency (CMA) that use activated carbon and consider the overall quantity and characteristics of the CMA HVAC secondary wastes
- assess the current plans and path forward for contaminated carbon management and disposition at Army chemical agent disposal facilities
- evaluate commercial and established industry alternatives for contaminated carbon disposal, i.e. best practices, processes and equipment suitable for use by the Army (considering both on-site and off-site usage), including characterization and pre-treatment requirements
- in the foregoing context, assess the scientific support needed for obtaining regulatory approvals at CMA facilities.

In response to this request, the NRC Board on Army Science and Technology assembled the Committee to Examine the Disposal of Activated Carbon from the Heating, Ventilation, and Air Conditioning Systems at Chemical Agent Disposal Facilities. After discussion with the sponsor, the committee undertook to consider the disposition of all the carbon, exposed or unexposed to chemical agent, at the facilities.

This report examines various approaches to handling carbon waste streams from the four operating chemical agent disposal facilities that use incineration technology developed by the Army. The approaches that will be used to dispose of carbon waste at each facility will ultimately be chosen bearing in mind local regulatory practices, facility design and operations, and the characteristics of agent inventories, along with other factors such as public involvement regarding facility operations. This report is intended to analyze and assess essential information on the various approaches for disposing of waste carbon from these facilities whether or not the carbon has been exposed to agent. This should enable readers to understand the technical reasoning underlying the committee's findings and recommendations. Specific findings and recommendations are found in the individual chapters; the key findings and recommendations (General Findings 1-5 and General Recommendations 1-5) derived from the individual

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[1] Note that what are termed "carbon filters" in Army parlance are more accurately termed "carbon adsorption beds."

chapters are presented at the end of this Summary and in Chapter 7.

Only three types of filter units are expected to ever be exposed to agents under normal operating conditions: (1) those that filter the heating, ventilation, and air conditioning (HVAC) air from the munitions demilitarization building (MDB), (2) the filters installed on the vent line from the agent collection system storage tanks, and (3) the canisters for the M-40 protective masks used by workers. The carbon from the initial banks of MDB HVAC air filters accounts for by far the largest share of exposed carbon. All of the other filter units installed to protect personnel or the environment will never have been exposed to agent unless some upset had occurred (e.g., release of agent to the atmosphere outside the MDB).

The MDB, which is where the munitions or containers are opened and treated, has a cascading HVAC system that is designed to move ventilation air from clean, uncontaminated areas to areas having increasing levels of agent contamination. The HVAC system then discharges the air through banks of activated carbon filters. Each bank of the filter units, which are arranged in series, contains 48 metal trays each holding approximately 50 lb of carbon. An important feature of the system design is that operational procedures normally allow only the carbon in Banks 1 and 2 of the multibank adsorber units filtering the plant HVAC air to ever be exposed to agent. The carbon from Banks 3-6 of the HVAC filter units and the carbon from the pollution abatement system (PAS) filtration system (PFS) on each of the incinerators make up the bulk of the unexposed carbon. Estimates of the amounts of carbon that must be disposed of from the indicated sources at each site are tabulated in Tables S-1 and S-2. The ratio of unexposed to exposed carbon is approximately 4 to 1.

The disposal of the exposed and unexposed carbon is regulated under the Resource Conservation and Recovery Act (RCRA) by the respective state regulatory agencies. Each facility has been issued a RCRA permit under the applicable state regulations. These permits establish waste characterization requirements, pertinent sampling/analysis methodologies, waste disposal methods, operating parameters, and closure requirements for each facility. The state-issued RCRA permits for all of the disposal facilities specify waste control limits (WCLs) or, for Oregon, permit compliance concentrations (PCCs) in parts per billion (ppb) of chemical agent below which a waste may be shipped off-site for disposal.

TABLE S-1 Summary of Sources and Estimated Inventories (in Pounds) of Carbon Exposed to Agent at CMA Incineration Sites During Operations and Closure[a]

Site	ACS	Laboratory	MDB HVAC	M-40 Mask Canisters[b]	Other
ANCDF	3,600	<100	153,800	1,400	
UMCDF	4,800	<100	47,500	2,100	
TOCDF	200	15,300[c]	159,000	3,100	20,800[d]
PBCDF	1,200	<100	95,600	<100	
Total	9,800	15,300	455,900	6,600	20,800

[a] Weights may include carbon, carbon tray materials, and packaging. Information is as of September 29, 2008. Estimates of exposed carbon made on basis of anticipated on-site treatment. Quantities have been rounded.

[b] Carbon from M-40 mask canisters, while normally not exposed to agent, is generally expected to be treated as exposed at most sites in view of the relatively small amounts involved.

[c] This carbon amount is the result of the significantly larger amounts and greater variety of materials tested over the longer duration of TOCDF operations compared to other sites.

[d] This carbon amount is the result of a ton container sampling operation unique to the site.

SOURCE: Adapted from information provided to the committee by Timothy Garrett, Site Project Manager, ANCDF, as of September 29, 2008.

The permits for the chemical agent disposal facilities at Anniston, Alabama, Pine Bluff, Arkansas, and Tooele, Utah (ANCDF, PBCDF, and TOCDF) set the WCL as 20 ppb for nerve agents GB and VX and 200 ppb for mustard agent, while the facility at Umatilla, Oregon (UMCDF) sets PCCs, which serve a similar purpose, at 13 ppb for VX, 16 ppb for GB, and 152 ppb for mustard.[2] The primary analytical methodology for characterizing a waste at most of the chemical agent disposal facilities is set forth in EPA Publication SW-846; it includes the toxic chemical leaching procedure (TCLP), which is required to determine if a waste meets the toxicity characteristic definition.[3]

The existing requirements to transport activated carbon off-site for disposal are stated in each facility's RCRA permit (Table S-3). Any changes require applying for a modification to the permit—the approval process takes approximately 1 year. Planned applica-

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[2] Brian O'Donnell, Chief, Secondary Waste, Closure Compliance, and Assessments, CMA, "Transportation risk assessment," Presentation to the committee, July 24, 2008.

[3] 40 C.F.R. 261.24(a). A waste is considered hazardous for toxicity if the extract from the procedure contains a listed contaminant above a specified concentration, with mercury listed at 0.2 mg/L (Table 1).

TABLE S-2 Summary of Sources and Estimated Inventories (in Pounds) of Unexposed Carbon Used at CMA Incineration Sites During Operations and Closure[a]

Site	PFS Carbon (Regular)	Laboratory	MDB HVAC	PFS Sulfur-Impregnated Carbon	Control Room	Other
ANCDF	115,500	15,400	414,700	69,300	15,400	12,400
UMCDF	270,000[b]	10,600	95,000	200,000[b]	5,300	17,300
TOCDF	0[c]	6,300	318,000	240,000[d]	5,000[d]	2,500[d]
PBCDF	80,800[e]	15,900	127,500	48,500[f]	8,000	14,400
Total	466,300	48,200	955,200	557,800	33,700	46,600

[a] Weights may include carbon, carbon tray materials, and packaging. Information is as of September 29, 2008, unless otherwise noted. Estimates of unexposed carbon made on basis of anticipated off-site treatment. Quantities have been rounded.

[b] Information updated as of March 17, 2009.

[c] PFS was only recently added at TOCDF for the processing of mercury-contaminated mustard agent and therefore only sulfur-impregnated carbon is to be used.

[d] Information updated as of March 19, 2009.

[e] Information updated as of March 18, 2009. Of this amount, 48,500 lb has already been shipped off-site.

[f] Information updated as of March 18, 2008.

SOURCE: Adapted from information provided to the committee by Timothy Garrett, Site Project Manager, ANDCF, as of September 29, 2008.

TABLE S-3 Current Status of Permit Requirements for Shipping Carbon Off-site from Chemical Agent Disposal Facilities

Facility	Requirement of the Existing Permit	Planned Modification Application
ANCDF	Carbon exposed to <1 STL may be shipped off-site.[a] Carbon exposed to >1 STL must undergo extractive analysis prior to shipment. Carbon that tests <WCL may be shipped off-site. Filters from the agent collection system will be incinerated on-site.	HVAC carbon >WCL after extractive analysis to be shipped off-site in accordance with bounding transportation risk assessment. Munitions demilitarization building HVAC Bank 1 carbon appears to be >WCL for GB.
UMCDF	Off-site shipment of agent-free carbon allowed if agent concentration is less than the PCC: 16 ppb for GB, 13 ppb for VX, and 152 ppb for mustard.	The UMCDF plans to submit a Permit Modification Request to incorporate the agent extraction method for spent carbon into the Hazardous Waste Permit WAP following the programmatic validation of the method.
TOCDF	All carbon must be processed by carbon microminiaturization system and subsequently combusted in the deactivation furnace system.[b]	Ship all carbon from the pollution abatement system filtration system and from the heating, ventilation, and air conditioning (HVAC) Banks 4-6 off-site. Considering using autoclave on remaining carbon until VSL <1 then shipping off-site.
PBCDF	The WAP requires on-site incineration of exposed carbon that is shown by extractive analysis to be greater than 20, 20, and 200 ppb for GB, VX, and H, respectively. The WAP allows off-site shipment to a TSDF for spent carbon that is shown by extractive analysis to be less than 20, 20, and 200 ppb for GB, VX, and H, respectively. Unexposed carbon can also be shipped, and generator knowledge is allowed in the determination of "unexposed."	None.
NECDF	Used agent-contaminated carbon is considered a listed hazardous waste (Waste Code 1001). However, extractive analysis was done to satisfy CMA bounding transportation risk assessment requirements. Agent-contaminated carbon has been shipped to a TSDF (a hazardous waste incinerator) for treatment.	None.

[a] The one STL for GB and VX is 20 ppb; for HD, it is 200 ppb.

[b] Although this is the existing requirement, the state and TOCDF have agreed that carbon will be stored until another treatment method is approved.

SOURCE: Personal communications between Timothy Garrett, Site Project Manager, ANCDF, and Margaret Novack, NRC study director, February 24, 2009, February 25, 2009, and February 27, 2009.

tions for permit modifications are also shown in the table. The regulations generally specify that the carbon will require extractive analysis to confirm that agent concentration(s) are below the respective WCLs or PCCs.

Although all three chemical agents are strongly adsorbed on coconut shell activated carbon, they all react with the moisture that is also adsorbed on the carbon to form the expected hydrolysis products. In 2007, several carbon samples from Banks 1 and 2 of the MDB HVAC filter unit at ANCDF were analyzed for residual GB and VX at both government and contractor surety laboratories.

These analyses verified that the agents GB and VX decompose by hydrolysis with the adsorbed water on the carbon. The amount of GB that must have been adsorbed on Bank 1 carbon during processing of GB munitions in the MDB is evidenced by the 13 wt percent of its hydrolysis product, isopropyl methylphosphonic acid (IMPA), which was found on the carbon by solid state magic angle spinning (MAS) nuclear magnetic resonance (NMR). In comparison, only a trace amount of the VX hydrolysis product, ethyl methylphosphonic acid (EMPA), was found on carbon from Bank 1. This small amount of the hydrolysis product is attributed to the low volatility of VX. Extractive analysis of HVAC filter unit carbon samples from NECDF by the system contractor laboratory indicated the presence of volatile VX impurities, hydrolysis by-products, and degradation products of the aminothiol group. At this time, no MDB HVAC carbon sample exposed to mustard agent HD from a chemical agent disposal facility is available for laboratory analysis.

The shipping of agent-exposed carbon to off-site disposal facilities will require determination of the loading of agent on the carbon on a mass basis (mass of agent per mass of carbon). For parts-per-billion levels of detection of residual agents on carbon, solvent extraction of the adsorbed phase from the carbon sample followed by gas chromatography/mass spectrometry (GC/MS) analysis is being pursued. The Bank 1 carbon removed at ANCDF was analyzed by this method at Southwest Research Institute to determine the amounts of GB and VX remaining on the carbon. VX was below the WCL, but GB was above it. The GB result has been interpreted as a sign that GB re-forms from the hydrolysis products in the solvent during the extraction process. A way was found to limit this re-formation to ~6 ppb, but this modification to the standard method is not considered valid until other laboratories have reproduced the results. Early (unvalidated) measurements on the ANCDF Bank 1 carbon indicate that the residual GB (~129 ppb) is above the WCL limit (20 ppb), which means the carbon will not be transportable under the present permit. However, carbon containing GB at more than 20 ppb could be transported off-site if the transportation risk assessment (TRA) approved by state regulators and procedures was implemented to satisfy the bounding TRA values. These values are a function of accidental release scenarios assumed in the assessment and the frequency established for such release scenarios.

In response to the third bullet in the statement of task for this study, the committee surveyed the common industrial practices for managing activated carbon. In commercial and industrial applications, activated carbon finds extensive use as an adsorbent for removal of a wide range of contaminants from liquids and gases. Demand for activated carbon in the United States was 363 million pounds in 2005, split approximately equally between granulated activated carbon and powdered activated carbon. The activated carbon used in chemical agent disposal facilities is granulated. Activated carbon is also used to adsorb a product such as a solvent from a process stream. In such applications, the adsorbed product is subsequently desorbed on-site for reuse. This last step, known as "carbon regeneration," differs from "carbon reactivation," which is a treatment process whereby adsorbed materials (adsorbates) on the carbon are destroyed and the structure of the activated carbon is restored for reuse. Reactivation is carried out in either a rotary kiln or multiple hearth furnaces where the carbon is heated in the presence of steam to 1800°F.

There are essentially three treatment and disposal methods used for treating activated carbon from commercial operations: (1) reactivation, (2) landfill, and (3) incineration. If carbon from commercial industrial operations has been reactivated, vendors offer two options. One is to return the reactivated carbon to its former user. The other is to combine it with reactivated carbon from other sources and resell it. Reactivation is attractive to industrial users principally because it is less costly than disposal and purchase of freshly made activated carbon.

When varying amounts of mercury were discovered in the mustard agent HD/HT ton containers at TOCDF, PBCDF, and UMCDF, CMA was required to develop a strategy to prevent emission of mercury during the incineration of HD/HT. Unlike agent, mercury persists in one form or another in the offgas leaving the PAS units of the incinerators. Testing results have shown that using sulfur-impregnated activated carbon in the PFS units during HD/HT processing is a good way to control mercury emissions.

The HD/HT stockpiles contain bulk storage ton containers and munitions. All HD/HT ton containers have been found to contain some amount of mercury. Some HD/HT munitions may also contain mercury. The semisolid heels in the ton containers at TOCDF are the largest sources of mercury. Given the diverse uses of activated carbons at chemical agent disposal facilities and the focus of this report on disposal options for activated carbon from these facilities, it is important to explain that the adsorption of mercury onto activated carbon and the adsorption of agent onto activated carbon occur in physically different carbon filter units and at separate locations during HD/HT thermal destruction operations. There is virtually no opportunity for both mercury and agent to be adsorbed onto the same carbon bed during normal operations at chemical agent disposal facilities. Activated carbon is expected to be exposed to mercury exclusively in the PFS units, while it will be exposed to agent primarily in the initial HVAC filter systems. Although the ton containers will be opened to the atmosphere in the MDB rooms, mercury volatilization will be negligible because the vapor pressure of mercury in its elemental form is very low. Mercury salts would not have any vapor pressure.

The closure plan for the Johnston Atoll Chemical Agent Disposal System (JACADS) required all used carbon to be incinerated on-site by micronization. The used carbon was first pulverized to a powdery consistency in a carbon micronization system and then blown into the deactivation furnace system, where it was incinerated. The committee has determined from the experience gained during the closure of JACADS that this process presents hazards, including the potential for serious dust explosions.

At the closure of the Aberdeen Chemical Agent Disposal Facility (ABCDF), the used carbon filters (carbon contained in metal trays) were double bagged in polyethylene. The bags that had agent vapor screening levels (VSLs)[4] of >1 were then placed in 95-gallon polyethylene drums, which were shipped by truck to the Veolia Environmental Services Facility in Port Arthur, Texas, where the used carbon and drums were incinerated without opening the drums. Bags containing carbon and agent at ≤1VSL were shipped to Veolia without drumming and incinerated as is.

The NECDF permit had no requirement for sampling and analysis of the used carbon before shipment to an off-site treatment, storage, and disposal facility (TSDF). Under this permit NECDF managed the carbon that had been exposed to VX as a designated hazardous waste and shipped it off-site to Veolia for incineration. NECDF also shipped approximately 220,000 pounds of used unexposed carbon to Calgon Carbon Corporation for reactivation. This used unexposed carbon came from Banks 3 through 6 of the HVAC filter units.

At ANCDF, PBCDF, and UMCDF, operating permits allow thermal treatment (1000°F for more than 15 minutes) of exposed carbon in the metal parts furnace. Presently, this practice is being used to treat the few carbon filter trays from the vent line of the agent collection system (ACS) storage tanks and carbon from the canisters of the M-40 protective masks. During this thermal treatment, the trays and canisters of carbon are held much longer than 15 minutes to ensure complete oxidation of the carbon and prevent it from smoldering when it is removed from the metal parts furnace. The TOCDF is planning to treat agent-exposed carbon in an autoclave to achieve decontamination sufficient for off-site shipment. This concept was being tested as this report was being written.

CMA has proposed managing the carbon by on-site disposal of the small quantities of highly contaminated carbon from the ACS storage tank vent lines and the carbon from M-40 gas mask canisters. Off-site shipment has been proposed for all of the other carbon (exposed and unexposed) for disposal at a qualified TSDF, either by incineration or in a landfill. For all unexposed carbon, shipment will be based on generator knowledge that the carbon has never been exposed to agent. For exposed carbon, off-site disposal is based on using approved sampling methods to determine the amount of agent present in each polyethylene drum and comparing that amount to the amount allowed by a bounding TRA prepared and approved by CMA for use on all agent-contaminated secondary waste ship-

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[4] Vapor screening levels (VSLs) and short-term limits (STLs) are equivalent names (specified in RCRA operating permits) for the limits used in waste transport and disposal. They also supplement short-term exposure limits (STELs) for protecting workers' health during plant operations as waste is generated and moved to storage areas within the plant. VSL and STL concentrations vary by agent and are the same values as STELs except that a VSL measurement is determined from air sampled for about 5 minutes instead of the 15 minutes of exposure applicable to STELs. A value of 1 VSL for GB, VX, and HD is equal to 0.0001 mg/m^3, 0.00001 mg/m^3, and 0.003 mg/m^3, respectively.

ments. Use of the bounding TRA at operating disposal facilities is expected to require acceptance by the state regulators for each site and for each state through which the materials are proposed to be moved.

Use of the bounding TRA for exposed carbon will require special sampling and analysis since the adsorptive properties of activated carbon prevent the application of vapor screening to determine the amount of agent in the container. This methodology poses at least two challenges: The CMA must validate a sampling technique that ensures that agent-exposed carbon samples are representative of the total mass of carbon in the shipping container. The CMA must also show that the extractive analysis procedure to be used accurately measures the agent present on the exposed carbon at the ppb level.

The committee believes that adding decontamination solution (NaOH) to the drums in which the exposed carbon would be shipped off-site is a potentially attractive method for ensuring the safety of off-site shipments. How much decontamination solution should be added must be determined as should how to ensure adequate wetting of carbon surfaces to achieve decontamination at levels safe for shipment.

An additional option applicable to unexposed carbon (approximately 80 percent of the total carbon) may be disposal by transfer to a reactivation contractor. This provides a path for the reuse of unexposed carbon, thereby reducing the cost of its disposal. Such an arrangement should be contingent on termination of the Army's ownership of and liability for the carbon as soon as it is transferred to the reactivation contractor.

GENERAL FINDINGS AND RECOMMENDATIONS

General Finding 1. About 80 percent of all the used activated carbon that has been or will be generated at the chemical agent disposal facilities operating under the Chemical Materials Agency has never been exposed to agent and can be treated as ordinary hazardous waste. This includes the carbon from Banks 3 to 6 of the heating, ventilation, and air conditioning filter units and the bulk carbon from the filter beds of the pollution abatement system filtration system.

General Recommendation 1. All unexposed carbon (as determined by generator knowledge) should be disposed of off-site as a hazardous waste without further chemical analysis for agent or sent for reactivation if a contractor will accept it and assume ownership and liability. The choice of disposal method and treatment, storage, and disposal facility will be dictated by whatever other contaminants are present on the carbon.

General Finding 2. Unless there is an unexpected upset resulting in contamination with agent, all of the sulfur-impregnated carbon that is to be used in the pollution abatement system filtration systems will not have been exposed to agent. Thus, based on generator knowledge the carbon can be sent off-site without further analysis for chemical agents. This carbon can be treated as a hazardous waste contaminated with mercury.

General Recommendation 2. All of the sulfur-impregnated carbon used in the pollution abatement system filtration systems and not involved in an unexpected upset condition at a chemical agent disposal facility should be sent off-site. This carbon should be treated as a hazardous waste that is contaminated with mercury.

General Finding 3. Treatment of all of the exposed carbon on-site in the metal parts furnace would seriously delay the closure of the currently operating Chemical Materials Agency chemical agent disposal facilities.

General Recommendation 3. Only the carbon filter trays from the agent collection system tank vent lines and the canisters from the M-40 protective masks should be treated on-site in the metal parts furnace when the metal parts furnace is not performing its primary function of treating metal parts or other wastes.

General Finding 4. Nerve agents GB and VX and mustard agent have been shown to degrade on activated carbon to their usual hydrolysis products by reacting with the moisture adsorbed on the carbon. This occurs both while the carbon is in use and after, during storage. Of the known analytical results, the concentrations of VX that remain on carbon samples from heating, ventilation, and air conditioning Bank 1 at the Anniston Chemical Agent Disposal Facility appear to be below the waste control limit (WCL) of 20 parts per billion. However, the remaining concentration of GB appears to be about 130 parts per billion, well above the WCL of 20 parts per billion. Thus, the carbon that has been exposed to GB cannot be sent off-site based on the waste control limits where those limits have been negotiated as permit compliance limits. The concentration of mustard that remains on the carbon filters had not been measured at the time this report was prepared.

General Recommendation 4. Carbon that has been exposed to agent should be sent off-site under one of the following arrangements:

- *Use of waste control limits (WCL) or permit compliance concentrations (PCC).* If the agent concentrations on the exposed carbon are below the waste control limits or the permit compliance concentrations, the carbon can be shipped off-site for proper disposal at a waste treatment facility licensed to receive and treat this waste under existing regulations. For this arrangement it will be necessary to develop and validate analytical methods that accurately measure agent concentration for both GB and mustard. The methods must be capable of analyzing the agents on carbon that has been exposed to all three agents and that will have both the agents and their respective degradation products from hydrolysis adsorbed on the carbon.
- *Use of a transportation risk assessment.* By using the precedent negotiated at Aberdeen Chemical Agent Disposal Facility, if the mass of the agent on the carbon in a drum is less than specified by the Chemical Materials Agency transportation risk assessment (see Table 7-1) but >1 VSL, the drum can be transported to a treatment, storage, and disposal facility. Each chemical agent disposal facility will have to negotiate with the appropriate regulatory authorities to ensure proper permit conditions to ship exposed carbon off-site based on the transportation risk assessment and the validated analytical methods.
- *Adding caustic solution to the drums.* If the addition of caustic (NaOH) decontamination solution to a drum of exposed carbon wets the carbon, the caustic will hydrolyze the agents remaining on the exposed carbon to below the WCL or PCC. The drum containing the decontaminated carbon and decontamination solution can then be shipped off-site. The method of applying the decontamination solution must be negotiated and approved by the facility's regulatory authority. Analysis for agent on the carbon should not be necessary with this arrangement.

General Finding 5. Environmental Protection Agency Method 3571 appears to have provided an improved method detection limit for extractive analysis of VX on the Bank 1 carbon sample from the Anniston Chemical Agent Disposal Facility, but it must still be validated. Neither Environmental Protection Agency Method 3571 for HD nor modified Method 3571 for GB, which appears to minimize re-formation of GB during extraction and analysis, had been validated at the time this report was being prepared.

General Recommendation 5. Both the original Environmental Protection Agency Method 3571 and the modified Method 3571 must be validated for use on carbon exposed to all three agents (GB, VX, and mustard) since the chemical agent disposal facilities expect to operate without changing out the heating, ventilation, and air conditioning filter units before closure.

1

Introduction

ACTIVATED CARBON AND CHEMICAL DEMILITARIZATION

For the past two decades, the United States has been destroying its complete stockpile of chemical agents. Nerve agents GB (sarin) and VX, and several forms of mustard agent (a blistering agent) were amassed and stored after World War II, during the Cold War. The U.S. Army's Chemical Materials Agency (CMA) is responsible for managing the program for the destruction and disposal of these agents and the munitions and containers in which they are stored. This program represents a major initiative through which the United States recognizes and complies with the international treaty known as the Chemical Weapons Convention (CWC), to which it is a signatory.

At the facilities where chemical agents are being destroyed, effluent gas streams pass through large activated carbon filters before venting to ensure that any residual trace vapors of agents and other pollutants do not escape into the atmosphere in exceedance of regulatory limits.[1] Most of these adsorber units have never been exposed to agent. Significantly in this regard, the system design and operational procedures are designed to limit agent exposure to the carbon in Banks 1 and 2 of the multibank adsorber units filtering the plant heating, ventilation, and air conditioning (HVAC) air.[2] The degree of agent contamination for carbon filters associated with process units (e.g., furnaces) varies from those having had no exposure to agent to those that are highly contaminated, such as the filter units on the vent lines of the agent collection system storage tanks in the facilities. The large amount of carbon (both exposed and unexposed) being stored at each of the sites awaits proper disposal in a safe manner in compliance with all applicable laws and regulations. All the carbon will have to be disposed of as a requirement for final closure of these facilities to take place. The applicable regulations are primarily related to satisfying requirements mandated by the federal Resource Conservation and Recovery Act (RCRA), and in some cases, more stringent requirements have been added by each state.

The National Research Council (NRC) Board on Army Science and Technology has provided advice and guidance to the Army's program for chemical stockpile destruction since its inception more than two decades ago and is very familiar with the technical, safety, health, and operational aspects of processes used for destroying chemical agents and munitions. Thus, in March 2008, the CMA requested the NRC to convene a committee to study, evaluate, and recommend the best methods for proper and safe disposal of the used carbon that continues to be accumulating at the operational disposal facilities.

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[1] Note that what are termed "carbon filters" in Army parlance are more accurately described as "carbon adsorption beds."

[2] The plant ventilation air moves through a cascade system starting with areas of the plant that are uncontaminated through areas that are progressively more contaminated with agent before entering the carbon filter units. Typically there are six sequential banks of carbon filters in the filter units that filter the munitions demilitarization building (MDB) HVAC air.

CHEMICAL STOCKPILE DISPOSAL PROGRAM

Overview

The United States manufactured and stockpiled about 31,000 tons of two nerve agents, GB and VX, and one blister agent, sulfur mustard agent. The mustard agent is in three forms: H mustard is an impure form of mustard agent containing other products produced during the chemical synthesis; HD is the distilled product of H, nominally pure mustard agent; and HT is a mixture of H with T, a related compound, which provides a eutectic that lowers its freezing point below cold winter temperatures because pure mustard agent freezes at 14.5°C. These chemical agents and munitions were stored at nine sites, eight of them in the continental United States and one at Johnston Atoll in the Pacific, about 700 miles southwest of Hawaii.

In 1985, Congress mandated that the Army establish a program to destroy at least 90 percent of the nation's unitary chemical stockpile (Public Law 99-145) with particular emphasis on M55 rockets. The U.S. Army selected incineration as the most effective method of destroying the chemical munitions in the stockpile. Incineration is very "democratic," i.e., it oxidizes chemical compounds to stable chemical forms such as water and carbon dioxide and inorganic salts of sulfur, phosphorus, and fluorine. The first site where an integrated prototype facility was built, namely, the Johnston Atoll Chemical Agent Disposal System, completed disposal operations in 2001. The plant has since been demolished and following closure of the site in 2003, the part of Johnston Atoll where the facility was located, Johnston Island, is now abandoned and is being allowed to return to its original natural condition. In August 1996, the Tooele Chemical Agent Disposal Facility (TOCDF) at the Deseret Chemical Depot in Tooele, Utah, which originally stored about 45 percent of the total stockpile, was the first continental U.S. site to begin destruction operations. It has completed the destruction of all the GB and VX munitions stored at the Deseret Chemical Depot, including all of the M55 rockets, which are considered to have the highest risk, and is presently destroying the remaining mustard agent stockpile. In the course of the mustard agent destruction campaign, analysis has revealed that some of the mustard agent ton containers contain varying amounts of mercury, a RCRA-controlled substance. This unexpected development has led to modifications in the plant and process designs, including the use of sulfur-impregnated activated carbon, which will adsorb mercury from the stack gases before they are released to the atmosphere. Three other sites that use incineration are now also in operation: the Umatilla Chemical Agent Disposal Facility (UMCDF) in Umatilla, Oregon, the Anniston Chemical Agent Disposal Facility (ANCDF) in Anniston, Alabama, and the Pine Bluff Chemical Agent Disposal Facility (PBCDF) in Pine Bluff, Arkansas.

Public Law 102-484 of 1993 mandated destruction of the entire chemical weapons stockpile and required the Secretary of the Army to evaluate potential alternatives to the Army's baseline disassembly and incineration process, considering whether—initially for a low-volume site—the application of such alternatives could complete demilitarization operations by December 31, 2004, the deadline set at that time, in a significantly safer manner than the baseline disassembly and incineration process and at least as cost-effective. This congressional directive led to the use of chemical neutralization (hydrolysis) at two sites where only bulk agent in ton containers was stored. Caustic NaOH solution at 194°F was the neutralization reagent used at the Newport Chemical Agent Disposal Facility (NECDF) in Newport, Indiana, where VX had been manufactured and stored. Hot water at 194°F was the neutralization reagent used at the Aberdeen Chemical Agent Disposal Facility (ABCDF) at Aberdeen Proving Ground, Maryland, where HD in ton containers had been stored. NECDF and ABCDF have completed destruction operations and ABCDF has completed closure.

Congress then mandated (Public Laws 104-201 and 104-208) that the facilities at the two remaining sites, the Pueblo Chemical Agent Destruction Pilot Plant (PCAPP) in Colorado and the Blue Grass Chemical Agent Destruction Pilot Plant (BGCAPP) in Kentucky, use a method other than incineration to destroy chemical agent. The Army has selected chemical neutralization, followed at PCAPP by bioremediation and at BGCAPP by supercritical water oxidation. Construction of these two plants was under way at the time this report was being prepared. At all operating sites, activated carbon continues to be used to filter the ventilation air and process gas streams prior to their release into the atmosphere and to protect personnel from accidental releases.

In 1997, the U.S. Congress ratified the CWC, an international treaty banning the use and stockpiling of chemical weapons. The CWC required that all signatory nations destroy their entire stockpiles within 10 years of signing the treaty, making the deadline April 29, 2007. However, later, both the United States and Russia applied for onetime 5-year extensions to this deadline, which were granted. Still, the United States is not expected to meet this date, because PCAPP and BGCAPP have not yet begun disposal operations.

Brief Description of the Chemical Agent Destruction Process

The following provides a generic description of the process facilities used to dispose of the Army's chemical agent stockpile. It includes a summary of the uses of activated carbon in those processes and the facilities used to house and control the processes. More detailed descriptions will be presented in Chapter 2.

Figure 1-1 is a schematic drawing that generically depicts the process that takes place in a typical chemical agent disposal facility using incineration technology. Differences in configuration exist because each site stores and destroys different types of agents and munitions, and also because the more recently constructed facilities have taken advantage of lessons learned during operations at the older sites. Facilities using chemical neutralization also have differences because the chemical processes must be specific to the particular agent being treated.

Whether incineration or neutralization technology is the primary method for agent destruction, a generic series of steps are taken to dispose of the stockpile. Munitions are moved from stockpile storage areas to the munitions demilitarization building (MDB) in on-site containers (ONCs) or enhanced on-site containers (EONCs), which are designed for retention and monitoring of any agent leakage that might occur during transport. The ONCs or EONCs are received at a container handling building connected to the MDB and are then moved to an unpack area, where the munitions and bulk items are removed and put on input conveyors to the MDB. Different conveyor systems transfer different types of munitions and agent containers from the unpack area to the explosives containment room(s) of the MDB, where the energetic materials are removed from the particular type of munition being processed—projectile, mortar, mine, or bomb. For ton containers and airplane spray tanks, there are no energetics to be removed.

The removed energetic components are then processed separately from the agent, which is subsequently drained or washed from munitions. When processing M55 rockets, the agent is drained before the rocket

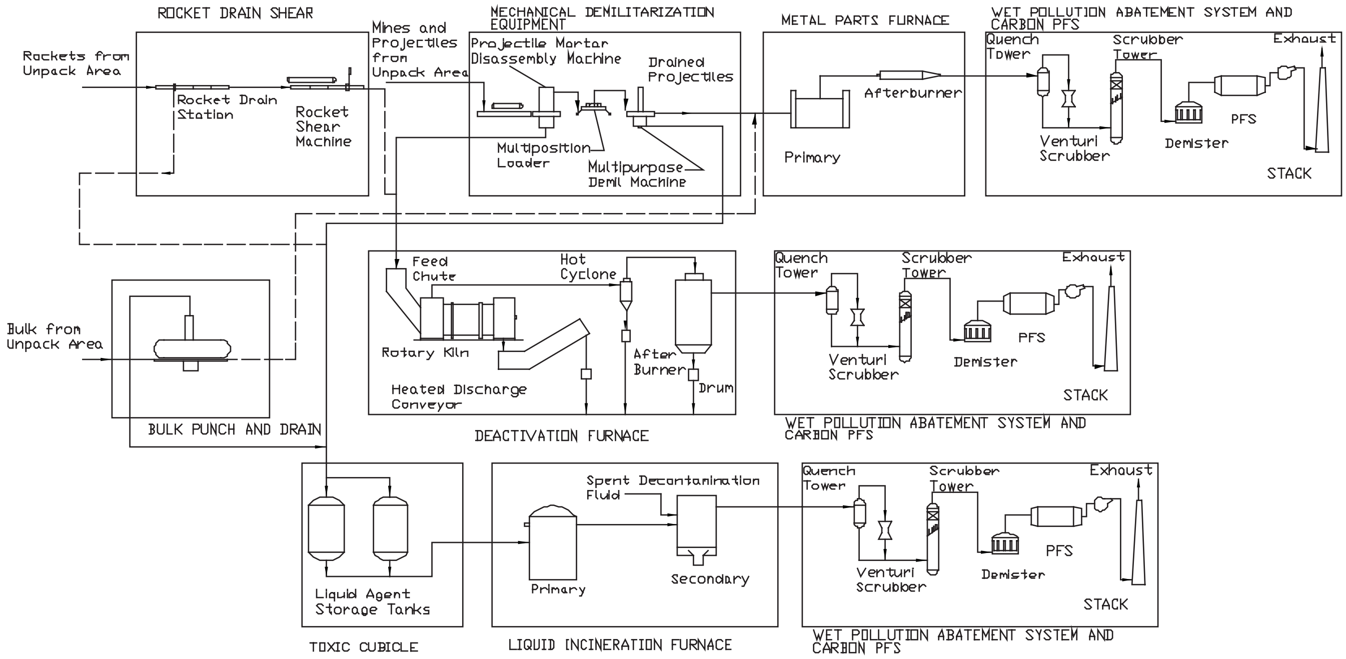

FIGURE 1-1 Schematic of the baseline incineration system. SOURCE: Personal communication between Timothy Garrett, Site Project Manager, ANCDF, and Margaret Novack, NRC study director, February 9, 2009.

(including the propellant in its motor) is sheared into segments. The rooms in which these operations are conducted become contaminated with agent vapors and liquid. Any personnel entering these rooms must be sealed in a demilitarization protective ensemble suit that includes a supply of breathing air under positive pressure.

Energetics are either burned or chemically destroyed by neutralization. The agent drained from munitions flows into agent collection tanks, which in turn feed a liquid agent incinerator where the agent is burned or, for plants using neutralization, reacted with a sodium hydroxide solution or hot water and subsequently processed further to convert reaction products to environmentally acceptable materials. Drained munitions, which in some cases may contain a solidified heel of agent, are processed in a metal parts furnace (MPF) at incineration sites or in an electrically heated metal parts treater (MPT) at the other sites. These munition casings are heated to at least 1000°F for no less than 15 minutes, which has become an established performance standard for achieving complete agent decontamination since the beginning of the chemical stockpile disposal program.

Use of Carbon Filtration Systems at Chemical Agent Disposal Facilities[3]

All of the preceding processing steps, from receipt of the ONCs or EONCs to destruction of agent and energetics, are housed in the MDB, which has a cascading HVAC system designed to move ventilation air from clean, uncontaminated areas to areas of increasing agent contamination in the MDB. The HVAC system then discharges the air through banks of activated carbon filters. In each unit, there are typically six separate filter banks arranged in series for removing airborne contaminants in ventilation air from process areas. Each bank contains approximately 2,200 lb of carbon.

In facilities using incineration processes, except TOCDF, exhaust gases from each furnace and afterburner system go to a high-performance pollution abatement system (PAS) that includes wet scrubbers and a PAS filtration system (PFS) containing activated carbon in horizontal beds. The PAS at TOCDF formerly consisted only of wet scrubbers, but a PFS using sulfur-impregnated carbon was being added to each PAS at the time this report was being prepared. The carbon filters at the other sites using incineration technology serve the same function as the MDB HVAC filters, although trial burns have validated that the incineration products are releasable to the atmosphere without the PFSs. The latter were added at ANCDF, UMCDF, and PBCDF in response to concerns expressed by the residents of the adjacent communities. These PFS filters have never been exposed to chemical agent.

In facilities using neutralization, vapor spaces in process vessels are discharged to an off-gas treatment system (OTS) whose stage is an activated carbon filter. A gas leaving the OTS then flows into the MDB HVAC system at the facility and passes through the HVAC carbon filters.

At every site, all process control rooms and occupied clean areas and laboratories have carbon filters on outside air flowing into these rooms to protect the workers inside. These filters preclude agent contamination of these areas in the event of a release of agent from munitions outside the MDB. In addition, each person working on-site is equipped with a protective mask containing an M-40 carbon cartridge. All these uses of carbon, other than the protective masks, are depicted schematically in Figure 1-2.

In summation, carbon filters are used extensively at all of the Army's chemical agent disposal facilities to protect workers and the public from the remote possibility that chemical agent in air or gas streams might be released to the environment. Only two of the types of filter units (which will be discussed in Chapter 2) are exposed to agent under normal operating conditions, those that filter the HVAC air from the MDB and the filters installed on the agent collection system vessels. The other filters (such as the PFS) would only be exposed to agent in the event of a serious upset. Each site will have nominally 500,000 lb of carbon to be disposed of after all of the chemical agents and munitions stored there have been destroyed.

STATEMENT OF TASK

As noted previously, the Army requested the NRC to assemble a committee to examine the characteristics of the spent carbon and alternatives for its disposal.

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[3] As noted previously, what the Army calls "carbon filters" are technically various configurations of carbon adsorption beds. No filtration processes are involved. However, for consistency with the language typically used for discussing U.S. chemical demilitarization, the terms carbon filters and carbon filtration have been used in this report.

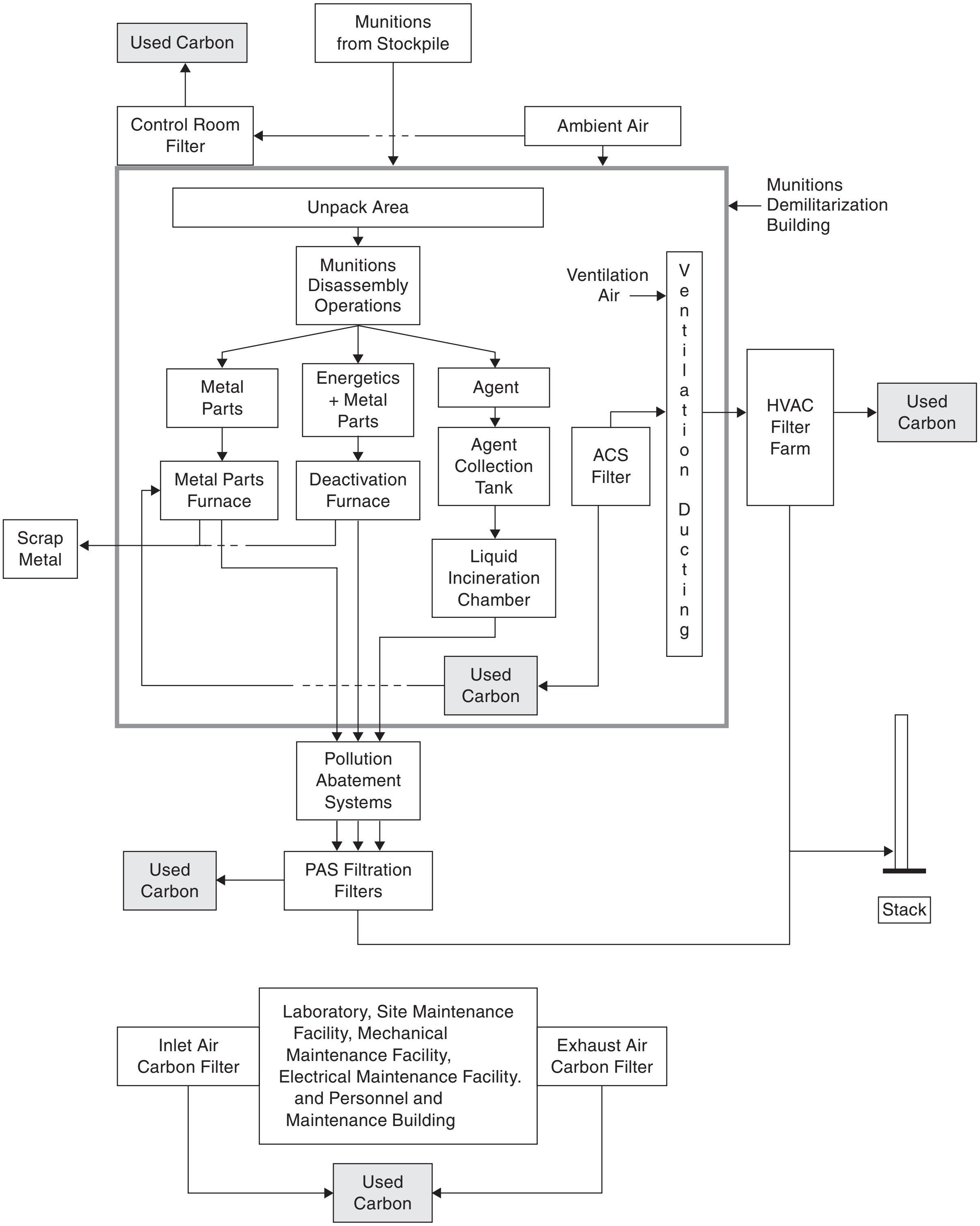

FIGURE 1-2 Sources of used carbon in a typical chemical agent disposal facility.

The full statement of task together with the preamble is as follows:

> The U.S. Army's Chemical Materials Agency has been engaged for nearly two decades in a program to destroy the nation's stockpile of obsolete chemical agents and munitions. At first, in the early 1990s, these efforts were limited to a single first-generation facility located on Johnston Island southwest of the Hawaiian Islands, where approximately 4 percent of the original stockpile of over 31,000 tons of agents was stored. In August 1996, agent disposal operations began at the first disposal facility in the continental United States at Deseret Chemical Depot in Tooele, Utah, where some 44 percent of the total stockpile tonnage was located. Since then, disposal operations have taken place at other facilities at five additional storage sites in the continental United States. Four of these sites use incineration technology and two have used or are using hydrolysis (neutralization) technology. At present, over 50 percent of the original stockpile tonnage has been destroyed.
>
> As program operations have progressed, so has the accumulation of large quantities of agent-contaminated activated carbon resulting from agent processing. This material is projected to be one of the largest secondary waste streams to remain in storage at the end of munitions destruction operations. Consequently, disposal of the HVAC carbon, which may require some pre-treatment prior to final disposition, could have a significant impact on closure costs and schedule for the Army's chemical agent destruction facilities.
>
> The National Research Council will establish an ad hoc committee to:
>
> - examine the current heating, ventilation, and air conditioning (HVAC) systems of the U.S. Army's Chemical Materials Agency (CMA) that use activated carbon and consider the overall quantity and characteristics of the CMA HVAC secondary wastes
> - assess the current plans and path forward for contaminated carbon management and disposition at Army chemical agent disposal facilities
> - evaluate commercial and established industry alternatives for contaminated carbon disposal, i.e. best practices, processes and equipment suitable for use by the Army (considering both on-site and off-site usage), including characterization and pre-treatment requirements
> - in the foregoing context, assess the scientific support needed for obtaining regulatory approvals at CMA facilities.

In response to this request, the NRC Board on Army Science and Technology assembled the Committee to Examine the Disposal of Activated Carbon from the Heating, Ventilation, and Air Conditioning Systems at Chemical Agent Disposal Facilities (CMA Carbon Committee). This committee was made up of individuals with expertise in the chemical demilitarization program, the chemistry of chemical agents on carbon, the surface chemistry of carbon, risk assessment, and environmental regulations. This would allow them to make recommendations on the proper disposal of the used carbon from chemical agent disposal facilities. Several members of the committee also had a perspective on the public interest aspects of the destruction of chemical munitions, notwithstanding that the scope of this report was limited to a technical and regulatory examination of alternatives for waste carbon.

STUDY SCOPE

The first bullet in the statement of task directs the committee to assess the current plans and path forward for the agent-contaminated activated carbon generated in the HVAC system at the sites. However, after conferring with the sponsor, the committee interpreted the second bullet to include the proper disposal of all carbon at the sites whether or not the carbon had been exposed to agent. Accordingly, the committee has restricted its assessment to the technological and permitting aspects of the carbon management and disposition at chemical agent disposal facilities under the authority of the CMA. The committee has given some consideration to the liability that may factor into a site's selection of certain alternatives over others that are also technically acceptable. The cost of the alternatives was not studied.

Importantly, the committee has used the following terminology throughout the report. If the carbon has not been exposed to agent, it is called "unexposed carbon." Any carbon that has been exposed to agent is called "exposed carbon." As discussed in Chapter 4, because the chemical agent degrades and forms hydrolysis products with the adsorbed moisture, exposed carbon may or may not contain agent. "Used carbon" or "carbon" refers to both exposed and unexposed carbon. Mustard agent exists in three forms: H, HD, and HT. The report may refer to HD when all three forms were intended.

Although all the chemical agent disposal facilities that use incineration are modeled after TOCDF, there are minor variations in the design and procedures from site to site. The descriptions given in this report focus on the ANCDF design and procedures. Where the committee was made aware of any variations, they are mentioned in footnotes.

ORGANIZATION OF THIS REPORT

In Chapter 1 the committee has provided a brief background and overview of the chemical stockpile disposal program, a short description of the facility designs, and a summary of the usage of carbon filtration at the sites. Also presented were the statement of task for the study and the scope of the study which the committee has adopted. In the next paragraph the committee turns to the organization of the rest of the report.

Chapter 2 gives details of the use and on-site management of activated carbon at the facilities. Chapter 3 discusses the regulatory issues that impact the usage and disposal of carbon. Chapter 4 describes adsorption fundamentals and discusses the chemistry and fate of the agents on activated carbon as well as analytical methods to measure their concentrations. Chapter 5 summarizes commercial and industrial practices for management of carbon being used in industrial settings. In Chapter 6, the committee addresses the issues unique to the disposal of activated carbon that has become contaminated with mercury, which is expected at some sites where mustard agent contaminated with mercury must be destroyed. Finally, Chapter 7 discusses and assesses the Army's past experience with the disposal of used carbon and the disposition options available for used carbon from chemical agent disposal facility operations. It also provides the committee's general findings and recommendations.

2

Uses and Management of Activated Carbon at Chemical Agent Disposal Facilities

USED CARBON SOURCES

Activated carbon is used at every site where chemical weapons are being destroyed in the United States. Its usefulness derives from its adsorptive properties that readily remove agent or other toxic chemicals from the air. Activated carbon is used at chemical agent disposal facilities to filter all air leaving agent-contaminated areas where remote processing of agent and munitions takes place and all vent gas streams from processing vessels. Activated carbon is used for other reasons as well:

- To filter ventilation air supplied to occupied work areas that are normally free of agent;
- To capture any agent vapors from leaking weapons in chemical weapon storage bunkers; and
- To protect all personnel working within the chemical limited area at each facility; it is contained in a canister that is inserted into a face mask.[1]

The activated carbon, which is granular, is used in three configurations:

- Filter trays that are used in all air filter units except the pollution abatement system (PAS) filtration system (PFS) and the M-40 gas mask canisters;
- In bulk form in horizontal filter beds in the PFS units; and
- In canister filters attached to M-40 protective masks.

Figure 2-1 is a picture of the nine filter units ("filter farm") for the air leaving a munitions demilitarization building (MDB) heating, ventilation, and air conditioning (HVAC) system. At least one of the filter units in the filter farm is a spare, which allows a filter tray changeout during operations by shutting down and isolating the unit where changeout is taking place. Figure 2-2 is a schematic of the airflow through the six filter banks that typically comprise each operational MDB HVAC filter unit. The automatic continuous air monitoring system (ACAMS) and the depot area air monitoring system (DAAMS) (not shown in Figure 2-2), which are located between Banks 1 and 2, 2 and 3, 3 and 4, and 4 and 5, monitor for the presence of agent. A filter tray is depicted in Figure 2-3, and the flow of air through the filter tray is shown in Figure 2-4. This filter tray is used in all filtering units except the PFS filters and the M-40 mask canisters.

Figure 2-5 shows a PFS. Figure 2-6 is a schematic of the PAS/PFS flow configuration including the PFS units, and Figure 2-7 is a schematic of the combustion gas flow through the PFS. The PFS beds, shown in a vertical orientation in the schematic, are actually horizontal in the PFS; however, the flow path sequence is as shown in Figure 2-7. Figure 2-8 shows an M-40 protective mask with the filter canister attached.

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[1] The "chemical limited area" is the fenced-in area at a facility subject to surety monitoring due to the presence of chemical agent(s).

FIGURE 2-1 The nine activated carbon filter units for the MDB HVAC system. SOURCE: Robie Jackson, Waste Management Manager, ANDCF, and Tracy Smith, Trial Burn Manager, ANCDF, "The use of carbon at ANCDF," Presentation to the committee, June 5, 2008.

A list of typical uses for carbon filter units in a chemical agent disposal facility using incineration for agent destruction is given in Table 2-1. The used carbon from most processes is not expected to be contaminated with agent. The only two places where used carbon is expected to become exposed to agent during normal operations are the unit filters for the agent collection system (ACS) and Banks 1 and 2 of the MDB HVAC filters. The semicontinuous monitoring (noted in Table 2-1) by a combination of near-real-time ACAMS and DAAMS after Banks 1, 2, 3, and 4 establishes that there is no exposure to agent beyond Bank 2.[2] This conclusion does not preclude plant management from changing out filters from Banks 1 and 2 for other reasons, e.g., to measure conditions of the carbon.

As indicated in Table 2-1, changeout of the carbon in Banks 1 and 2 would take place if agent breakthrough above the short-term limit is detected between Banks 2 and 3 at the Tooele, Anniston, and Pine Bluff Chemical Agent Disposal Facilities (TOCDF, ANCDF, and PBCDF). At Umatilla Chemical Agent Disposal Facility (UMCDF), the policy is that changeout would occur if agent breakthrough above the short-term limit is detected between Banks 3 and 4. However, as has been and continues to be the case at the other sites, the committee does not expect that it would ever become necessary for MDB HVAC Bank 3 carbon at UMCDF to be changed out due to contamination. For this reason, for each site covered in this report the first two banks of MDB HVAC carbon will be considered to be exposed to agent and the last four banks will be considered to be unexposed carbon.

The PFS filters are not expected to be exposed to agent during normal operation of the liquid incinerator (LIC), the metal parts furnace (MPF), or the deactivation furnace system (DFS) and their respective PAS units. The PFS units at the more recently constructed ANCDF, PBCDF, and UMCDF were not required by the regulations applicable to these facilities that implement the Resource Conservation and Recovery Act (RCRA), but they were included in the design of these facilities as an extra precaution to relieve public concerns about the possibility of uncontrolled gaseous emissions. The report *Carbon Filtration for Reducing Emissions from Chemical Agent Incineration* examined various technical and risk-related aspects surrounding the use of PFSs at chemical agent disposal facilities (NRC, 1999). From the start of operations in 1996, TOCDF has operated without a PFS but was adding units downstream of the two LICs and the MPF as this report was being prepared. Sulfur-impregnated carbon is being installed in these units to capture mercury from the incineration of mercury-containing mustard agent. The PFS at ANCDF, PBCDF, and UMCDF will also use sulfur-impregnated carbon when these facilities are processing mustard agent-containing munitions and ton containers.

Table 2-2 estimates total quantities of used carbon expected to be generated during disposal operations and site closure for each of the incineration-based chemical agent disposal facilities currently operating and for the neutralization (hydrolysis)-based Newport

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[2] The DAAMS monitors consist of adsorption tubes that confirm the ACAMS monitors since they sample any agent in the airstream on a continuous basis but are analyzed only periodically (several times daily). Measurements to date beyond Bank 2 have been nondetect for agent.

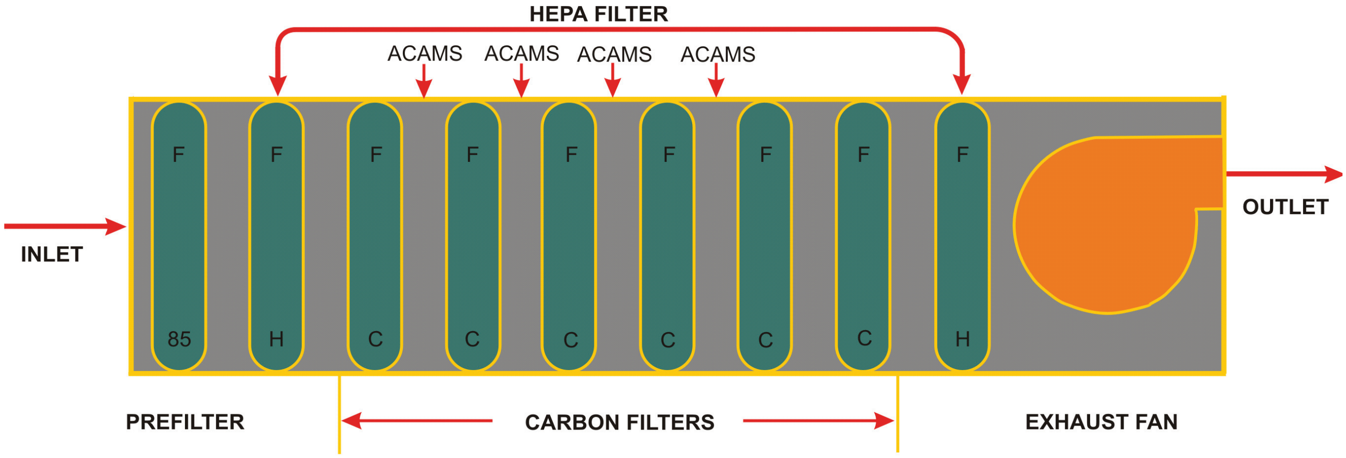

FIGURE 2-2 Schematic representation of airflow through the six filter banks that make up each MDB HVAC filter unit. Carbon filters each contain 48 filter trays arrayed in six columns and eight rows, with each tray oriented in horizontal position. The 85 indicates 85 percent efficiency for the particulate prefilter; H indicates HEPA filter; F indicates filter; and C indicates carbon filter. SOURCE: Robie Jackson, Waste Management Manager, ANCDF, and Tracy Smith, Trial Burn Manager, ANCDF, "The use of carbon at ANCDF," Presentation to the committee, June 5, 2008.

Chemical Agent Disposal Facility (NECDF), which recently completed destruction of the stockpile of bulk VX nerve agent stored in ton containers at the site. Table 2-2 also indicates the quantities of carbon that the Army currently anticipates for off-site and on-site treatment.

Table 2-3 estimates the quantities of carbon anticipated to be exposed to agent and the operations that produce them at each of the Chemical Materials Agency (CMA) incineration facilities. Table 2-4 provides complementary estimates of the quantities of carbon that can be considered unexposed to agent and the operations where this carbon was used. These estimates include used carbon from both operations and closure and are based on data provided by the Army showing which carbon it expects will be treated on-site in the MPF (exposed) and which can be slated for off-site shipment (unexposed.)

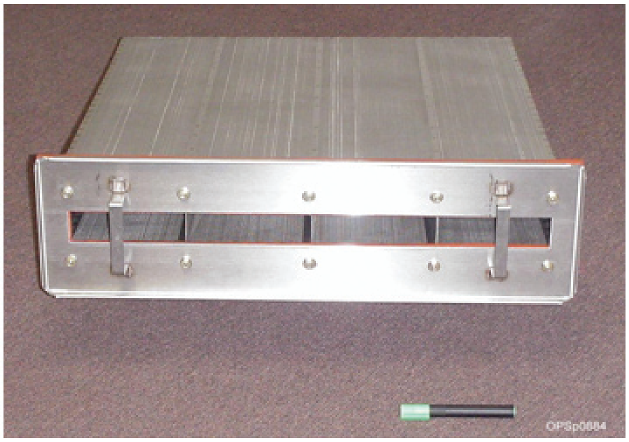

FIGURE 2-3 A filter tray. SOURCE: Robie Jackson, Waste Management Manager, ANCDF, and Tracy Smith, Trial Burn Manager, ANDCF, "The use of carbon at ANCDF," Presentation to the committee, June 5, 2008.

It is important to note that the numbers in Tables 2-3 and 2-4 represent calculated estimates as of September 2008 and are subject to changes based on operational factors, design modifications, and ongoing developments and negotiations concerning permitting and regulatory requirements for on-site analysis and treatment and off-site shipment and disposal. There is also some variation in how the data from which these tables were generated was compiled at each site (e.g., dry weight or actual weight, frame and hardware weight included or not). However, the main point made by Tables 2-3 and 2-4 is that the anticipated total amount of exposed carbon (~508,400 lb) is about one-fourth the anticipated total amount of unexposed carbon (~2,107,800 lb), or only about one-fifth the total used carbon (~2,616,200 lb) expected from operations and closure at the four incineration sites.

Also evident from Table 2-3: The overwhelming majority of exposed carbon comes from the MDB HVAC system, which is also the source of about half the unexposed carbon, as shown in Table 2-4. The PFS

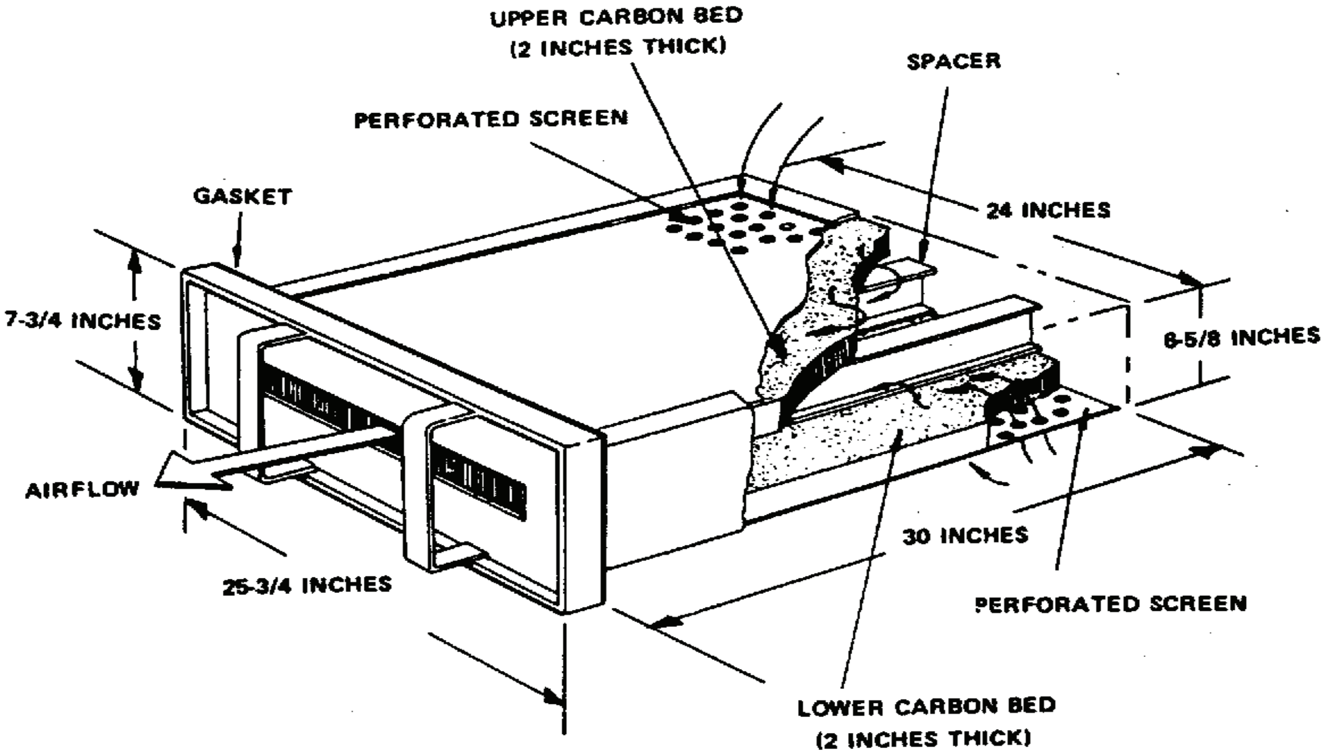

FIGURE 2-4 Airflow path through a filter tray. SOURCE: Susan Ankrom, SAIC Task Manager, ANCDF, "Published values for agent loading capacity of MDB and PFS carbon," Presentation to the committee, June 6, 2008.

carbon, including the sulfur-impregnated carbon that will be used to capture mercury emissions from the processing of mustard agent munitions, constitutes the bulk of the remaining carbon that can be considered unexposed to agent, as discussed later. It is also worthwhile noting that RCRA regulations at 40 CFR 261.10(a)(2)(ii) allow generators of solid waste to use the "knowledge of their waste" to determine whether the RCRA regulations apply to it.[3]

FIGURE 2-5 PFS filter unit. SOURCE: Robie Jackson, Waste Management Manager, ANCDF, and Tracy Smith, Trial Burn Manager, ANCDF, "The use of carbon at ANCDF," Presentation to the committee, June 5, 2008.

The data provided from the neutralization-based NECDF indicate that the used carbon generated during the now-completed disposal operations and ongoing facility closure comes primarily from MDB HVAC and process filters (270,000 lb) but also from other sources (nearly 11,000 lb). At the time this report was being prepared, 200,000 lb of this carbon had been shipped to Calgon Carbon Corporation, a carbon supplier, for reactivation and has never been returned to the NECDF inventory. The Army has released it for sale on the open market. There is no requirement for NECDF to sample and analyze the used exposed carbon, which is managed as a listed hazardous waste under the Indi-

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[3] What is commonly termed "generator knowledge" as applicable to used carbon from chemical agent disposal facilities is discussed further in Chapter 3 and later chapters.

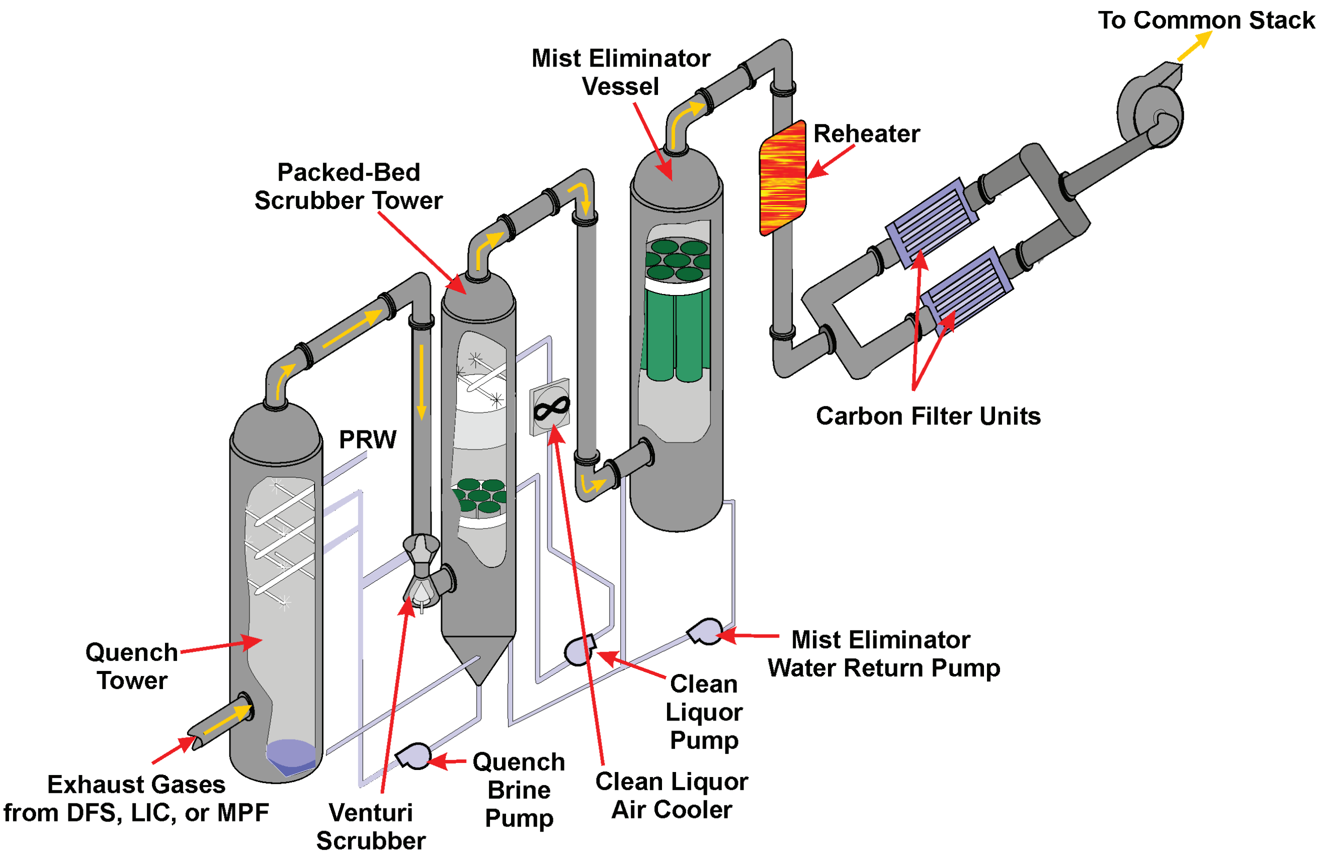

FIGURE 2-6 Schematic of the PAS/PFS flow configuration including the PFS filter unit. The carbon filter units refer to two zones of the PFS unit, which are actually in series and not in parallel as shown. SOURCE: Robie Jackson, Waste Management Manager, ANCDF, and Tracy Smith, Trial Burn Manager, ANCDF, "The use of carbon at ANCDF," Presentation to the committee, June 5, 2008.

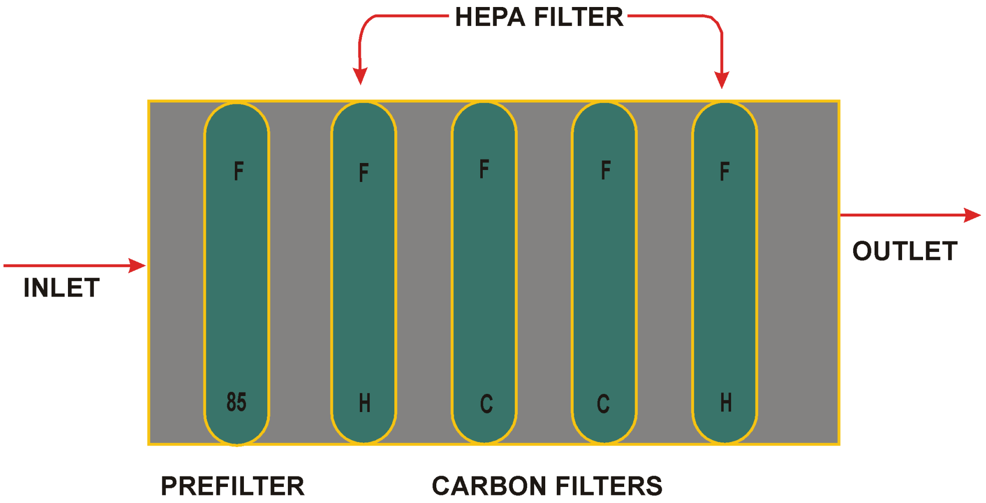

FIGURE 2-7 Schematic representation of the combustion gas flow path through the PFS. The carbon filters, denoted by "C," are actually horizontal beds with gas flow from the first bed through the second bed and then out through the HEPA filter, denoted by "H." "F" is a generic denotation for various types of filters. The efficiency of the particulate prefilter is 85 percent. SOURCE: Robie Jackson, Waste Management Manager, ANCDF, and Tracy Smith, Trial Burn Manager, ANCDF, "The use of carbon at ANCDF," Presentation to the committee, June 5, 2008.

FIGURE 2-8 An M-40 protective mask with the filter C-2 canister attached. SOURCE: Robie Jackson, Waste Management Manager, ANCDF, and Tracy Smith, Trial Burn Manager, ANCDF, "The use of carbon at ANCDF," Presentation to the committee, June 5, 2008.

ana Department of Environmental Management 1001 waste code and is to be disposed of accordingly, at an approved treatment, storage, and disposal facility (TSDF).

MANAGEMENT OF USED CARBON

Two considerations dictate how used carbon is handled on-site:

- Is the carbon contaminated with agent?
- How much agent is present on the carbon?

The current practice when a filter tray containing exposed carbon is removed from operation is to first bag the tray in two plastic bags and then place the double-bagged tray in a 95-gallon polyethylene drum (see Figure 2-9), which is stored for future disposal. This practice avoids unnecessarily exposing personnel to agent as would be the case if the carbon were to be removed from the filter trays prior to packaging for storage and disposal. While this approach minimizes any chance of exposure to agent during packaging, it makes it difficult to characterize the amount of agent that might be present on the used carbon. Recall from Table 2-1 that each MDB HVAC filter unit typically consists of six banks and each bank consists of 48 filter trays. Each filter tray is specified to contain 48.3 lb of carbon.

Only the used activated carbon from the PFS is handled in bulk form; i.e., the used carbon is not contained in filter trays. The used carbon from PFS filters is emptied as a loose solid into plastic bags, and the bags are placed in polyethylene drums for storage and disposal. The PFS filter beds are arranged in two horizontal zones in series in the process vent gas stream with ACAMS monitoring between the zones. In some facilities, combustion gas flowing to Zone 1 is not monitored for agent because it is expected to be free of agent during normal plant operation based on tests performed when the facility was licensed for operation. While the PFS carbon is not expected to be exposed to agent, each disposal facility has installed a DAAMS monitor downstream of Zone 1. The sampling tubes in this monitor are regularly removed and analyzed in the laboratory.

Finding 2-1. At some chemical agent disposal facilities, no depot area air monitoring system monitor has been installed in front of Zone 1 of the pollution abatement system filtration system.

Recommendation 2-1. If the activated carbon in a pollution abatement system filtration system unit at a chemical agent disposal facility is ever to be changed out, consideration should be given to installing a depot area air monitoring system (DAAMS) upstream of Zone 1 (the first carbon bed) of the pollution abatement system filtration system if none exists now. The addition of this DAAMS unit would document the absence of agent in the gas stream flowing to the carbon in Zone 1, even though no agent is expected to be released as a result of incineration and subsequent scrubbing of the incineration flue gases.

While current management philosophy dictates handling the used carbon as contaminated material, most of the used carbon will be unexposed even at the end of agent disposal operations, barring an airborne release on-site. Furthermore, standard operating procedures may preclude the exposure of filters in air streams that contain agent. Four key factors that reduce the agent loading on the MDB HVAC filter are these:

1. Keeping agent vapor levels low in Level A (the most contaminated) process areas by periodic decontamination with caustic to clean up spills and leaks.
2. Providing ACAMS and DAAMS monitoring between zones. A vestibule is provided to change

TABLE 2-1 Uses of Activated Carbon Filters at Chemical Agent Disposal Facilities

Use	Typical Configuration	Expected Agent Exposure Level
ACS filter	1 filter tray per ACS	High. Filters are exposed to vent gases flowing from headspace of the agent collection tanks, which feed agent to the LIC.
Banks 1 and 2 of each filter unit of the MDB HVAC system filters[a]	Each filter unit bank contains 48 horizontal filter trays typically arranged in 6 columns and 8 rows. Bank 1 is the first bank that MDB air encounters and Bank 2 is the second bank. Semicontinuous monitoring (ACAMS/DAAMS) is used after Banks 1 and 2.	High. Filters in Banks 1 and 2 are exposed to any agent vapors in air from the processing rooms. Filters in Banks 1 and 2 are changed if agent breakthrough above the short-term limit is detected between Banks 2 and 3. A filter housing vestibule is installed for removal of Bank 1 and 2 filter trays in a controlled environment.[b]
Banks 3, 4, 5, and 6 of each unit of the MDB HVAC system filters	Each filter unit bank contains 48 horizontal filter trays typically arranged in 6 columns and 8 rows. Air from Bank 2 flows through Banks 3 to 6 before flowing to the plant stack. Semicontinuous monitoring (ACAMS/DAAMS) is used after Banks 3, 4, and 5.	None. ACAMS monitoring between Banks 2 and 3 provides data that demonstrate the lack of exposure.[b]
PAS/PFS filters	3 filter units; 2 banks of bulk carbon/unit	None. By design, agent is destroyed by incineration in the DFS, LIC, and MPF. Agent would only be present in offgas during upset operations.
DFS cyclone enclosure filter	1 filter unit; 2 filter banks; 12 trays/bank	None. Agent could be present in ash during upset operations. At TOCDF the cyclone ash collection system enclosure has no filter and is vented to the MDB HVAC system filters.
Laboratory hood exhaust filter	1 filter unit; 2 banks/unit; 48 filter trays/bank	None. Normally not expected based on laboratory procedures.
M-40 mask canisters	1 canister/mask	None unless a mask used in area where agent vapors are present.
Control room ventilation air supply filter	1 filter unit; 2 banks/unit; 48 filter trays/bank	None. No agent expected in ambient air.
Laboratory ventilation air supply filter	1 unit; 2 banks/unit; 48 filter trays/bank	None. No agent expected in ambient air.
Personnel and maintenance building ventilation air filters	1 filter unit; 1 bank/unit; 36 filter trays/bank	None. No agent expected in ambient air.
Site maintenance facility; mechanical maintenance facility; electrical maintenance facility, protection facility ventilation air supply filters	2 filter units each; 5 filter trays/unit	None. No agent expected in ambient air.

[a] Typically, there are 9 MDB HVAC filter units each consisting of 6 banks of filters arranged in series with respect to airflow.

[b] At UMCDF, the policy is to change the filters in Banks 1, 2, and 3 if agent breakthrough above the short-term limit is detected between Banks 3 and 4. However, in this report, the committee has formulated its findings and recommendations and supporting text on the expectation that MDB HVAC Bank 3 filter at UMCDF will not experience agent exposure above the short-term limit. This expectation is based on the monitored experience to date concerning Banks 1 and 2 carbon at all sites.

SOURCE: Adapted from Timothy Garrett, Site Project Manager, ANCDF, “Carbon management by site,” Presentation to the committee, July 23, 2008.

out the filter trays in Banks 1 and 2 when agent breakthrough is detected at the outlet of Bank 1 filters. Figure 2-10 shows a vestibule on the side of an MDB HVAC unit. Thus, used activated carbon from Bank 3 and higher is never exposed to chemical agent during normal operation.[4]

3. The low volatility of VX and distilled mustard agent, HD, which results in low carbon filter loading. The nerve agent GB, which is more volatile, presents the potential for high carbon filter loading.
4. The degradation of agent on activated carbon at varying rates in the presence of moisture in the filtered gas stream (see Chapter 4).

Current evaluations of the long-term behavior of agents on activated carbon indicate that chemical agents are hydrolyzed by the water adsorbed on the carbon. (See Table 2-5 for information on properties of

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[4] See footnote *b* in Table 2-1.

TABLE 2-2 Estimated Carbon Waste Inventories (in Pounds) for CMA Chemical Agent Disposal Facilities as of September 29, 2008[a]

Site	Existing Inventory	Changeout Prior to Closure	Total Generated at Closure	Off-site Shipment	On-site Treatment in MPF
ANCDF	18,000	209,700	573,700	642,700	158,700
UMCDF	148,100	60,400	304,000	598,200[b]	54,400
TOCDF	367,700	40,000	325,000	537,400	195,300
PBCDF	33,100	48,500	302,400	295,100[c]	96,900
NECDF	235,000	0	35,000	270,000	0

[a] Weights may include carbon, carbon tray materials, and packaging. Quantities have been rounded.

[b] Information updated as of March 17, 2009. Includes 140,000 lb additional PFS carbon since September 29, 2008, estimate.

[c] Information updated as of March 18, 2009.

SOURCE: Adapted from information provided to the committee by Timothy Garrett, Site Project Manager, ANCDF, as of September 29, 2008.

TABLE 2-3 Summary of Sources and Estimated Inventories (in Pounds) of Carbon Exposed to Agent at CMA Incineration Sites During Operations and Closure[a]

Site	ACS	Laboratory	MDB HVAC	M-40 Mask Canisters[b]	Other
ANCDF	3,600	<100	153,800	1,400	
UMCDF	4,800	<100	47,500	2,100	
TOCDF	200	15,300[c]	159,000	3,100	20,800[d]
PBCDF	1,200	<100	95,600	<100	
Total	9,800	15,300	455,900	6,600	20,800

[a] Weights may include carbon, carbon tray materials, and packaging. Information is as of September 29, 2008. Estimates of exposed carbon made on basis of anticipated on-site treatment. Quantities have been rounded.

[b] Carbon from M-40 mask canisters, while normally not exposed to agent, is generally expected to be treated as exposed at most sites in view of the relatively small amounts involved.

[c] This carbon amount is the result of the significantly larger amounts and greater variety of materials tested over the longer duration of TOCDF operations compared to other sites.

[d] This carbon amount is the result of a ton container sampling operation unique to the site.

SOURCE: Adapted from information provided to the committee by Timothy Garrett, Site Project Manager, ANCDF, September 29, 2008.

agents.) Chapter 4 provides a detailed discussion of the chemical reactions of agent on activated carbon.

At chemical agent disposal facilities using incineration to destroy agent, the ACS filters and personnel protective equipment canister carbon are expected to be disposed of on-site in the MPF. CMA plans to dispose of all other used carbon by bagging and drumming it and eventually shipping it to a qualified TSDF. As noted previously, the bulk carbon from the PFS will be bagged and drummed as loose material. All other used carbon will be contained in metal filter trays similar to those used in the MDB HVAC (see Figures 2-3 and 2-4).

The ACS filter trays and gas mask canisters, including the metal canister frames and canister bodies, are double bagged, placed in 95-gallon polyethylene drums, and sent to storage. Subsequently, when operating schedules permit, they are removed from the drums, placed in waste incineration containers, and treated in the MPF. In the MPF, the spent carbon and container are treated to an agent-free condition for several hours as they pass through each zone. The MPF process meets

TABLE 2-4 Summary of Sources and Estimated Inventories (in Pounds) of Unexposed Carbon Used at CMA Incineration Sites During Operations and Closure[a]

Site	PFS Carbon (Regular)	Laboratory	MDB HVAC	PFS Sulfur-Impregnated Carbon	Control Room	Other
ANCDF	115,500	15,400	414,700	69,300	15,400	12,400
UMCDF	270,000[b]	10,600	95,000	200,000[b]	5,300	17,300
TOCDF	0[c]	6,300	318,000	240,000[d]	5,000[d]	2,500[d]
PBCDF	80,800[e]	15,900	127,500	48,500[f]	8,000	14,400
Total	466,300	48,200	955,200	557,800	33,700	46,600

[a] Weights may include carbon, carbon tray materials, and packaging. Information is as of September 29, 2008, unless otherwise noted. Estimates of unexposed carbon made on basis of anticipated off-site treatment. Quantities have been rounded.

[b] Information updated as of March 17, 2009.

[c] PFS was only recently added at TOCDF for the processing of mercury-contaminated mustard agent and therefore only sulfur-impregnated carbon is to be used.

[d] Information updated as of March 19, 2009.

[e] Information updated as of March 18, 2009. Of this amount, 48,500 lb has already been shipped off-site.

[f] Information updated as of March 18, 2008.

SOURCE: Adapted from information provided to the committee by Timothy Garrett, Site Project Manager, ANCDF, September 29, 2008.

FIGURE 2-9 A 95-gallon drum for storage of used carbon filter trays. SOURCE: Robie Jackson, Waste Management Manager, ANCDF, and Tracy Smith, Trial Burn Manager, ANCDF, "The use of carbon at ANCDF," Presentation to the committee, June 5, 2008.

the temperature and time criteria, 1000°F for at least 15 minutes, to allow the treated residual materials leaving the MPF to be safely released to a commercial disposal facility. However, any carbon must be kept in the MPF until it has finished smoldering. Treating all the carbon filter units in the MPF would seriously delay the schedule for completion of facility operations and closure.

FIGURE 2-10 Vestibule on the side of an MDB HVAC unit. SOURCE: Photograph taken at ANCDF and provided courtesy of ANCDF.

For the used carbon that is to be shipped to a qualified TSDF, a permitted protocol is needed. At the time this report was being written, CMA was working on such a protocol that uses sampling, extractive analysis, and transportation risk assessment (TRA) guidelines to establish the conditions under which the carbon can be safely transported to an off-site qualified TSDF without prior on-site treatment (see Chapter 4 for further discussion on an analysis protocol). The waste control limits for off-site shipment at operating sites other than UMCDF are 20 parts per billion (ppb) for GB and VX and 200 ppb for mustard agent; for UMCDF, the state has set permit compliance concentrations that serve a similar purpose: at 13 ppb for VX, 16 ppb for GB, and 152 ppb for HD (see Chapter 3). The CMA TRA approach requires the chemical agent disposal facility

TABLE 2-5 Pertinent Physical Properties of the Chemical Agents and Mercury

	Nerve Agent		Blister Agent	
Property	GB	VX	HD	Elemental Mercury
Vapor pressure (torr)	2.48 at 25°C 0.410 at 0°C	8.78×10^{-4} at 25°C 4.22×10^{-5} at 0°C	0.106 at 25°C	1.2×10^{-6} at 20°C
Volatility (mg/m^3)	18,700 at 25°C 3,370 at 0°C	12.6 at 25°C 0.662 at 0°C	75 at 0°C 906 at 25°C	0.884
Boiling point (°C)	150	292	218	357
Freezing point (°C)	−56	<−51	14.45	−38.87
Solubility (g/100 g water)	Miscible	5% at 21.5°C	0.092 at 22°C	Insoluble

SOURCE: Lide (1985) and U.S. Army (2005).

to estimate the maximum amount of agent that might be present in each carbon container. This amount will then be compared to the maximum amount determined for safe shipment by a "bounding" TRA prepared for the anticipated size and method of shipment (see Chapter 7).

Finding 2-2. Carbon is used at many locations in a chemical agent disposal facility. However, it will be exposed to agent-contaminated air or process vent streams in only two locations during normal operation: the agent collection system vent filters and Banks 1 and 2 of the heating, ventilation, and air conditioning filter units.

Recommendation 2-2. A recognized means for characterizing hazardous waste for regulatory purposes is known as "generator knowledge" (as described in Chapter 3). It should be the basis for determining which used carbon can be considered unexposed to agent and thereby minimizing the use of sampling and analysis for final disposition of the carbon.

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U.S. Army. 2005. Potential Military Chemical/Biological Agents and Compounds. FM3-11.9/MCRP3-37.1 B/NTRP3-11.32/AFTTP (I) 3-2.55, January. Fort Monroe, Va.: U.S. Army Training and Doctrine Command.

3

Regulations Governing Carbon Disposal

REGULATORY FRAMEWORK AND CONSIDERATIONS

The generation, accumulation, treatment, storage, and disposal of hazardous wastes are regulated under the Resource Conservation and Recovery Act (RCRA). Wastes derived from the management and destruction of chemical agents and munitions must be assessed under this authority and, if determined to be hazardous, managed under it. This includes waste activated carbon from all air- and gas-filtering units at each chemical agent disposal facility. In this chapter, the committee summarizes the regulations applying at each facility, demonstrates their complexity, and points out some differences from one state to another to clarify the legal constraints impacting carbon disposal options. These are the rules by which the facilities must abide, notwithstanding that some public interest groups may advocate more stringent requirements.

Regulation under RCRA is triggered once it has been determined that a material is a hazardous waste, which is dependent on the material being a solid waste. Solid waste is defined as "garbage, refuse, sludge from an . . . air pollution control facility or other discarded material, including solid, liquid, semisolid, or contained gaseous material resulting from industrial . . . operations."[1] RCRA then requires generators of solid waste to determine if a particular solid waste is hazardous and, if it is, to manage the hazardous waste in accordance with the regulations. Hazardous wastes are solid wastes that because of "quantity, concentration, or physical, chemical, or infectious characteristics may (a) cause, or significantly contribute to an increase in mortality or an increase in serious irreversible, or incapacitating reversible, illness; or (b) pose a substantial present or potential hazard to human health or the environment when improperly treated, stored, transported, or disposed of, or otherwise managed."[2] The statutory definition is implemented for a specific waste through a series of regulations that require a stepwise process for determining if the solid waste is a hazardous waste. First, if a waste is included on one of several lists of substances or constituents provided in the regulations, it is a hazardous waste (each list has a letter designation (F, K, P, and U)) (40 CFR 261.31-261.33). Second, a waste is hazardous if it is ignitable, corrosive, reactive, or toxic (40 CFR 261.20-261.24). A state that has received authorization from the U.S. Environmental Protection Agency (EPA) may define additional wastes as hazardous. With some exceptions, solid wastes generated during the treatment, storage, or disposal of a listed hazardous waste or their mixture with a listed hazardous waste are also hazardous waste. A hazardous waste remains such for the duration of its existence except if it is a characteristic waste that no longer has the characteristic.

RCRA requires operators of facilities that treat, store, or dispose of hazardous wastes to obtain a permit.

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[1] 42 U.S.C. 6903(27).

[2] 42 U.S.C. 6903(5).

A facility must meet design, operational, performance, insurance, and financial responsibility standards issued by the EPA or an authorized state to obtain a permit. RCRA specifically bans land disposal of uncontained liquid wastes and of specified wastes unless they are first treated to reduce their risk.[3]

At the Tooele Chemical Agent Disposal Facility (TOCDF) and the Umatilla Chemical Agent Disposal Facility (UMCDF), operations are known to include the destruction of certain mustard agent munitions that are contaminated with mercury. The processing of these munitions will cause some of the used carbon at these facilities to become contaminated with mercury. If the mercury concentration levels in a waste are found to exceed 0.2 mg/L by EPA's toxic chemical leaching procedure (TCLP), the waste is hazardous based on its toxicity characteristic. Hazardous wastes containing mercury are covered by the land disposal restriction regulations, which establish two categories: low mercury (<260 mg/kg total mercury) and high mercury (≥260 mg/kg total mercury). Low mercury wastes require treatment to 0.20 mg/L for residues from retorting and 0.025 mg/L for all other wastes (using the TCLP) (40 CFR 268.40 and 268.48). EPA states that stabilization or solidification is generally used to meet these standards. High mercury wastes must generally be treated by retorting or roasting in a thermal processing unit capable of volatilizing the mercury and subsequently condensing the volatilized mercury for recovery (40 CFR 268.42). The residual waste from this treatment is then required to meet the above standards; if it does not, the same process must be repeated until there is compliance.

EPA authorizes states to regulate hazardous wastes within their borders under RCRA. A state must adopt a program that is no less stringent than the requirements adopted by the EPA (40 CFR 271). All of the states with operating chemical agent disposal facilities—Alabama, Arkansas, Indiana, Oregon, and Utah—have obtained such EPA authorization.

Each of the states has adopted laws and regulations essentially the same as the EPA hazardous waste management regulations, including regulations for identification and listing of hazardous wastes; requirements applicable to generators and transporters of hazardous waste; requirements for hazardous waste treatment, storage, and disposal facilities (TSDFs); and restrictions for the land disposal of some hazardous wastes.

Each state grants permits for the construction and operation of TSDFs. Permits stipulate the general requirements governing the design, construction, and operation of a TSDF and also establish appropriate site-specific conditions for all aspects of hazardous waste management at the facility. Activated carbon waste from the chemical agent disposal facilities covered in this report is governed by the permits issued by the respective states in which these facilities are located.

In addition to regulation under RCRA, the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA), or Superfund,[4] requires a responsible party to clean up the release of any hazardous substance into the environment. A hazardous substance is defined to include any substance specifically designated by EPA, hazardous wastes as defined under RCRA, toxic pollutants listed under the federal Clean Air Act, and imminently hazardous substances under the federal Toxic Substances Control Act.[5] Liability under Superfund is strict and joint and several and applies to the generator of the hazardous substance regardless of what treatment or disposal may have occurred.[6] Thus, if any hazardous substance remains

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[3] 42 U.S.C. 6924(d)-(m).

[4] 42 U.S.C. 9601-9675.

[5] 42 U.S.C. 9601(14).

[6] Environmental regulatory law has its roots in common law tort law, particularly strict liability principles. This is a complex area of law. A few of the basic principles concerning liability are outlined below to provide context. In tort law, strict liability is the imposition of liability on a party without a finding of fault (such as negligence or tortious intent). The plaintiff needs to prove only that the tort happened and that the defendant was responsible. For example, in the context of a release of chemical agent, a plaintiff needs only to prove that an injury was caused by the chemical agent and the defendant's actions resulted in a level of exposure that caused that injury. Strict liability is imposed for legal infractions that are *malum prohibitum* rather than *malum in se*; therefore, neither good faith nor the fact that the defendant took all possible precautions is a valid defense. Strict liability often applies to those engaged in hazardous or inherently dangerous ventures. In joint liability, parties are each liable up to the full amount of the relevant obligation. In several liability, the parties are liable for only their respective obligations. In joint and several liability, a claimant may pursue an obligation against any one party as if they were jointly liable, and it becomes the responsibility of the defendants to sort out their respective proportions of liability and payment. This means that if the claimant pursues one defendant and receives payment, that defendant must then pursue the other obligors for a contribution to their share of the liability.

after treatment or disposal of wastes generated from the chemical agent treatment or destruction processes and that hazardous substance is released or there is a substantial threat of a release into the environment, then the generator would be liable for remediation of the site of the release.

Finding 3-1. The Army's Chemical Materials Agency will retain liability for the release or threatened release of residual hazardous wastes or hazardous substances adsorbed on activated carbon if that activated carbon is disposed of in a landfill.

OVERVIEW OF STATE-SPECIFIC REGULATORY REQUIREMENTS

Each state has adopted its own waste characterization regulations. Alabama and Arkansas have generally adopted the federal regulations for hazardous waste characterization and listing. Oregon and Utah have issued additional regulations specifically addressing chemical agents or munitions.

Each chemical agent disposal facility has been issued a RCRA permit under the applicable state regulations. These permits establish waste characterization requirements, pertinent sampling and analysis methodologies, waste disposal methods, operating parameters, and closure requirements for each facility. To deviate from any of the provisions set forth in its permit, a chemical agent disposal facility must first obtain approval for the permit modification from the state. The individual facility permit requirements for specific secondary waste streams are discussed below.

The state-issued RCRA permits for all of the disposal facilities specify waste control limits (WCLs) or permit compliance concentrations (PCCs) in parts per billion (ppb) of chemical agent, below which a waste may be shipped off-site for additional treatment or disposal. The permits for the Anniston Chemical Agent Disposal Facility (ANCDF), the Pine Bluff Chemical Agent Disposal Facility (PBCDF), and TOCDF all set WCLs as 20 ppb for nerve agents GB and VX and 200 ppb for distilled mustard agent HD, while the UMCDF permit sets PCCs, which serve a similar purpose, of 13 ppb for VX, 16 ppb for GB, and 152 ppb for HD.[7] The WCL values of 20 ppb for the nerve agents and 200 ppb for mustard agent were derived from Army chemical agent regulations for drinking water standards. The primary analytical methodology for characterizing a waste at most of the chemical agent disposal facilities is set forth in EPA Publication SW-846. This includes the TCLP, which is required to determine if a waste meets the toxicity characteristic definition.[8]

Finding 3-2. The existing state permits issued to chemical agent disposal facilities allow for on-site thermal treatment of all used carbon.

Finding 3-3. The existing state permits issued to chemical agent disposal facilities allow the off-site transportation of agent-contaminated waste if the agent concentration is below the waste control limits established by each state.

Alabama

The Alabama Department of Environmental Management (ADEM) has adopted hazardous waste regulations that mirror the federal RCRA program.[9] ADEM has not specifically listed chemical agents or munitions, or the wastes derived from their destruction, as listed hazardous wastes. Therefore, activated carbon wastes from the treatment or management of chemical agents or munitions at ANCDF must be managed as RCRA hazardous waste only if they exhibit hazardous characteristics.

ADEM issued a permit (AL3210020027) to the U.S. Department of the Army, Anniston Army Depot; the U.S. Department of the Army, ANCDF Field Office (ANCDF site); and Westinghouse Government Environmental Services Company LLC to operate a hazardous waste storage and treatment facility. The permit defines "chemical agent free" as agent concentrations below the lowest achievable method detection limits for the specified analytical method used. ADEM recently approved a permit modification under which certain solid wastes not exposed to chemical agent liquids or to vapors at concentrations greater than the

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[7] Brian O'Donnell, Chief, Secondary Waste, Closure Compliance, and Assessments, CMA, "Transportation risk assessment," Presentation to the committee, June 4, 2008.

[8] 40 C.F.R. 261.24(a): A waste is considered hazardous for toxicity if the extract from the TCLP contains a listed contaminant above the concentration specified in Table 1 of Part 261.24(a); mercury is listed at 0.2 mg/L.

[9] Alabama Administrative Code Revised 335-14-2.

short-term limit (STL) are deemed to be nonhazardous with respect to chemical agent and may be disposed of off-site in accordance with the applicable solid waste regulations.[10] According to the ADEM requirements, only combustible nonporous solid wastes or objects that do not possess internal cavities can be evaluated for off-site disposal using chemical agent vapor monitoring; thus, activated carbon is excluded (ADEM, 2006). Under the ANCDF waste analysis plan (WAP), if an EPA analytical methodology exists, that methodology must be used to determine whether a material contains agent or other toxic constituents. Methods developed by the Army are to be used for those materials for which no EPA methods exist.

Arkansas

The Arkansas Department of Environmental Quality (ADEQ), like ADEM, has promulgated hazardous waste regulations that essentially are the same as the federal RCRA program.[11] Similarly, ADEQ has not listed specific designated chemical agents or munitions as hazardous wastes. As a result, activated carbon wastes from the treatment or management of chemical agents or munitions at PBCDF must be managed as RCRA hazardous waste only if they exhibit hazardous characteristics.

ADEQ issued a permit (Permit No. 29-H) to Pine Bluff Arsenal to operate a hazardous waste management facility at Pine Bluff Circle, Jefferson County, Arkansas. At PBCDF, process knowledge, quality assurance data, and analytical data are used to make waste characterization decisions. Under the PBCDF RCRA permit, the term “chemical agent-free” refers to contaminated or potentially contaminated solid materials that have been tested per the PBCDF WAP and found to be below the WCL or to have been thermally treated for 15 minutes at 1000°F. Under the WAP, waste may be shipped off-facility for treatment and/or disposal only if

- The waste was not agent contaminated, or
- The waste meets the criteria for chemical agent free, or
- The waste has been decontaminated and/or monitored to a vapor concentration equivalent to less than the short-term exposure limit (STEL) for agent.[12]

According to the PBCDF WAP, each batch of waste from areas where chemical agent may be present will either be sampled and tested for agent or the vapor space above the waste will be monitored for agent. For those batches characterized by sampling and analysis, the TCLP extraction method will be used to determine concentrations of substances of regulatory concern.

Agent vapor space monitoring is performed by placing the wastes in a container (e.g., drum or bag) and allowing at least 4 hours at 70°F for the agent vapor in the container to reach equilibrium. After equilibrium is reached, the concentration of agent in the vapor space will be measured using near-real-time monitoring (e.g., automatic continuous air monitoring systems). The characterization methodology for each secondary waste stream destined for off-site shipment is detailed in the WAP (ADEQ, 2006).

Oregon

The Oregon Department of Environmental Quality (ODEQ) has incorporated by reference the federal RCRA regulations for the identification and listing of hazardous wastes (Oregon Administrative Rules 340-101-001). In addition to the federally listed acute hazardous wastes, ODEQ regulations include the following as state-specific listed hazardous wastes:

- Blister agents (such as mustard agent) (Hazardous Waste Code P998) and
- Nerve agents (such as GB and VX) (Hazardous Waste Code P999).

Oregon regulations also include the following as additional state-specific listed hazardous wastes from nonspecific sources:

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[10] The STL is a concentration typically expressed in milligrams of a specific agent per cubic meter of air. For GB, 1 STL is 0.0001 mg/m^3; for VX, 0.00001 mg/m^3; and for HD, 0.003 mg/m^3.

[11] ADEQ Regulation No. 23.

[12] The STEL is the maximum vapor concentration to which unprotected workers can be exposed for up to 15 minutes (as often as four times in an 8-hour workday) without adverse health effect. These values for chemical agents GB, VX, and HD are the same as the STL values but include as well the aforementioned time component.

- Residues from demilitarization, treatment, and testing of blister agents (such as mustard agent) (Hazardous Waste Code F998)[13] and
- Residues from demilitarization, treatment, and testing of nerve agents (such as GB and VX) (Hazardous Waste Code F999).

The Oregon Environmental Quality Commission issued a permit (ORQ 000 009 431) to the U.S. Army, as represented by the Umatilla Chemical Depot and the Washington Demilitarization Company, LLC, to operate a hazardous waste treatment and storage chemical demilitarization facility located in Umatilla County, Oregon. At UMCDF any nerve, military, and chemical agents or any residues from demilitarization, treatment, and testing of nerve, military, and chemical agents are a state-listed hazardous waste. According to the UMCDF WAP, wastes must be agent free before they are shipped to an off-site facility. Samples will be considered agent free if they contain less than 13 ppb VX, 16 ppb GB, and 152 ppb mustard. These PCCs, included in the UMCDF permit, were adopted based on process knowledge, previous results for similar waste streams at the Johnston Atoll Chemical Agent Disposal System (JACADS) or TOCDF, and existing RCRA land disposal restriction notification requirements. These values are modestly lower than the 20 ppb criterion for GB and VX at the other chemical agent disposal facilities.

Under the UMCDF WAP, compliance of waste streams with PCCs is determined using EPA SW-846 unless another characterization methodology is approved. For the detection of chemical agent, UMCDF standard operating procedure UM-0000-M-559, "Agent Extraction and Analyses," is used. This procedure tailors the analyses to different sample matrices; if a process stream is not listed, the matrix that the sample most resembles is to be used (ODEQ, 1997).

Utah

The Utah Department of Environmental Quality (UDEQ) regulations generally restate the federal RCRA regulations for the identification and listing of hazardous wastes (Utah Administrative Rules R315-2). In addition to the EPA list of acute hazardous wastes, the UDEQ regulations add the following state-specific listed wastes: nerve, military, and chemical agents (i.e., CX, GA, GB, GD, H, HD, HL, HN-1, HN-2, HN-3, HT, lewisite, T, and VX) (Hazardous Waste Code P999). The UDEQ regulations also incorporate by reference the federal list of hazardous waste from nonspecific sources and then add the following state-specific listed wastes: residues from demilitarization, treatment, and testing of nerve, military, and chemical agents CX, GA, GB, GD, H, HD, HL, HN-1, HN-2, HN-3, HT, lewisite, T, and VX (Hazardous Waste Code F999).

The Utah Solid and Hazardous Waste Control Board issued a permit (UT 3213820894) to Tooele Army Depot to operate a hazardous waste treatment and storage facility located approximately 3 miles south of Tooele, on State Highway 36, in Tooele County, Utah. Under the TOCDF WAP, only secondary wastes having a chemical agent concentration below the WCL of 20 ppb for GB and VX and 200 ppb for mustard agent may be transported to an off-site RCRA TSDF. These wastes are designated as process wastes (Utah F999). Wastes above the WCL are designated as acute wastes (Utah P999). The vapor space above certain other wastes is monitored for agent to determine if the waste is (1) a Utah process waste (Utah F999) that may be shipped off-site for treatment and ultimate disposal if it meets the WCL or (2) an acute waste (Utah P999), which must be treated on-site (UDEQ, 2004).

COMMONALITIES AND DIFFERENCES SPECIFIC TO ACTIVATED CARBON PRACTICES AND PERMIT REQUIREMENTS

At the four operating Chemical Materials Agency (CMA) incineration facilities, exposed carbon is either disposed of on-site by thermal treatment in the metal parts furnace or stored on-site for future treatment and disposal. CMA management has identified a need to develop better analytical methods for analyzing porous

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[13] ODEQ regulations define demilitarization as all processes and activities at the Umatilla Chemical Depot and Umatilla Chemical Agent Disposal Facility from February 12, 1997, through ODEQ approval for closure of all permitted treatment, storage, and disposal units and facility-wide corrective actions.

Demilitarization residue is defined as any solid waste generated by demilitarization processes and activities, except for waste streams generated from processes or activities prior to the introduction of nerve or blister agent into the treatment unit and waste streams generated from the maintenance or operation of process utility systems not contaminated by agent (Oregon Administrative Rules 340-100-0010).

materials to help facilitate additional off-site carbon disposal.[14]

The current ANCDF operating permit states that used carbon will be evaluated for chemical agent contamination if it has been exposed to agent concentrations of ≥1 STL. If generator knowledge[15] is not sufficient to establish the exposure history, extractive analysis can be used to measure the level of chemical agent if the waste is being considered for off-site disposal. Used carbon that experiences agent breakthrough of ≥1 STL will not be sampled and is to be treated on-site. Used carbon considered for off-site disposal must also be tested for EPA's TCLP organics and TCLP metals.

The means and permit requirements for managing used activated carbon disposal at PBCDF are currently similar to those at ANCDF. The PBCDF WAP states that agent-contaminated carbon will be incinerated on-site in an appropriate manner. Used carbon that has not been exposed to agent is disposed of off-site.

Originally, on-site carbon micronization and incineration was the only disposal option allowed at TOCDF (UDEQ, 2004). Micronization is a process in which carbon is ground to a fine powder prior to incineration. Micronization and incineration were used in the JACADS closure operation to dispose of used activated carbon (Jordan and Kaminski, 2001). The systems contractor at JACADS, the Washington Demilitarization Group, experienced many difficulties with the micronization system and wrote various lessons-learned reports. Based on that experience, micronization followed by incineration appears to be a highly problematic method of disposal, but no on-site alternative to the micronization technology has so far been permitted by Utah.

The contamination of the mustard agent stockpiled at TOCDF with significant amounts of mercury could be another problem. TOCDF is implementing a pollution abatement system (PAS) filtration system (PFS) that will trap the mercury on sulfur-impregnated carbon, but the resulting secondary waste stream will contain carbon with adsorbed mercury.[16] This same issue will arise at ANCDF and UMCDF.

Mustard agent accounts for the largest fraction of chemical agent yet to be processed at UMCDF. The used carbon from the mustard campaign at UMCDF will be managed in much the same way as at TOCDF, including following the TOCDF lead for disposal of carbon waste that is potentially mercury contaminated. The UMCDF WAP requires carbon to be treated on-site and simply states that the treatment method for used carbon has not yet been determined (ODEQ, 1997).

Finding 3-4. Carbon that has not been exposed to agents, based on generator knowledge, or exposed carbon that meets the waste control limit (or, in Oregon, the permit compliance concentrations) may be shipped off-site for treatment or disposal. However, where the carbon is sent depends on whether it is determined to be a hazardous waste.

Finding 3-5. Upon a determination that carbon from a chemical agent disposal facility is not a hazardous waste, it may be sent to a solid waste disposal facility or carbon reactivation facility. If there is a determination that the carbon is a hazardous waste but has not been exposed to agent or that the concentration of agent is below the waste control limit, it must be sent to a permitted hazardous waste treatment, storage, and disposal facility. The TSDF itself may require additional testing or certification. This does not apply at the Tooele Chemical Agent Disposal Facility, where the permit currently requires on-site storage until a treatment system is approved.

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[14] Timothy Garrett, Site Project Manager, ANCDF, "ANCDF secondary waste initiative," Presentation to a fact-finding team of the Committee on Review of Chemical Agent Secondary Waste Disposal and Regulatory Requirements, October 16, 2006.

[15] "Generator knowledge" is a hazardous waste evaluation method commonly accepted and defined by EPA (2005) and individual states based on some or all of the following information:

1. Facility process flow diagram or narrative description of the process generating the waste (should be used in most cases).
2. Chemical makeup of all ingredients or materials used in the process that generates the waste (should be used in most cases).
3. List of constituents that are known or believed to be by-products of side reactions to the process that produces the waste.
4. Material Safety Data Sheets and/or product labels for substances used in the process that generates the waste.
5. Data obtained from approved methods of sampling and laboratory analysis of waste generated from the same process using the same ingredients/materials.
6. Data obtained from literature on waste produced from a similar process using the same ingredients/materials.
7. Documentation of product specifications or input materials and output products.

[16] Wastes contaminated with >0.2 mg/L of mercury are hazardous wastes (D009). Mercury-contaminated hazardous wastes must meet the land disposal restrictions of <0.025 mg/L (for nonwastewater) prior to disposal.

TABLE 3-1 Current Status of Permit Requirements for Shipping Carbon Off-site from Chemical Agent Disposal Facilities

Facility	Requirement of the Existing Permit	Planned Modification Application
ANCDF	Carbon exposed to <1 STL may be shipped off-site.[b] Carbon exposed to >1 STL must undergo extractive analysis prior to shipment. Carbon that tests <WCL may be shipped off-site. Filters from the agent collection system will be incinerated on-site.	HVAC carbon >WCL after extractive analysis to be shipped off-site in accordance with bounding transportation risk assessment. Munitions demilitarization building HVAC Bank 1 carbon appears to be >WCL for GB.
UMCDF	Off-site shipment of agent-free carbon allowed if agent concentration is less than the PCC: 16 ppb for GB, 13 ppb for VX, and 152 ppb for mustard.	The UMCDF plans to submit a Permit Modification Request to incorporate the agent extraction method for spent carbon into the Hazardous Waste Permit WAP following the programmatic validation of the method.
TOCDF	All carbon must be processed by carbon microminiaturization system and subsequently combusted in the deactivation furnace system.[a]	Ship all carbon from the pollution abatement system filtration system and from the heating, ventilation and air conditioning (HVAC) Banks 4-6 off-site Considering using autoclave on remaining carbon until VSL <1 then shipping off-site
PBCDF	The WAP requires on-site incineration of exposed carbon that is shown by extractive analysis to be greater than 20, 20, and 200 ppb for GB, VX, and H, respectively. The WAP allows off-site shipment to a TSDF of spent carbon that is shown by extractive analysis to be less than 20, 20, and 200 ppb for GB, VX, and H, respectively. Unexposed carbon can also be shipped, and generator knowledge is allowed in the determination of "unexposed."	None
NECDF	Used agent-contaminated carbon is considered a listed hazardous waste (Waste Code 1001). However, extractive analysis was done to satisfy CMA bounding transportation risk assessment requirements. Agent-contaminated carbon has been shipped to a TSDF (a hazardous waste incinerator) for treatment.	None

[a] Although this is the existing requirement, the state and TOCDF have agreed that carbon will be stored until another treatment method is approved.
[b] The one STL for GB and VX is 20 ppb; for HD, it is 200 ppb.

SOURCE: Personal communications between Timothy Garrett, Site Project Manager, ANCDF, and Margaret Novack, NRC study director, February 24, 2009, February 25, 2009, and February 27, 2009.

REQUIREMENTS RELATING TO TRANSPORTATION

General

Transportation of hazardous materials is regulated by the Pipeline and Hazardous Materials Safety Administration within the U.S. Department of Transportation (DOT) under the Hazardous Waste Material Transportation Act.[17] The administration establishes uniform standards for the shipment of all hazardous materials, including hazardous wastes, and generally preempts state and local requirements unless such requirements (1) may be complied with in addition to the federal requirements; (2) as applied do not present an obstacle to compliance with the federal requirements; or (3) are substantively the same as the federal requirements. DOT may waive preemption of state or local requirements if it determines that the nonfederal requirement (1) provides the public with "at least as much protection" as the federal requirements and (2) is not "an unreasonable burden on commerce."[18]

Existing Requirements for Transporting Carbon Off-site

The existing requirements to transport activated carbon off-site for disposal are stated in each facility's RCRA permit. Any changes desired by the facility require applying for a modification to the permit—a process that takes approximately a year. The existing requirement and planned requests for permit modifications are given in Table 3-1. It is expected that the ship-

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[17] 49 U.S.C. 5101-5127.

[18] 49 U.S.C. 5235.

ping of exposed carbon will require extractive analysis to confirm that the agent concentration is below the permitted levels.

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4

Interactions of Chemical Agents with Activated Carbon

Application of activated carbon and other adsorbents for removal of chemical constituents from commercial and industrial gas streams has been a widespread practice for many decades. Carbon use in chemical agent disposal facilities was discussed in detail in a previous National Research Council report (NRC, 1999). This chapter explains some adsorption fundamentals and the known reactions of agents on activated carbon. These are prerequisites for understanding the chemical fates and levels of agent loadings on carbon. Also examined in this chapter is the ability to analyze such agent loadings.

FUNDAMENTALS OF ADSORPTION

Adsorption processes generally involve the partitioning of a chemical solute (such as the agents of concern here) between the bulk fluid phase (e.g., water or air) and the surface of the solid adsorbent material. Gas-phase applications of adsorption typically involve physical adsorption (physisorption) and chemical adsorption (chemisorption). Physical adsorption entails the attraction of molecules to surfaces via dispersion-repulsion forces, termed London–van der Waal forces, and hydrogen bonding. Gas-phase molecules condense in these force fields and adhesion to the surfaces is described in terms of Lennard-Jones and electrostatic potentials (Mattson and Mark, 1971). When the forces involved are relatively weak, the adsorbate (e.g., agent) molecules remain intact and are held in close proximity to adsorbent surfaces. In microporous adsorbents such as activated carbon, molecules entering the micropores can also be attracted by functional groups on the surrounding adsorbent pore walls. These functional groups are formed on the surface during the activation process and greatly enhance physical adsorption. They also contribute to pore filling with adsorbate molecules at liquid-like densities. In contrast to physical adsorption, chemical adsorption involves the formation of chemical bonds between adsorbate molecules and functional groups on the adsorbent surfaces, interactions that often lead to dissociation of the adsorbate molecules. Such interactions—for example, hydrolysis by water adsorbed on the carbon—are important in determining and understanding the ultimate fate of adsorbed agents.

Both equilibrium processes and rate processes must be considered to understand adsorption processes (Mattson and Mark, 1971; Weber and DiGiano, 1996). Adsorption isotherms quantitatively describe equilibrium loadings of solutes on solid adsorbents in liquid- and gas-phase applications, respectively, as functions of their liquid-phase concentrations or partial pressure at a fixed temperature. Equilibrium is a dynamic phenomenon, involving molecules adsorbing and desorbing simultaneously at equal rates. Adsorption of mixtures of different chemical vapors is complicated by different molecular species competing for available adsorbent surface sites and the possible replacement of some adsorbed molecules by others that are more strongly adsorbed. In some cases, the adsorption of molecules of one chemical species can enhance the adsorption of another—for example, the adsorption of low molecular weight alcohols is enhanced by adsorbed water vapor. Such cooperative mechanisms involving water generally occur only for water-soluble chemicals adsorbed at low loadings.

Overall rates of adsorption of agents by activated carbon involve both mass transfer and chemical reaction rates. Mass transfer mechanisms influencing process performance in adsorption beds include (1) external mass transfer from the bulk fluid phase passing through the bed to exterior surfaces of adsorbent particles contained in the bed, (2) intraparticle mass transfer by fluid-phase diffusion within pore fluids and/or adsorbed-phase diffusion along pore wall surfaces, and (3) hydrodynamic axial dispersion of adsorbate through the bed within the external fluid phase. The length of an adsorption wave front, which is the adsorbate fluid-phase concentration profile, passing through a bed of carbon in a fixed-bed adsorber is characterized as the active mass transfer zone (Figure 4-1). The mass transfer zone by definition extends from a performance-designed maximum allowable fluid-phase concentration at its furthest depth of penetration into the bed to a concentration slightly less than the feed concentration near the influent end of the bed (Weber and DiGiano, 1996). When the wave has passed through the bed to the point that the maximum allowable effluent concentration has reached the end of the bed, "breakthrough" of the bed with respect to prespecified effluent constraints is said to have occurred.

Activated carbon surfaces are generally populated by oxygen-containing functional groups (e.g., –OH, =O, and –COOH). These groups are formed during the activation process and by exposure to air afterwards, and they are instrumental in both chemisorption-driven adsorption and adsorbate transformation. This is particularly the case for small polar molecule adsorption at ambient temperatures in moist air. The transformation reactions, which include hydrolysis, dissociation, oxidation, complexation, and acid-base reactions, depend in large measure on the molecular properties of the adsorbates and the properties of the adsorbent precursor and its activation conditions (Bandosz and Ania, 2006).

These functional groups cause the activated carbon surfaces to exhibit some polarity, which plays a specific role in attracting chemical agents containing oxygen, sulfur, nitrogen, halogens, and phosphorus and in enabling the retention of water. The presence of water in carbon pore systems is crucial for achieving the hydrolysis reactions that occur at pore wall surfaces. Significant quantities of water—loading up to 70 weight percent—are adsorbed on virgin carbon surfaces when the relative humidity exceeds 50 percent (McCallum et al., 1999). The principal centers for water adsorption are the micropores, in which water is attracted to functional groups and/or forms clusters by hydrogen bonding, which results in condensa-

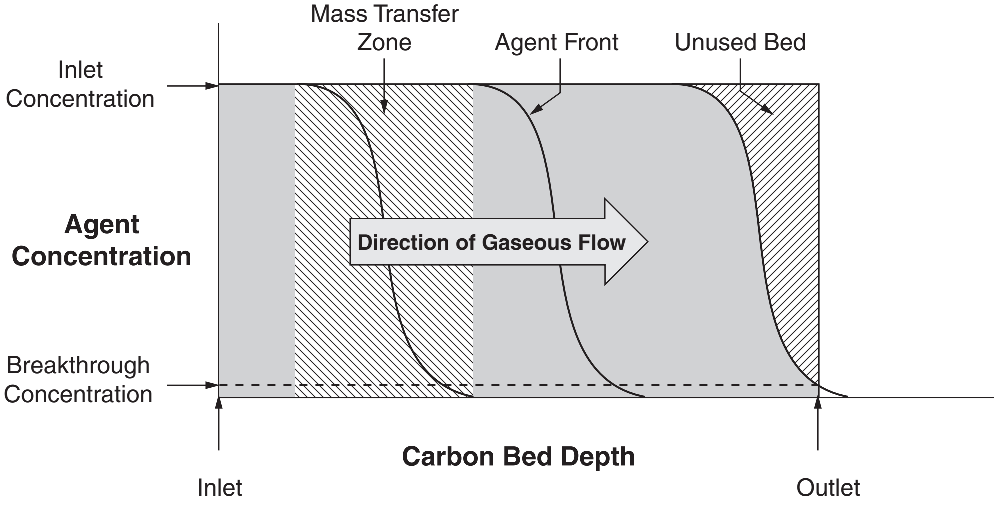

FIGURE 4-1 Mass transfer zone in a carbon adsorption bed. The three curves represent the agent front after progressive periods of time. The breakthrough concentration typically represents the maximum acceptable effluent concentration; once the breakthrough concentration has been achieved, the filter has reached the end of its useful protective life and requires changeout. SOURCE: Adapted from Holgate et al., 1993.

tion (McCallum et al., 1999). Figure 4-2 illustrates the S-shaped isotherm commonly exhibited by water adsorbed on wood- and coal-based carbons.

Finding 4-1. Because moisture is always present in the air that continually flows through the carbon beds at chemical agent disposal facilities, water is always available on the carbon to hydrolyze adsorbed chemical agents.

The presence of ash in activated carbons is also known to enhance surface reactivity by causing catalytic reactions (Hsu and Teng, 2001). Before they are used, activated carbons usually contain from 2 to 15 percent inorganic matter such as oxides of alkali and alkaline earth elements, other oxides, aluminum, iron, and silicon. For many applications, a low level of inorganic impurities in activated carbon is desirable. For other applications, however, higher ash content may be beneficial because certain ash constituents may selectively chemisorb specific types of metals, inorganic species, and some synthetic organics, as well as play a beneficial role by catalyzing surface reactivity.

ADSORPTION OF CHEMICAL AGENTS ON HEATING, VENTILATION, AND AIR CONDITIONING CARBON

Activated carbons are produced from various precursors, including petroleum residues, coal, wood, fruit pits, and shells of various nuts. The choice of precursor and of activation process determines pore size distributions, surface areas, and surface chemistries of the activated carbon product. The carbon used in the adsorption-based filters at the Chemical Materials Agency (CMA) chemical agent disposal facilities is made from coconut shells. Activated carbons made from this material typically have more micropores per unit mass (volumes of <2 nm^3), greater surface areas, and greater crush strengths than carbons produced from more common materials such as bituminous coal and wood. Moreover, they often have greater adsorption capacities for specific adsorbates.

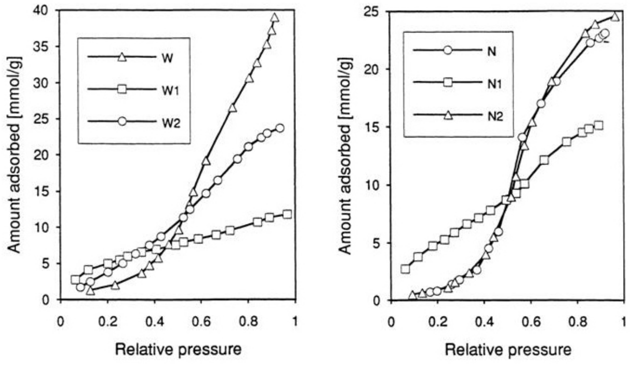

FIGURE 4-2 Water adsorption isotherms on activated carbons made from different types of wood (W, W1, and W2) and coals (N, N1, and N2) at 25°C. Relative pressure is the ratio of the actual pressure over the vapor pressure at the temperature of measurement and ranges from 0 to 1. SOURCE: Reprinted with permission from Bandosz et al., 1996. Copyright 1996 American Chemical Society.

As discussed in Chapter 2, the large carbon adsorption-based filter units installed at the chemical agent disposal facilities were manufactured by IONEX Research Corporation. The units contain several banks of filter trays in series, each containing IONEX 03-001 (formerly C-800) 8 × 16 mesh coconut shell carbon, trade named Cocoanut. Each filter tray contains two thin beds of carbon in series. IONEX carbons possess surface areas of 1,150 m^2/g and a bulk density of 520 kg/m^3. As designed, agent in the first carbon bank of a multiple-bank system will break through into the next carbon bank in the series after the first bank has been exposed to a quantity of adsorbate sufficient to exceed its adsorption capacity. In this case, the first bank provides the bulk of agent removal and the next bank is said to "polish" the effluent.

As shown in Table 4-1, all three chemical agents—GB, VX, and HD—are adsorbed effectively by coconut shell activated carbon up to about 30 weight percent. However, as discussed below, the agents all react with the moisture on the carbon to form the expected hydrolysis products. In 2007, several carbon samples from the Anniston Chemical Agent Disposal Facility (ANCDF) were analyzed for residual nerve agents GB and VX at government and contractor surety laborato-

TABLE 4-1 Agent Loadings on Cocoanut Activated Carbon

Agent	Relative Humidity (%)	Maximum Loading (g agent/g carbon)
GB	Dry	0.318
GB	66	0.383
VX	Dry	0.298
HD	Dry	0.379

SOURCE: Adapted from material from by Susan Ankrom, SAIC Task Manager, ANCDF, "Published values for agent loading capacity of MDB and PFS carbon," Presentation to the committee, June 6, 2008.

ries. They included (1) carbon samples taken from both Bank 1 and Bank 2 during the changeout on December 1, 2006, following completion of all GB agent and VX rocket and projectile campaigns, (2) a carbon sample from the pollution abatement system (PAS) filtration system (PFS), and (3) a sample of unused carbon as a control. No agent was detected on Bank 2 carbon.

The analytical results from the U.S. Army Edgewood Chemical and Biological Center (ECBC) are shown in Table 4-2 (Buettner et al., 2008). The amount of GB that must have been adsorbed on Bank 1 carbon during processing of GB munitions in the munitions demilitarization building (MDB) is indicated by the 13 weight percent of its hydrolysis product, isopropyl methylphosphonic acid (IMPA), that was found on the carbon by solid-state magic angle spinning (MAS) nuclear magnetic resonance (NMR). Because the molecular mass of GB and IMPA are approximately the same and one mole of IMPA is produced for each mole of GB, the mass percent of IMPA is approximately equivalent to the amount of GB to which the carbon was exposed. The MAS NMR method was not sensitive enough to detect trace amounts of GB if any remained.

In comparison, only a trace amount of the VX hydrolysis product, ethyl methylphosphonic acid (EMPA), was found on carbon from Bank 1. This small amount of the hydrolysis product is attributed to the low volatility of VX in the ambient air stream. (The vapor pressures and volatilities of the agents are given in Table 2-5.) Because the vapor pressure of VX is much lower than that of GB, only a comparatively smaller amount of VX was ever in the gas phase and available to be transported through the heating, ventilation, and air conditioning (HVAC) system to the HVAC filters and, finally, adsorbed on the carbon filters in any given time interval. The chemistry of the adsorbed agents with the water on the carbon is discussed in detail in the next section.

The carbon samples from ANCDF discussed above are from a chemical agent disposal facility that uses incineration technology. At disposal facilities such as the Newport Chemical Disposal Facility (NECDF), VX was instead destroyed by a chemical neutralization (hydrolysis) process. When a chemical agent is destroyed by neutralization (as was the case at NECDF) instead of incineration, hydrolysis products are formed (none are formed by incineration). At NECDF, the HVAC carbon had been exposed to the neutralization reactor venting system for the duration of NECDF disposal operations, so volatile hydrolysis and thermal degradation (90°C) products of VX were adsorbed on the HVAC carbon in addition to VX itself.

Extractive analysis of HVAC carbon samples from NECDF by a Southwest Research Institute (SwRI) laboratory indicated the presence of volatile VX impurities, hydrolysis by-products, and degradation products

TABLE 4-2 Analytical Results of HVAC and PFS Carbon Samples Collected from ANCDF in January 2007

	HVAC Bank 1	HVAC Bank 2	PFS Carbon	New Carbon
Headspace vapor analysis	GB $< 1.5 \times 10^{-5}$ mg/m^3 VX $< 5.1 \times 10^{-7}$ mg/m^3	Same as Bank 1	Not analyzed	Not analyzed
Thermal desorption followed by GC/MS/FPD[a]	GB $< 1.0 \times 10^{-4}$ mg/m^3 VX $< 1.0 \times 10^{-4}$ mg/m^3	Same as Bank 1	Not analyzed	Not analyzed
Solid-phase NMR, MAS ^{31}P or MAS ^{1}H	GB < 1,500 ppm VX < 1,500 ppm IMPA = 13 wt percent[b] EMPA = Nondetect[b]	No phosphorus compound was detected at a detection limit of 1,500 ppm	Relatively large water peaks	Relatively small water peaks
Solvent extraction followed by GC/MS	GB[c] VX < 20 ppb	Not analyzed	Not analyzed	Not analyzed
Remaining filter capacity[d]	12 percent	100 percent	Not analyzed	100 percent (control)

[a] Thermal desorption up to 100°C and 1 L processing volume. FPD, flame photometric detection.

[b] The sample was also extracted in CD_3CN to resolve the IMPA peak in the ^{31}P NMR MAS spectra. NMR analysis of the liquid extract gave 92 percent IMPA, 7 percent MPA (methyl phosphonic acid, $CH_3P(O)(OH)_2$), and a trace of EMPA.

[c] Analytical procedures and results for GB are being revised and validated.

[d] Adsorption capacity was determined by conducting DMMP (dimethyl methylphosphonate, $CH_3P(O)(OCH_3)_2$) breakthrough tests at 3,000 mg/m^3 DMMP concentration and 0.016 m^3/min flow rate.

SOURCE: Adapted from Buettner et al., 2008.

of the aminothiol group.[1] These VX-related adsorbates were extracted into solvent and became potential interferences for the gas chromatography (GC)/mass spectrometry (MS) analysis that was conducted. However, analysis of the extracts by GC/MS indicated the VX to be below 95 parts per billion (ppb).

At the time this report was being prepared, no MDB HVAC carbon sample exposed to distilled mustard agent HD from a chemical agent disposal facility had been available for laboratory analysis. Of the currently operating facilities, only the Tooele Chemical Agent Disposal Facility (TOCDF) had destroyed mustard munitions by incineration, but the Bank 1 and Bank 2 carbon filter units had not yet been removed.

Finding 4-2. The level of GB degradation product found on the Anniston Chemical Agent Disposal Facility munitions demilitarization building heating, ventilation, and air conditioning system Bank 1 filter samples demonstrates that the filter had been exposed to high levels of volatile GB, had adsorbed the GB, and that all or most of the GB had hydrolyzed to its degradation products.

Finding 4-3. Based on the analytical results of the changeout of the Anniston Chemical Agent Disposal Facility munitions demilitarization building heating, ventilation, and air conditioning system Bank 1 carbon filter, very little VX degradation product, ethyl methylphosphonic acid, was detected on the carbon sample. Therefore, it can be concluded that very little of the low-volatility VX was transported by the heating, ventilation, and air conditioning system and adsorbed on the carbon during the processing of the VX munitions at Anniston Chemical Agent Disposal Facility.

Finding 4-4. Chemical agent has not been observed beyond the munitions demilitarization building heating, ventilation, and air conditioning system Bank 2 filter units at the Anniston Chemical Agent Disposal Facility. Furthermore, the changeout of Bank 2 on December 1, 2006, showed that it had retained adsorption capacity equivalent to new (unused) carbon, indicating that Bank 2 was not exposed to any significant amount of agent.

Recommendation 4-1. Banks 3-6 at the Anniston Chemical Agent Disposal Facility have not been exposed to agent and can be disposed of using procedures for unexposed carbon.

REACTIONS OF CHEMICAL AGENTS ON ACTIVATED CARBON

As mentioned above, it has been widely reported that adsorbed chemical agents GB, VX, and HD degrade on activated carbon with time (Brevett et al., 1998; Karwacki et al., 1999; Wagner et al., 2001; McGarvey et al., 2003; Columbus et al., 2006). Degradation generally increases as the relative humidity of the vapor phase increases. The time to reach 50 percent degradation ranges from days to weeks at ambient temperatures. Most of the studies used indirect thermal desorption GC/MS methods for measuring the desorbed agent concentrations in the vapor phase (Karwacki et al., 1999). However, hydrolysis products and intermediates of the reactions of these agents on carbon are usually ionic compounds, which are not detectable by GC. Starting in the 1990s, the reactions of agents on carbon have also been investigated by solid-state MAS NMR techniques that can identify and quantify agents and agent reaction products on the surfaces of carbon directly and simultaneously. The following sections summarize these direct MAS NMR observations of agent reactions on wet carbon.

GB Reactions

Figure 4-3 shows ^{31}P MAS NMR spectra from a recent study.[2] A reaction-time profile is revealed for 10 weight percent GB on wet coconut shell carbon containing 13 weight percent water at room temperature. In the initial spectrum, only the doublet GB peaks ($\delta P = 27.5$ and 18.8 ppm due to P-F splitting, $J_{PF} = 1046$ Hz) were observed. Spectra taken at 6, 13, and 16 days show a decrease in the GB peaks and the emergence of an IMPA peak at $\delta_P = 20.5$ ppm (IMPA is the main hydrolysis product of GB). At 16 days, only a small amount of GB (the shoulder on the main IMPA

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[1] Brian O'Donnell, Chief, Secondary Waste, Closure Compliance, and Assessments, CMA, "NECDF carbon shipment decision," Presentation to the committee, July 24, 2008.

[2] Leonard Buettner, John Mahle, George Wagner, Tara Sewell, and Nicole Fletcher, all of the U.S. Army Edgewood Chemical and Biological Center, and David Friday, Houston Advanced Research Center, "Adsorbent analysis of Anniston Chemical Agent Disposal Facility MDB Bank 1 and Bank 2 filter samples," Presentation to the committee, July 23, 2008.

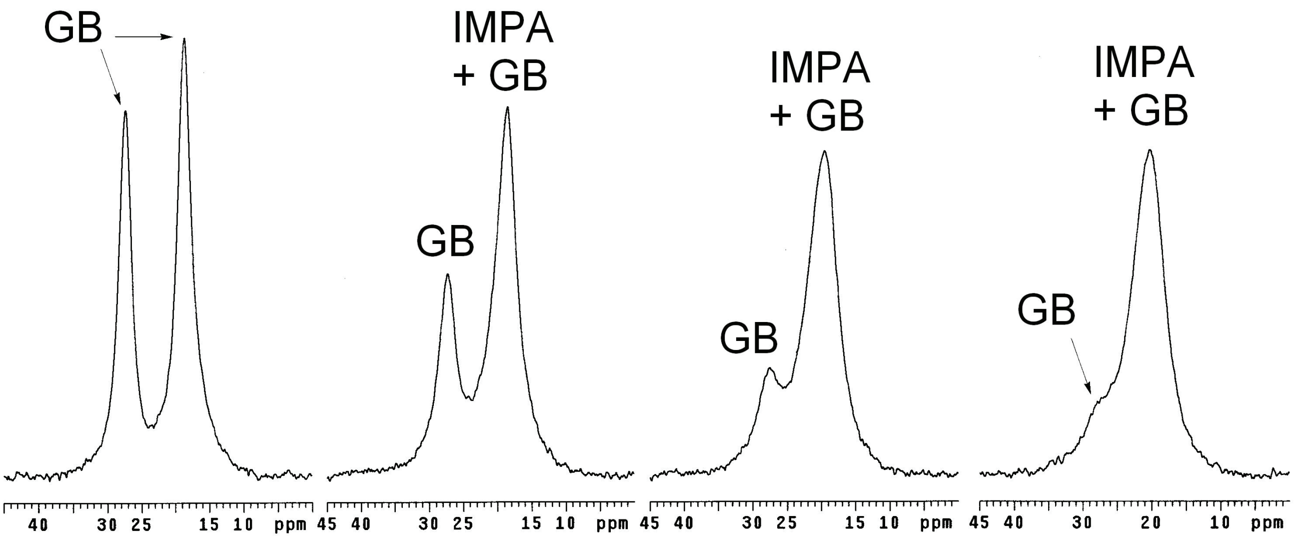

FIGURE 4-3 Phosphorus-31 magic angle spinning (MAS) nuclear magnetic resonance (NMR) spectra of 10 wt percent sarin (GB) on humidified (13 weight percent water) activated carbon over time: initial and after 6, 13, and 16 days, left to right. SOURCE: Leonard Buettner, John Mahle, George Wagner, Tara Sewell, and Nicole Fletcher, all of the U.S. Army Edgewood Chemical and Biological Center, and David Friday, Houston Advanced Research Center, “Adsorbent analysis of Anniston Chemical Agent Disposal Facility MDB Bank 1 and Bank 2 filter samples,” Presentation to the committee, July 23, 2008. IMPA, isopropyl methylphosphonic acid.

peak) remained. GB is known to react with water to form IMPA by the following equation:

$$\underset{\text{GB}}{\mathrm{CH_3P(O)(O}\mathit{i}\mathrm{C_3H_7)F}} + \mathrm{H_2O} \rightarrow$$

$$\underset{\text{IMPA}}{\mathrm{CH_3P(O)(O}\mathit{i}\mathrm{C_3H_7)OH}} + \mathrm{HF} \qquad (1)$$

It should be noted that the initial GB hydrolysis reaction was relatively rapid because it was base-catalyzed (samples of new unused carbon added to deionized water gave pH readings of around 10). As more GB was adsorbed and hydrolyzed, the pH of the adsorbed phase on the carbon was reduced and the acid-catalyzed hydrolysis rate was slower than the base-catalyzed hydrolysis rate. Consequently, the hydrolysis of GB on carbon decreased as the carbon became more acidic. According to analyses by SwRI, the Anniston exposed Bank 1 samples gave pH readings around 3.0 when the carbon was added to deionized water.[3]

In developing the current solvent extraction method for the Anniston carbon samples, the detection of GB at a concentration in excess of the amount that was expected on the carbon—in effect, a false positive—was similar to what Rohrbaugh et al. (2006) had observed in analyzing aqueous acidic samples composed of GB hydrolysis products. Furthermore, with an improved analytical method, GB was detected in the GB hydrolysate when the pH of the hydrolysate was adjusted to below 5 (Malloy et al., 2007)). Accordingly, when developing analytical methods for exposed carbon that would allow it to be cleared at the waste control limit (WCL) or the permit compliance concentration (PCC) level, it is important to avoid conditions that can cause the false positive detection of GB. As GB on the carbon hydrolyzes, the pH decreases because the degradation products are acids, and the rate of hydrolysis becomes slower. The Army interprets this as a sign of re-formation. At the time this report was being written, it was not at all clear to the committee from the available data whether re-formation was in fact occurring.

Finding 4-5. The degradation of GB on carbon produces isopropyl methylphosphonic acid and hydrofluoric acid. In aqueous solutions and at a pH of less than 5, these compounds may slow the rate at which

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[3] The pH measurements were provided in a personal communication between Matthew Blais, SwRI, and the committee, March 17, 2009.

GB hydrolyzes, as previously reported by Malloy et al. (2007). Under such conditions, GB on carbon may not degrade completely.

VX Reactions

As illustrated in Figure 4-4, the reaction of 10 weight percent VX on wet coconut shell carbon containing 13 weight percent water was also monitored by ^{31}P MAS NMR at room temperature (Karwacki et al., 1999; Wagner et al., 2001). In the initial spectrum, as VX was added to the carbon, the broad VX peak at δ_P = 49.4 ppm was reduced and replaced by a sharp major product peak at δ_P = 16.4 ppm, which was identified as diethyl dimethylpyrophosphonate (VX-pyro). The minor broad shoulder peak at δ_P = 20 ppm was produced by the hydrolysis product EMPA (see equations 2 and 3). In the final spectra, taken at 24 days, VX disappeared and the VX-pyro peak increased significantly. The toxic hydrolysis product EA-2192 was not detected. This pair of spectra recorded at reaction times close to 0 and 24 days clearly demonstrated that VX reacted rapidly on the wet carbon.

The degradation of VX occured through an autocatalytic chain. After a small amount of the initial hydrolysis product, EMPA, was produced, the VX primarily reacted with the EMPA to give the diphosphonate compound VX-pyro (equation 2) as the only observed initial product. The VX-pyro, an anhydride of EMPA, subsequently reacted with water adsorbed on carbon to produce more EMPA (equation 3), which reacted with the remaining VX to form more VX-pyro. Thus, an autocatalytic chain reaction was propagated. Also, because the hydrolysis of VX-pyro (equation 3) was much slower than its production, VX-pyro accumulated as the main product during the 24-day monitoring period. These observations are consistent with the rates and mechanisms of VX reacting with less than 10 weight percent water in the bulk organic VX phase (Yang et al., 1996). It can therefore be concluded that on carbon, the main reaction occurred in the adsorbed VX phase, in which only a small amount of water was present.

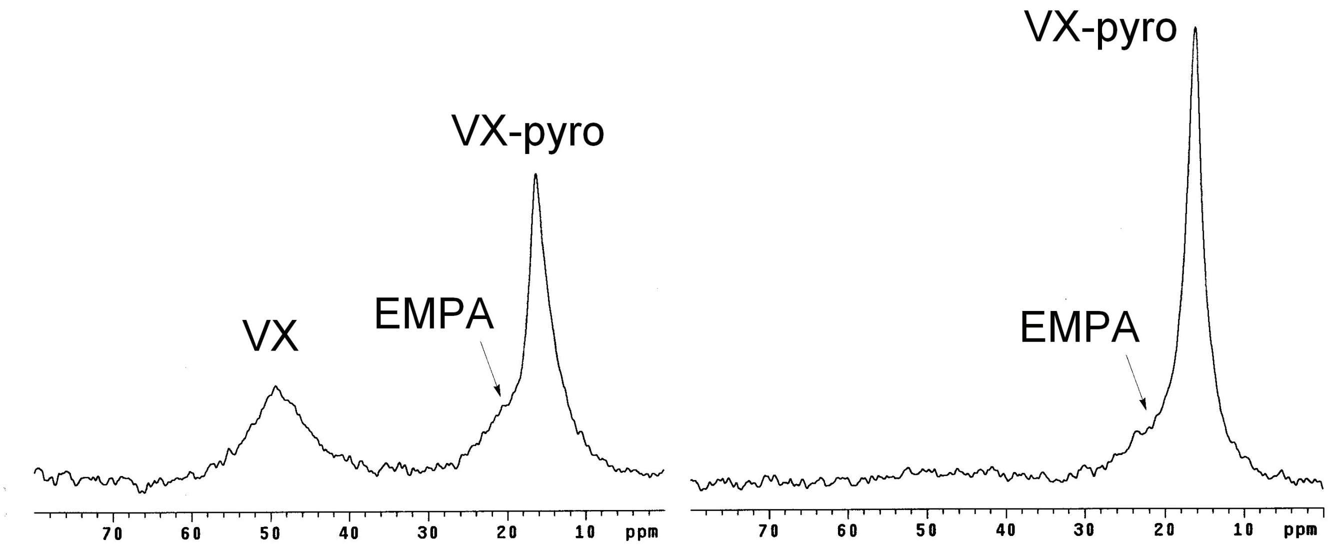

FIGURE 4-4 MAS NMR spectra for 10 weight percent nerve agent VX absorbed on humidified (13 weight percent water) carbon, left to right: initial and at 24 days showing heterogeneous autocatalytic hydrolysis of VX over 24 days, left to right. SOURCE: Leonard Buettner, John Mahle, George Wagner, Tara Sewell, and Nicole Fletcher, all of the U.S. Army Edgewood Chemical and Biological Center, and David Friday, Houston Advanced Research Center, "Adsorbent analysis of Anniston Chemical Agent Disposal Facility MDB Bank 1 and Bank 2 filter samples," Presentation to the committee, July 23, 2008. EMPA, ethyl methylphosphonic acid.

$$\underset{\text{VX}}{CH_3P(O)(OC_2H_5)(SCH_2CH_2N(iC_3H_7)_2)} + \underset{\text{EMPA}}{CH_3P(O)(OC_2H_5)OH} \rightarrow \underset{\text{VX-pyro}}{[CH_3P(O)(OC_2H_5)]_2O} + HSCH_2CH_2N(iC_3H_7)_2 \quad (2)$$

$$\underset{\text{VX-pyro}}{[CH_3P(O)(OC_2H_5)]_2O} + H_2O \rightarrow \underset{\text{EMPA}}{2\ CH_3P(O)(OC_2H_5)OH} \quad (3)$$

After most of the VX is converted to VX-pyro, which is soluble in water, this product will continue to react with the water adsorbed on carbon surfaces to eventually give EMPA (equation 3) as the final product. This was confirmed in 2006 by a study of the reaction of VX adsorbed on a range of carbon samples (Columbus et al., 2006). The authors reported that the VX reaction was complete in less than 20 days. When the final carbon sample was extracted in ethanol, EMPA was detected by ^{31}P NMR as the only phosphorus-containing product.

It should be noted that VX dissolves in acidic water but the protonated VX does not react with water under acidic pH (Yang, 1999). The above VX degradation reaction with water occurs in pH ranges close to neutral—from weakly acidic to weakly basic. If the water adsorbed on the carbon sample becomes strongly acidic, adsorbed VX may dissolve readily in the acidic water in the pores, and the protonated VX in the water phase will neither hydrolyze nor react via the above autocatalytic reaction mechanism (Yang, 1999).

Finding 4-6. Although VX is barely soluble in water, it reacts to form water-soluble VX-pyro, which then reacts in the water phase to produce ethyl methylphosphonic acid. The initial degradation of VX on carbon follows an autocatalytic hydrolysis mechanism that occurs exclusively in the bulk VX phase. Ethyl methylphosphonic acid is the only phosphorus-containing final product. The toxic EA-2192 hydrolysis product has not been detected.

Recommendation 4-2. The Chemical Materials Agency should determine the length of time required for the VX concentration to degrade below the waste control limit or permit compliance concentration.

Mustard Agent Reactions

The ^{13}C MAS NMR from carbon in normal isotopic abundance is not sufficiently sensitive to detect mustard agent HD and its degradation products on carbon directly. However, as reported by Karwacki et al. (1999), ^{13}C MAS NMR has been used to examine the reaction of a ^{13}C-enriched HD compound (0.1 g/g loading) on wet coconut shell carbon containing 13 weight percent water. As the ^{13}C-enriched HD peaks decreased, the hydrolysis products mustard chlorohydrin (CH), thiodiglycol (TG), and sulfonium ion (CH-TG) were detected (see Table 4-3).[4] The reported reaction was slow, with 71 percent of the HD remaining on the carbon after 115 days at 30°C. In comparison, reaction of the same ^{13}C-enriched HD on BPL[5] carbon containing 38.8 weight percent water was complete in less than 24 hours at 50°C (McGarvey et al., 2003). The rate of degradation thus appears to be markedly dependent on the type of carbon used and the temperature.[6]

When adsorbed HD reacts on wet carbon, the main products are TG, hydrochloric acid, and a range of branched sulfonium ions produced from the reaction of HD with TG. The production of the sulfonium ions indicates that HD degradation reactions can occur in mixtures with high HD to water ratios.

With the same ^{13}C-enriched HD loaded onto wet carbon fibers, Brevett et al. (1998) identified another linear sulfonium ion, H-2TG, produced from the reactions of HD and TG (see Table 4-2). These sulfonium ions do not contain 2-chloroethyl groups and therefore do not have vesicant properties. The authors reported that the rate of HD degradation on these carbon samples was much faster than the degradation times reported by Karwacki et al. (1999). The Brevett results showed that after about 6 weeks at room temperature, most of the HD was converted to TG and H-2TG.

The formation of sulfonium ions CH-TG and H-2TG indicates that TG was present in the adsorbed water phase and was able to compete with water in reacting

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[4] The CH-TG was detected only after the carbon sample had been extracted into a solvent.

[5] BPL, a trademarked product of Calgon Carbon Corporation, is a bituminous coal-based granular activated carbon.

[6] Note that 50°C would not be a practical temperature for HVAC air at a chemical agent disposal facility.

TABLE 4-3 Chemical Formulas for Mustard Agent and Its Hydrolysis Products

Abbreviation	Chemical Formula
HD	$ClCH_2CH_2SCH_2CH_2Cl$
CH	$ClCH_2CH_2SCH_2CH_2OH$
TG	$HOCH_2CH_2SCH_2CH_2OH$
CH-TG	$HOCH_2CH_2SCH_2CH_2S^+(CH_2CH_2OH)_2$
H-TG	$ClCH_2CH_2SCH_2CH_2S^+(CH_2CH_2OH)_2$
H-2TG	$(HOCH_2CH_2)_2S^+CH_2CH_2SCH_2CH_2S^+(CH_2CH_2OH)_2$

with insoluble HD at the HD-water interface. Sulfonium ions have frequently been observed in two-phase liquid mixtures of HD and water at relatively high HD to water ratios (Yang et al., 1988). Once produced, they are soluble and relatively stable in water but react more rapidly if NaOH is present (Yang et al., 1988). In previous studies sponsored by the Aberdeen Chemical Agent Disposal Facility, these sulfonium ions present in acidic aqueous solutions made it difficult to prove that batches of HD hydrolysate had the required levels of agent destruction. It is believed that if sufficient HCl is present during solvent extraction and subsequent GC/MS analysis, some of the major sulfonium ions such as CH-TG may decompose and react with chloride ion to form HD. The hydrolysate batches were found to contain less than 20 ppb HD only after aqueous NaOH solutions were added to the acidic hydrolysates.[7] It may therefore be that these sulfonium ions and hydrochloric acid also cause problems in clearing carbon samples to the required WCL or PCC level.

Finding 4-7. Experimental data indicate that it takes weeks to months at room temperature for mustard on carbon to degrade.

Recommendation 4-3. The Chemical Materials Agency should determine the rate of degradation of mustard on carbon under controlled constant conditions with greater accuracy in order to predict if and when the concentration of mustard on carbon will be minimal, or below the waste control limit or permit compliance concentration. For example, any acceptable analytical method needs to be verified by a high level (about 80 percent or more) of agent spike recovery.

Finding 4-8. Analytical studies have shown that sulfonium ions interfere with the analysis of trace amounts of mustard in aqueous solutions.

Recommendation 4-4. The Army should establish definitively whether or not the presence of sulfonium ions interferes with the analysis of mustard on carbon.

Summary of Studies of Agent Reactions on Carbon

As discussed above, direct MAS NMR measurements have shown that all three agents (GB, VX, and mustard) are unstable on wet carbon surfaces and degrade with time. In the case of water-soluble GB, IMPA was the only phosphorus-containing compound detected. For the sparingly soluble VX and practically insoluble HD, more complicated products were obtained from reactions with water and the initial hydrolysis products. Given the relatively high concentrations needed for detection (approximately 0.1 to 1.0 percent g/g) by solid-state MAS NMR, it is uncertain whether the reactions continue to completion or trace amounts of agent remain on the carbon samples. To determine ppb levels of detection of residual agents on carbon, other analytical approaches, such as extraction of the adsorbed phase from the carbon sample, possibly followed by GC/MS detector analysis, are required. During this type of analysis, caution must be exercised to verify that agent is not re-formed during the analytical process, particularly when the carbon samples are acidic. Based on the MAS NMR measurements of the initial stages of degradation, the committee estimates, by extrapolation, that at room temperature it will take approximately 1 month following removal of the carbon from the filter units for GB and VX to degrade to minimal levels and several months for mustard to do the same. Of course, these reactions proceed even while the carbon is in place during disposal operations.

Finding 4-9. The chemical agents VX, GB, and mustard all degrade on wet carbon, with VX and GB degrading faster than mustard. Increasingly rapid rates of agent decomposition occur with increasing temperature and humidity. Also, the final concentrations of agents on the carbon are dependent on the pH of the water adsorbed on the carbon. Under acidic conditions, the hydrolysis of GB is equilibrium controlled, so the GB may not degrade to the waste control limit or permit compliance concentration.

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[7] Although the WCL is 200 ppb, a value of 20 ppb was used to ensure destruction to a 99.9999 percent level.

Recommendation 4-5. The Chemical Materials Agency should determine the time necessary for each of the three agents (GB, VX, and mustard) to degrade on carbon to minimum values and determine if that value is below the respective waste control limits or permit compliance concentrations. Given that mustard is the last agent scheduled for processing at chemical agent disposal facilities, it should be determined if the slow rate of degradation of HD on carbon will impact the schedule for facility closure.

METHODS FOR DETERMINING CHEMICAL AGENT LOADING ON ACTIVATED CARBON

The shipping of agent-exposed carbon to off-site disposal facilities will require a determination of the loading of agent(s) on the carbon on a mass basis (mass of agent per total mass of carbon and all adsorbates). The levels adopted in the Resource Conservation and Recovery Act permits for the Pine Bluff Chemical Agent Disposal Facility (PBCDF), ANCDF, and TOCDF are 20 ppb for GB and VX and 200 ppb for mustard, where the total mass considered is the adsorbent plus all adsorbates, including water and hydrolysis products. The levels that have been adopted at the Umatilla Chemical Agent Disposal Facility (UMCDF) are 16 ppb for GB and 13 ppb for VX, which are the practical quantitative limits.

Because each bank in the MDB HVAC filter units contains 48 filter trays with two layers of carbon in each tray, a statistically reliable method is needed for the selection of a few trays from the location of highest flow in each bank. This sampling approach would be sufficient to determine the maximum loading of agent on the carbon in each bank. At ANCDF it was decided to sample at several different locations within the trays and then mix the samples to produce a homogenized standard sample, an approach found to be acceptable.[8]

Headspace vapor analysis provides a valid measure of the inhalation threat from agents. However, to use this method to accurately measure agent loading on carbon requires measurement of the gas-phase concentration in equilibrium with the carbon and also requires knowledge of the adsorption isotherm for that agent under relevant conditions. In principle, if the adsorption isotherm is known, then the adsorbed-phase concentration or loading can be determined from the gas-phase concentration. Three issues associated with the use of headspace analysis must be considered to achieve a reliable analysis of agent loading on carbon. First, the gas-phase concentration of agent that would be in equilibrium with an agent loading of 20 ppb at ambient, and even moderately elevated temperatures could be undetectable by headspace analysis. Second, the adsorption isotherm would be needed to correlate loadings with gas-phase concentrations at agent loadings near 20 ppb. Third, a pure-component adsorption isotherm would not even apply to the real system, which would contain coadsorbed amounts of other components, such as water and degradation products.

As mentioned earlier, several carbon samples from ANCDF were analyzed for residual GB and VX at both government and contractor surety laboratories in 2007 by extracting agent into a solvent. The samples included (1) a carbon sample from the changeout on December 1, 2006, of Banks 1 and 2 of HVAC filter unit 102 following completion of all GB agent and VX rocket and projectile campaigns, (2) a PFS carbon sample,[9] and (3) an unused carbon sample as a control. Again, no detectable agent was found on Bank 2 carbon.

The HVAC Banks 1 and 2 carbon samples were analyzed at SwRI, first by solvent extraction (Environmental Protection Agency [EPA] SW-846 Method 3571) and then by GC/MS (EPA SW-846 Method 8271) to determine the levels of GB and VX remaining on the carbon. This method showed the results for VX to be valid and below the WCL or PCC, but the results for GB on the carbon were unexpectedly high. As described earlier in this chapter, GB can react with the water on the carbon to form the hydrolysis products IMPA and hydrofluoric acid (HF). In a previous study (Malloy et al., 2007), these products were assumed to be able to react to re-form GB in GB hydrolysate when the pH of the hydrolysate samples was adjusted to below 5. For carbon samples containing these products, the re-formation is believed to occur in the solvent after extraction. Thus, without modification, EPA SW-846 Method 3571 was not able to determine the actual concentration of GB on the carbon at the 20 ppb level.

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[8] Matthew Blais, SwRI, "Carbon analysis for GB," Presentation to Robert Beaudet and Yu Chu Yang, committee members, January 13, 2008.

[9] The PFS carbon sample was analyzed not by SwRI but rather by ECBC; however, SwRI did analyze a sample from HVAC Banks 1 and 2 via NMR, with results indicating less than 1,500 ppm for GB and VX.

Since August 2008, CMA has undertaken to enhance this method to prevent or minimize GB re-formation by modifying the conditions under which the extraction is performed. A working group consisting of staff from SwRI, Battelle, ECBC, and the laboratories at ANCDF, UMCDF, and PBCDF was formed to address this problem, and the experimental work to modify Method 3571 was performed at SwRI. Because the work was not complete when this report was being written and the progress report was made available to the committee only after it had completed its fact finding, the committee was not able to evaluate whether the modified method could validate that the carbon was below the WCL for GB. However, the committee reports the preliminary findings of the SwRI working group below.

Unlike previous analyses of Bank 1 samples, a standard sample from the ANCDF Bank 1 filter was prepared at SwRI. This standard sample was a well-mixed composite sample of carbon samples taken from the Bank 1 filter at different locations. Three replicates of this sample were analyzed for GB, and the results were closely similar, indicating that the standard sample was indeed a homogeneous sample and representative of the Bank 1 filter. This step ensures experimental reproducibility.

Re-formation was minimized by careful choice of solvent (dichloromethane), pH control (use of a pH = 7 buffer), a longer extraction time (30 minutes), and the addition of 1.0 M calcium nitrate, which sequesters fluoride ions.

SwRI has determined the method detection limit (MDL) for this procedure to be 5 ppb. It did this by loading unused carbon with IMPA/HF to simulate Bank 1 carbon, spiking it with GB, and then analyzing it.

Finding 4-10. The method detection limit of 5 ppb for GB obtained by Southwest Research Institute from new unused carbon samples loaded with isopropyl methylphosphonic acid and hydrofluoric acid is the best indication of the extent of re-formation for the current recommended analytical procedures.

The modified Method 3571 is being validated at ECBC and the laboratories at ANCDF, UMCDF, and PBCDF. When this modified method is applied to the ANCDF Bank 1 sample, it shows that the concentration of GB on the carbon is 129 ppb (see Table 4-4). Early results indicate that the MDL is about 5 ppb, but this value has not yet been validated.[10]

TABLE 4-4 Analysis of GB and VX on Carbon and Method Detection Limits (MDLs)[a]

Agent	Type of Carbon Sample	Analytical Method	MDL (ppb)	Agent Detected (ppb)
GB[b]	IMPA- and HF-loaded new, unused carbon	SwRI modified extraction method 3571 (being validated)	5 (SwRI) 4 (ECBC)	—
	ANCDF Bank 1, standard carbon batch	Same as above	—	129
VX	New, unused carbon	SwRI extraction method 3571 for VX for ANCDF	4	—
	ANCDF Bank 1 carbon	Same as above	—	17
	New, unused carbon	SwRI extraction method 3571 for VX for NECDF	14[c]	—
	NECDF Bank 1 carbon	Same as above	—	80

[a] No MDL for mustard on carbon had been established at the time this report was prepared.

[b] The new, unused, loaded carbon was spiked with GB.

[c] A different carbon mass was used for the NECDF MDL determination.

SOURCE: Personal communication between Michael MacNaughton, SwRI, and Robert Beaudet, committee chair, January 15, 2009.

Other methods could be investigated to determine the concentration of agents on carbon if the extraction method cannot be validated to show acceptable recovery of agent. However, direct methods involving measuring concentrations in the adsorbed phase are not sensitive to low levels of agent. Indirect methods involving the removal of the adsorbates from the carbon and analyzing them separately could be investigated: These include chromatography, solid-liquid extraction, or thermal/vacuum desorption (LeVan and Carta, 2007). Of the chromatographic methods—specifically, elution and displacement chromatography—displacement

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[10] Matthew Blais, SwRI, "Carbon analysis for GB," Presentation to Robert Beaudet and Yu Chu Yang, committee members, January 13, 2008.

chromatography would provide the most conclusive measurement of total residual agent. In displacement chromatography, a sample of the exposed carbon could be placed in a small column, probably after grinding, and a strongly adsorbed solvent (the "displacer") passed through the column. The displacer is adsorbed more strongly than any of the adsorbed agent and will displace the agent from the carbon, so that the entire adsorbed phase (all desorbed agent plus some of the displacer solvent) is eluted from the column. A liquid chromatography apparatus can be used for this purpose to provide the desired low flow rates. The extract from the column (adsorbates plus displacer solvent) could be analyzed to determine the agent concentration on the exposed carbon. This can be done either temporally during the chromatographic displacement process by measuring time-dependent concentrations as the agent is eluted, provided that the detector is sufficiently sensitive, or it can be performed on aliquot portions of the extract (or on the entire extract) after completion of the process. Thus, with the measured agent effluent concentration passing through a maximum and declining to zero, it can be determined positively by displacement chromatography that the agent has been entirely removed from the exposed carbon.

Another alternative for indirect analysis, solid-liquid extraction (also referred to as leaching), requires careful application. As with liquid-liquid extraction, the process would normally be performed with multiple contacts in a batchwise mode to make sure that essentially all residual agent has been extracted from the carbon for analysis. As with displacement chromatography, the best solvent would be one that is adsorbed more strongly than the adsorbates, so that essentially the entire adsorbed phase is removed efficiently in no more than a few batches. Thermal desorption is another indirect method, one that has been used by ECBC as mentioned above. However, heating a sample may cause thermal decomposition, and a method using a vacuum and capture in liquid nitrogen may prove more promising.

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5

Commercial and Industrial Practices for Activated Carbon Management

COMMERCIAL AND INDUSTRIAL USE OF ACTIVATED CARBON

Overview

Activated carbon finds extensive use as an adsorbent for the removal of a wide range of contaminants from liquids and gases. It is also used to adsorb a product, such as a solvent, from a process stream, with the adsorbed product being subsequently desorbed on-site for reuse. This last step, known as "carbon regeneration," differs from "carbon reactivation," which is a treatment process whereby adsorbed materials (adsorbates) on the carbon are destroyed and the structure of the activated carbon is restored for reuse. The term "spent carbon" is commonly used in commercial and industrial applications to denote used carbon whose adsorptive performance has diminished to the point that it can no longer be used for its intended application without reactivation.[1]

Demand for activated carbon in the United States was 363 million pounds in 2005, split approximately equally between granulated activated carbon (GAC) and powdered activated carbon (PAC). About 173 million pounds of activated carbon was produced domestically; the remainder was imported. Demand grew at an average annual rate of 1.3 percent from 2000 to 2005. Annual growth of 2.3 percent is expected through 2009.

Liquid-phase applications greatly exceed gas-phase applications. The three largest liquid-phase applications are treatment of potable water (37 percent), treatment of wastewater (21 percent), and decolorization of sugar (10 percent). The three largest gas-phase applications are air purification (40 percent), automotive emission control (21 percent), and solvent vapor recovery (12 percent). The three largest producers of activated carbon in the United States are Calgon Carbon, MeadWestvaco, and Norit Americas (Kirschner, 2006).

Mercury Removal as an Emerging Market for Activated Carbon

In 2005, the U.S. Environmental Protection Agency issued the Clean Air Mercury Rule, which proposed to extend emissions limits for mercury beyond municipal waste incinerators (MWIs) to fossil-fueled power plants. Because coal contains roughly two orders of magnitude more mercury than petroleum (Linak et al., 2000), the Clean Air Mercury Rule affected mainly coal-fired power plants, which account for slightly less than half of the stationary electric generating capacity

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[1] Although sometimes used in the context of chemical agent demilitarization operations, the term "spent carbon" has not been used in this report to refer to the degree of adsorption of chemical agents on carbon because the adsorptive capacities of the various agent-exposed carbon sources under consideration have not necessarily been exhausted. Moreover, agents are not the only materials that are adsorbed on the carbon used at chemical agent disposal facilities, and these other materials could possibly make the carbon "spent" in the sense used in commercial applications. For these reasons, and to avoid confusion, this report has instead used the terms "exposed" or "unexposed" to distinguish carbon that has "seen" chemical agent at least once from carbon that has never been exposed to agent but may contain other contaminants.

in the United States.[2] Although the experience of MWI operators was initially expected to be instructive in controlling mercury emissions at power plants, dozens of demonstration tests have shown that controlling mercury emissions from coal-fired power plants is both more difficult and more complex than had been expected. Mercury concentrations resulting from coal combustion are several orders of magnitude lower than those typical of MWIs. Whereas MWIs typically inject PAC into a fabric filter to form a fixed sorbent bed, 90 percent of power plants operate without such filters (Brown et al., 1999) and instead seek to adsorb the mercury on PAC suspended within the flue gas. Coal combustion produces different species of mercury in proportions that vary by type of coal burned and the configuration of the power plant. Each mercury species exhibits different adsorption kinetics on activated carbon, kinetics that can be enhanced or inhibited by the other species present in the flue gas. For this and other reasons, the control of mercury emissions from power plants by the use of activated carbon is an area of active research.

Activated carbon has been used for several decades to treat the gaseous products of combustion resulting from medical and municipal waste incineration facilities (collectively termed MWIs). These MWIs use activated carbon to adsorb volatile heavy metals such as mercury that survive the combustion process and are present in the waste stream as well as unwanted combustion products such as dioxins and furans that may be formed in the postcombustion region of an incinerator. In MWI applications, flue gas treatment with activated carbon most often occurs in conjunction with a fabric filter (baghouse). The filter material may be constructed from fibers embedded with PAC or may be continuously injected into the flue gas upstream of the baghouse, forming a sorbent bed on the filter that grows over time until it is dislodged during periodic baghouse cleaning. In either case, the physical configuration can be described as a fixed sorbent bed in which long exposure times of the sorbent to the waste stream result in the near-complete utilization of the adsorptive capacity of the carbon.

Disposal issues for spent PAC at power plants are largely overshadowed by the disposal issues associated with residual fly ash. PAC used to control mercury emissions ends up mixed with much larger quantities of fly ash. Because the concentration of PAC in the admixture as well as the concentrations of mercury on the PAC are low, overall concentrations of mercury in the admixture do not prohibit disposal in a landfill. Tests conducted on the fly ash-PAC mixture have shown that leaching of the mercury once deposited in a landfill is not an issue (Gustin and Ladwig, 2004; Senior et al., 2004; Wang et al., 2007). Some power plants can also sell their fly ash as a replacement for portland cement in concrete, although they must limit the PAC content. These factors all contribute to the conclusion that the disposal of activated carbon by the electric power industry offers little useful insight for the disposal of used activated carbon from the destruction of mercury-contaminated mustard agent (which is described in Chapter 6).

TREATMENT AND DISPOSAL OF ACTIVATED CARBON FROM COMMERCIAL AND INDUSTRIAL APPLICATIONS

There are essentially three commercial treatment/disposal methods for the spent activated carbon resulting from its commercial and industrial use:

- Reactivation,
- Landfill, and
- Incineration.

Figure 5-1 summarizes the choices for disposition of the approximately equal amounts of GAC and PAC used in commercial and industrial applications. Of the spent GAC generated from industrial and commercial use, approximately 10 percent is hazardous and 90 percent is nonhazardous. Ninety percent of hazardous GAC is disposed of by reactivation, 7 percent by incineration, and 3 percent in landfill; the reactivation is done entirely off-site at Resource Conservation and Recovery Act (RCRA) permitted facilities. Disposition of the nonhazardous GAC is 66 percent by reactivation, 7 percent by incineration or thermal destruction at cement kilns or waste-to-energy plants, and 27 percent by landfill. Of the nonhazardous GAC that is reactivated, approximately 40 percent is reactivated on-site by sweetener manufacturers like Cargill and Archer Daniels Midland Company, and the remainder is reactivated off-site. Spent wood-based GAC, used in automotive applications, is not well suited to reactivation and is mainly sent to landfills.

Spent PAC cannot be reactivated. About 5 percent of

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[2] For additional information, see the Energy Information Agency Web site at http://www.eia.doe.gov/kids/energyfacts/sources/electricity.html#Generation. Last accessed March 25, 2009.

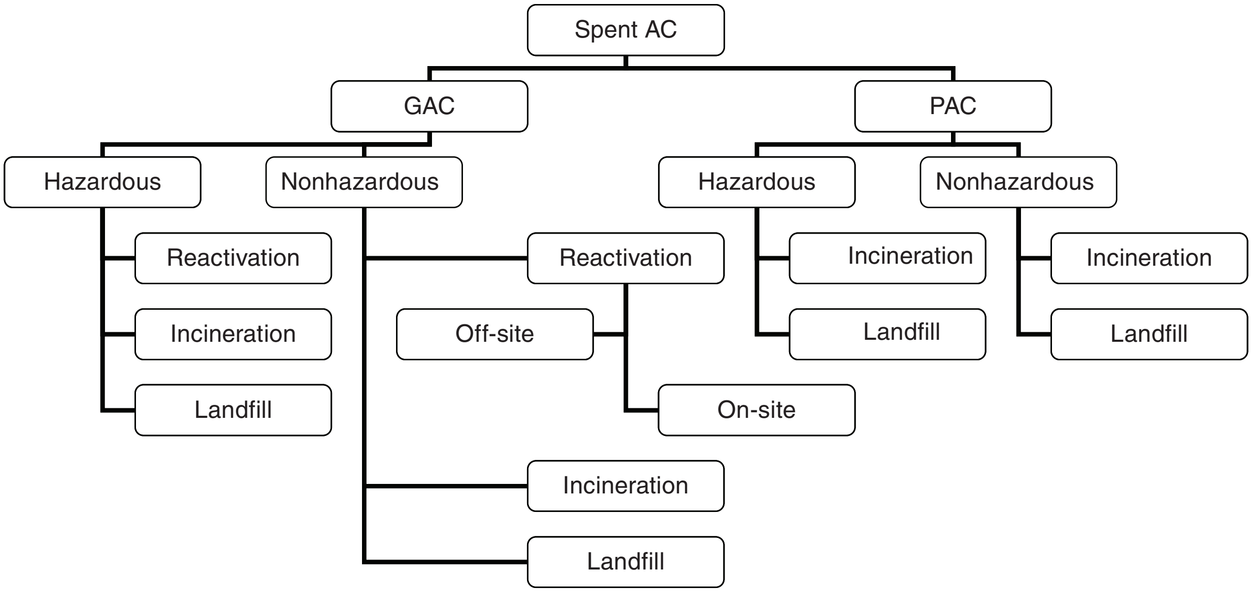

FIGURE 5-1 General schematic of the fate of spent activated carbon from commercial and industrial sources.

it is hazardous (it comes mainly from the pharmaceutical industry) and is incinerated. The other 95 percent is nonhazardous and goes to landfills.

Figure 5-2 is a schematic diagram for carbon reactivation, which is carried out in either a rotary kiln or a multiple hearth furnace. As the carbon travels through the furnace, water and other solvents evaporate, volatile halides and hydrocarbons vaporize, and other impurities are destroyed by calcination or pyrolysis. The calcined product is reactivated by steam gasification at around 1800°F (980°C). The process is carried out in a low-oxygen environment consisting of flue gas and steam. Offgases go through an afterburner and a scrubber prior to discharge to the atmosphere. Approximately 10-15 percent of the carbon is lost through oxidation during reactivation.

Appendix A provides tabulated criteria from Calgon Carbon Corporation for determining if used GAC is suitable for reactivation. It is noteworthy that Calgon does not accept material contaminated with mercury at any concentration and has limits on the acceptable concentration of sulfur. If Calgon accepts a material for reactivation, the company will, on request, pick it up from the site of generation and assume responsibility and liability for the reactivated product. If Calgon rejects a material for reactivation, the company will assist the generator in finding an alternative method of disposition, but liability remains with the generator.

Companies other than Calgon Carbon Corporation that provide reactivation services include Norit Americas; Westates Carbon, a division of Siemens Water; and Cameron Carbon. These vendors offer two options. One is to return the reactivated material to the generator. The other is to combine it with the reactivated carbon from other sources for reuse or resale. Of the hazardous spent carbon reactivated off-site,

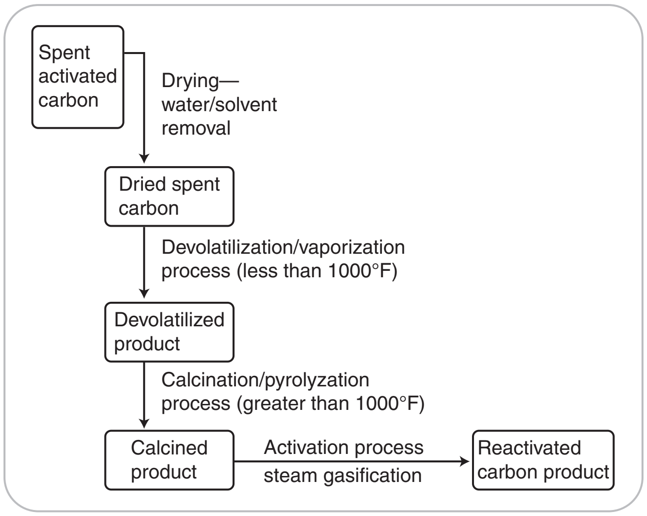

FIGURE 5-2 Calgon Carbon's process for reactivation of spent carbon.

approximately 80 percent is released for resale and the vendor assumes all subsequent liability. Reactivation is attractive principally because it is less costly than disposal and/or the purchase of freshly made activated carbon.

Landfilling is less expensive than incineration and is the preferred option if the carbon is not suitable for reactivation. However, the contaminants adsorbed on the carbon can leach out, and the generator can be expected to retain liability for the landfill operation. Permitted hazardous waste landfills suitable for disposal of spent activated carbon include several operated by Clean Harbors, Waste Management Inc., and American Ecology.

Incineration is the most expensive of the three options but the one with the least potential liability. At least two commercial hazardous waste incinerators, Clean Harbors in Aragonite, Utah, and Veolia in Port Arthur, Texas, are permitted to burn spent activated carbon and have experience in doing so. Permits might be required to handle activated carbon contaminated with the agent by-products discussed in Chapter 4, although there is no question that they would be destroyed by incineration. The agent by-products are similar to those in the hydrolysate from Newport that are being burned successfully at Veolia's incinerator in Port Arthur, Texas.

Finding 5-1. Reactivation is an attractive alternative to landfilling or incineration for disposing of unexposed carbon if the carbon reactivation contractor accepts liability for subsequent use and disposal.

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6

Use and Disposal of Sulfur-Impregnated Carbon for Mercury Adsorption

As noted in Chapter 2, the pollution abatement system (PAS) filtration systems (PFSs) for the process gas streams from the liquid incinerators (LICs), metal parts furnace (MPF), and deactivation furnace system (DFS) at the Anniston, Pine Bluff, and Umatilla Chemical Agent Disposal Facilities (ANCDF, PBCDF, and UMCDF) were added to reassure the public that residual agent would not escape from the incineration pollution abatement systems. A PFS was not included at the Johnston Atoll Chemical Agent Disposal System, but one was being added at the Tooele Chemical Agent Disposal Facility (TOCDF) to control mercury as this report was being prepared.

When mercury was discovered in the mustard agent HD/HT ton containers at TOCDF, PBCDF, and UMCDF, the U.S. Army's Chemical Materials Agency (CMA) was required to develop a strategy to control the emission of mercury during the incineration of HD/HT. Unlike the agent, mercury is not destroyed in the LIC, MPF, or DFS or their associated PAS units but persists in one form or another throughout these processes. CMA has concluded that using sulfur-impregnated activated carbon in the PFS during HD/HT processing is an effective method of controlling mercury emissions during the processing of mercury-contaminated HD/HT. Mercury adsorption by sulfur-impregnated carbon has been studied extensively (Liu et al., 1998; Hsi et al., 1998; Karatz et al., 2000; Dsi et al., 2001; Jurng et al., 2002; Kilgroe and Senior, 2003; Feng et al., 2006; Uddin et al., 2008). Tests of mercury adsorption from simulated coal combustion flue gases indicate that sulfur-impregnated carbon is able to capture about 2.5 mg metallic mercury per gram carbon and about 1.5 mg of $HgCl_2$ per gram carbon (Hsi et al., 1998).

At UMCDF, ANCDF, and PBCDF, the existing activated carbon beds in the PFS units will be replaced with sulfur-impregnated carbon before HD/HT processing. At TOCDF, a PFS with sulfur-impregnated carbon is being installed before the remaining mustard ton containers and munitions are destroyed. The configuration of the PFS units at UMCDF, ANCDF, and PBCDF is identical. The TOCDF PFS is different from a design perspective.

The expected presence of mercury in the sulfur-impregnated carbon beds poses a new issue for disposal of activated carbon from chemical agent disposal facilities.

KNOWN CHARACTERISTICS OF MUSTARD AGENT STOCKPILES

The HD/HT stockpiles contain bulk storage ton containers and munitions; all of the HD ton containers have been found to contain some mercury, although the amount varies. The semisolid heels of mustard agent at TOCDF are the largest sources of mercury-contaminated mustard agent.

All 6,398 HD/HT ton containers at TOCDF have now been sampled, and some sampling has also been conducted at PBCDF. At TOCDF, 906 (13.5 percent) of the containers registered mercury concentrations in the liquid agent that were above the practical quantification limit and 1,602 had high amounts of solids (heels).[1] At the time this report was prepared, the committee had no definitive information on the mercury content in mustard agent munitions.

Fewer samples have been taken of the heels than of the liquid-phase agent. In general, despite significant scatter in the data, high concentrations of mercury in liquid-phase agent suggest even higher mercury concentrations in the accompanying heel. When the amount of the mercury in the heels of 96 ton containers was measured, 18 of them averaged mercury levels of 2,440 mg/kg (2,440 parts per million (ppm_w)), while the average concentration of mercury in liquid-phase agent was 22 ppm_w. CMA believes that many munitions and ton containers contain some heel (UDEQ, 2008). Based on historical documentation, the mercury contamination in ton containers at UMCDF should be similar to that at TOCDF. Information on the mercury content of munitions at UMCDF as well as HD/HT stockpiles at ANCDF and PBCDF was not available when this report was being prepared.

Destruction of the heel portion of HD/HT requires special processing because it is generally too viscous to be extracted from the containers or munitions by simply pumping or draining. Also, early test burns of containers with large heels revealed that boiling over of the contents was a problem.[2] TOCDF is permitted to destroy ton containers holding up to 632 lb heel in the MPF, but it has set a more conservative upper limit of 550 lb per container.[3] Also, it has developed a special procedure for handling ton containers with heels exceeding this limit—namely, it mobilizes and dissolves the heel by flushing with jets of hot water. Then the rinsate is transferred to empty ton containers, which are treated in the MPF. This flushing process completely dissolves the heel. UMCDF is adopting the same processes to identify and flush ton containers having a high content of heel and to transfer the resultant rinsate into transfer ton containers.

FATE OF MERCURY WITHIN THERMAL DESTRUCTION PROCESSES AT CHEMICAL AGENT DISPOSAL FACILITIES

Given the diverse uses of activated carbon at chemical agent disposal facilities and the focus of this report on disposal options for activated carbon from these facilities, it is important to understand that the adsorption of mercury and the adsorption of agent onto activated carbons occur in physically different carbon filter units in separate locations during HD/HT thermal destruction. There is virtually no opportunity for both mercury and agent to be adsorbed onto the same carbon bed during normal operations at chemical agent disposal facilities.

As shown in Table 2-1, activated carbon is expected to be exposed to agent when the latter volatilizes into the ambient air during disassembly and preprocessing of munitions and ton containers in Level A areas. This contaminated air flows through the heating, ventilation, and air conditioning (HVAC) systems of the munitions demilitarization building (MDB) to the HVAC filter units, where the agent is captured.

However, no mercury is expected in the MDB HVAC air. Although the ton containers will be opened to the atmosphere in the MDB rooms, the volatilization of elemental mercury will be negligible. The tendency of a liquid to evaporate at a specified temperature depends on its vapor pressure at that temperature. The vapor pressure of elemental mercury is 2.47×10^{-4} kPa at 27°C. Any mercury salts would be insoluble or ionized in solution. Thus, the low vapor pressure of elemental mercury and the nonvolatility of ionic mercury salts in solution virtually eliminate the possibility that the MDB HVAC air would contain mercury in concentrations of any significance with respect to human health and safety, nor would the activated carbon in the MDB HVAC system filters be exposed to mercury over the duration of the mustard agent disposal campaign to an extent that would be of regulatory concern with respect to mercury.

No agent is expected to be found on the PFS carbons because in normal operation, the two-stage design of the LIC, MPF, and DFS provides a more than sufficient time-temperature history for the constituent elements of mustard agent—hydrogen, carbon, sulfur, and chlorine—to be fully converted to common gaseous combustion products such as HCl, SO_x, NO_x, H_2O, and CO_2. Because HCl and SO_2 are soluble in aqueous solu-

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[1] Personal communication between Gary McCloskey, TOCDF General Manager, URS Corporation, EG&G Division, and Robert Beaudet, committee chair, March 4, 2009.

[2] Information gathered from committee site visit to TOCDF, September 4, 2008.

[3] Information gathered from committee site visit to TOCDF, September 4, 2008.

tions, they are efficiently removed by the wet venturi and tower scrubbers in the PAS (see Chapter 1, Figure 1-1). The PAS does not offer any control of NO_x, and trial burns to destroy HD/HT in the MPF at TOCDF have demonstrated NO_x concentrations on the order of 30 ppm.[4]

The exposure of activated carbon to mercury is expected to occur exclusively in the PFS units. PFS carbon beds at the disposal facilities are situated downstream of the PAS units for the LIC, MPF, and DFS and will not be exposed to any agent under normal operation. Furthermore, because the PFS carbon beds are situated downstream of the wet scrubbing processes in the PAS, trace concentrations of water-soluble compounds are found in the gas phase; however, no water-insoluble products of agent thermal destruction (e.g., CO_2) and contaminant thermal oxidation (e.g., Hg^0) would be found.

If an upset were to occur (unlikely) and agent were to pass through the incinerator's PAS, then both agent and mercury would be present on the carbon. This would pose a problem, because regulations might not allow the carbon to be shipped to a TSDF, and the TSDF might not accept waste containing both agent and mercury. Then, the mercury or the agent would have to be separated from the carbon.

Finding 6-1a. Carbons exposed to agent will not be exposed to mercury in the gas streams handled by the heating, ventilation, and air conditioning system of the munitions demilitarization building. No agent will be present in the gas streams handled by the pollution abatement system filtration system under normal operating conditions.

Finding 6-1b. When mercury-containing mustard agent HD/HT is being destroyed, no agent will be present in the gas streams exiting the pollution abatement system units for the liquid incinerator, deactivation furnace system, and metal parts furnace. However, mercury will be present, so the Army is installing sulfur-impregnated carbon in the pollution abatement system filtration system to capture it.

Recommendation 6-1a. The pollution abatement system filtration system sulfur-impregnated carbon containing mercury should be disposed of separately from other activated carbons used at chemical agent disposal facilities. If generator knowledge confirms that mercury-containing carbon has not been exposed to agent, it should be shipped off-site for disposal in compliance with existing regulations governing mercury-containing solid wastes.

Recommendation 6-1b. In the unlikely event that an operational upset were to cause both mercury and agent to be deposited on the sulfur-impregnated carbon of the pollution abatement system filtration system, the permit might not allow shipping the carbon off-site for disposal, even if sufficient time had elapsed for agent on the carbon to degrade. In this case, fresh carbon should be installed in the pollution abatement system filtration system. The agent- and mercury-contaminated carbon should be processed through the metal parts furnace, thereby destroying the agent and transferring the mercury to the fresh (agent-free) carbon of the pollution abatement system filtration system. This mercury-containing carbon, no longer having agent, could then be shipped off-site for disposal.

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[4] Information gathered from committee site visit to TOCDF, September 4, 2008.

7

Disposal of Carbon from Chemical Agent Disposal Facilities

The preceding chapters of this report have indicated the sources, amounts, and properties of activated carbon; described how it is actually used and managed at chemical agent disposal facilities and other industrial operations; and discussed the chemical fate of the agents on the carbon. This chapter addresses disposal options for all of the used carbon (exposed and unexposed) from chemical agent disposal facilities, including methods that have been used or proposed by both closed and operating chemical agent disposal facilities. It also assesses the type of scientific support required for the disposal facilities to obtain regulatory approvals.

The central theme of this report is that the used activated carbon from chemical agent disposal facilities can be assigned to one of two categories: (1) carbon that has been exposed to chemical agent(s) in the course of its utilization ("exposed carbon") and (2) carbon that has not been so exposed ("unexposed carbon"). Analyses performed on samples of exposed carbon have confirmed that contamination with agents decreases over time because the agents react with the moisture adsorbed on the carbon and form degradation products via hydrolysis. However, the analytical evidence suggests that a small, parts-per-billion level of agent may always remain on the carbon after normally expected storage times following removal from service and storage.

PAST EXPERIENCE WITH DISPOSAL OF USED ACTIVATED CARBON

The first integrated chemical agent disposal facility was the Johnston Atoll Chemical Agent Disposal System (JACADS), which used incineration technology and completed 10 years of disposal operations in 2000. In 2005, the Aberdeen Chemical Agent Disposal Facility (ABCDF), which used neutralization technology to destroy agent, was the first integrated disposal facility in the continental United States to complete agent disposal operations. JACADS and ABCDF have already disposed of their entire inventory of used carbon by incineration, the former on-site and the latter off-site. The Newport Chemical Agent Disposal Facility (NECDF), another facility that used neutralization, completed agent disposal operations in 2008. It had a regulatory permit allowing shipment of all of its exposed carbon as a listed secondary waste to a qualified treatment, storage, and disposal facility (TSDF) for incineration. NECDF was in the process of shipping its exposed carbon off-site as this report was being prepared. It has also shipped approximately 220,000 lb unexposed carbon to Calgon Carbon Corporation for reactivation and resale. The determination that this carbon had not been exposed to agent was based on generator knowledge. Further details of these disposal activities and their relevance to future carbon disposal at other facilities are provided below.

Incineration of Used Carbon at JACADS

The closure plan for JACADS required that all used carbon be incinerated on-site. This was accomplished by a process known as carbon micronization. The used carbon was first pulverized to a fine powder in a carbon micronization system (CMS) and then blown into the deactivation furnace system, where it was incinerated.

The experience was summarized as follows (NRC, 2007, p. 60):

> The micronization process proved difficult to operate, and throughputs were much lower than expected. In addition, while being transported in pipes from the micronizer to the deactivation furnace system, the resulting powder could under some circumstances become an explosive mixture. Fortunately, no explosive event happened at JACADS, but the possibility is real and must be considered. A prudent course now would be for the Chemical Materials Agency to immediately pursue alternative disposal options for treating spent activated carbon resulting from current operations as well as for the large amounts of spent activated carbon that will [be] generated during closure operations.

On p. 45 the same report stated that "depending on the organic contaminants adsorbed, spent carbon may be classified as hazardous or nonhazardous." In this context, "spent carbon" is a more generalized term than "exposed carbon" because it refers to activated carbon that has been exposed either to agent or to other airborne contaminants.

The JACADS experience demonstrated that activated carbon exposed to agent can be incinerated. As well as oxidizing the carbon, this process destroys any agent that may be present. However, use of the micronization process to prepare the carbon for incineration created an explosion hazard associated with the handling of the finely divided carbon. The carbon dust also created operational problems that extended JACADS' operating time and necessitated additional maintenance. Also, CMS processing required many demilitarization protective ensemble (DPE) entries by personnel to conduct maintenance operations. At times, CMS maintenance operations accounted for 85 percent of DPE entries, which increased the risk to personnel and created additional secondary waste for disposal. Used DPE suits were a major source of secondary waste. This had a direct impact on closure decontamination operations and schedule.

Finding 7-1. The micronization of carbon before it is incinerated in the deactivation furnace system is a hazardous operation with operational problems and a lot of maintenance. Fine pulverized carbon is susceptible to dust explosions.

Recommendation 7-1. If a chemical agent disposal facility must dispose of any carbon on-site, micronization should not be used to prepare the carbon for incineration.

Disposal of Used Carbon at ABCDF

At ABCDF, after their removal from service, the used carbon filters were double bagged in polyethylene. The vapor space in the bag was then sampled for agent. Bags with >1 vapor screening level (VSL)[1] agent levels of mustard agent HD were placed in 95-gallon polyethylene drums and shipped by truck to the Veolia Environmental Services Facility in Port Arthur, Texas, where the used carbon was incinerated without opening the drums. There were 482 drums with >1 VSL contamination.

The remaining filter trays from the heating, ventilation, and air conditioning (HVAC) Banks 2 through 6 were placed in bags and shipped without drumming since they had agent levels <1 VSL. The total weight of carbon filters with <1 VSL contamination was 94,720 lb.

Since the polyethylene drums and bagged filters were not to be opened before being fed to a rotary kiln and incinerated at the Veolia facility, the metal filter frames became part of the kiln discharge solid residue. Kiln flue gases were processed through the Veolia facility's gas scrubbing system. Carbon at ABCDF was contaminated only with mustard agent HD, with the worst-case loading of HD estimated to be 16 weight percent, the HD saturation level.[2] The waste was transported based on a transportation risk assessment (TRA).

Finding 7-2. The use of a transportation risk assessment provides a methodology to assist the permitting regulatory authority in making a determination of whether the proposed method of shipment is safe.

Recommendation 7-2. The Chemical Materials Agency should explore with the appropriate regulatory

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[1] Vapor screening levels (VSLs) and short-term limits (STLs) are names for equivalent measurements (specified in RCRA operating permits) for control limits used to help plan for waste transport and disposal. They also supplement short-term exposure limits (STELs) for protecting workers' health during plant operations as waste is generated and moved to storage areas within the plant. VSL/STL concentrations vary by agent and are the same values as STELs except that VSL is measured in air sampled for about 5 minutes instead of 15 minutes for STELs. For GB, VX, and HD, 1 VSL is equivalent to 0.0001 mg/m^3, 0.00001 mg/m^3, and 0.003 mg/m^3, respectively.

[2] Brian O'Donnell, Chief, Secondary Waste and Closure Team, CMA, "CMA carbon management," Presentation to the committee, June 4, 2008.

authorities the use of a transportation risk assessment as a method of permitting the transportation of exposed carbon for off-site disposal.

Disposal of Used Carbon at NECDF

The NECDF permit had no requirement for sampling or analyzing the used carbon before its shipment to an off-site TSDF. NECDF managed the carbon, which had been exposed to the nerve agent VX, as a designated hazardous waste and shipped it off-site to Veolia for incineration using this permit. Bank 1 carbon from the NECDF HVAC filter units was analyzed by the extractive method and found to contain less than 95 ppb of VX. The Bank 2 carbon would have even less contamination. Based on generator knowledge, carbon from Banks 3 through 6 had not been exposed to agent.

Approximately 70,000 lb of carbon that had been exposed to VX was shipped to Veolia during closure of NECDF. A TRA had been prepared in July 2008 for the shipment of VX-exposed carbon to Veolia. All of the documentation to meet National Environmental Policy Act requirements for the shipments was completed, and the Indiana Department of Environmental Management and the Centers for Disease Control were informed of the planned shipments. The TRA was based on concentrations determined for Bank 1 HVAC filter trays (the most heavily contaminated trays).[3] As of August 2008, NECDF had 792 polyethylene drums containing carbon filters in bags ready for shipment. In September 2008, all drums containing exposed carbon filters had been shipped to the Veolia facility for incineration.[4] NECDF has already shipped approximately 220,000 lb of used unexposed carbon from Banks 3 through 6 of the HVAC filter units to Calgon Carbon Corporation for reactivation. Generator knowledge confirmed that this carbon had not been exposed to VX. The used (unexposed) carbon from Banks 3 through 6 also met Calgon's acceptance criteria for physical condition and amount of other contaminants. The reactivated carbon was stored at Calgon pending a decision for its final disposition. The Chemical Materials Agency (CMA) obtained permission from the Army Material Command to allow Calgon to sell the reactivated carbon on the open market for nonfood use. Calgon assumes any liability.

Finding 7-3. Used carbon that qualifies as unexposed to agent based on generator knowledge can be reactivated at a commercial carbon activation facility if it meets the reactivation contractor's requirements for physical condition and chemical contamination.

Recommendation 7-3. The Chemical Materials Agency should consider the reactivation and sale of unexposed used carbon on the open market provided that the Army's liability terminates with transfer of the carbon to the reactivation contractor.

On-site Disposal of Exposed Carbon at Operating Disposal Facilities

Treatment in the Metal Parts Furnace

At the Anniston, Pine Bluff, and Umatilla Chemical Agent Disposal Facilities (ANCDF, PBCDF, and UMCDF respectively), operating permits allow thermal treatment of exposed carbon (1000°F for at least 15 minutes) in the metal parts furnace (MPF). However, while this is an accepted decontamination procedure used for steel munition bodies and certain other secondary wastes, it results in smoldering carbon. At present, only the small amounts of carbon from the filter units of the agent collection system (ACS) vent line and M-40 protective mask canisters are treated in the MPF. These filter trays are placed in waste incineration containers that are fed to the MPF. Since the carbon would not be completely oxidized at the end of normal thermal treatment, processing times were established for achieving complete oxidation of carbon during the UMCDF ACS Filter Processing Evaluation—namely, 90 minutes in Zone 1 of the MPF, 90 minutes in Zone 2, and 1,260 minutes in Zone 3, for a total of 24 hours.[5] The material exiting the MPF is agent-free metal and ash. The amount of used carbon that can be processed in the MPF in this manner is limited by overall facility scheduling because the primary function of the MPF

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[3] Brian O'Donnell, Chief, Secondary Waste and Closure Team, CMA, "NECDF carbon shipment decision," Presentation to the committee, July 24, 2008.

[4] Timothy Garrett, Site Project Manager, ANCDF, "CMA's efforts on carbon management disposal," Presentation to the Committee on Chemical Demilitarization, September 17, 2008.

[5] Robie Jackson, Waste Management Manager, ANCDF, and Tracy Smith, Trial Burn Manager, ANCDF, "The use of carbon at ANCDF," Presentation to the committee, June 5, 2008.

is to thermally treat the casings and other metal parts from munition disassembly.

Some additional heavily exposed carbon filters could be processed in the MPF without adversely impacting the throughput rate for treating munition casings and the like during operations or during plant closure, but processing all the Bank 1 and Bank 2 filter units of the HVAC filter units in the MPF would seriously delay the overall operating schedules of the disposal facilities.

Finding 7-4. On-site thermal treatment in the metal parts furnace has been demonstrated to be a satisfactory method for disposing of exposed carbon and is being used at some chemical agent disposal facilities. However, the residence time must be sufficient to fully oxidize the carbon or prevent smoldering. The solid metallic filter trays and ash that remain afterward can be disposed of with other thermally decontaminated secondary waste.

Recommendation 7-4. Although carbon can be successfully treated in the metal parts furnace, on-site disposal treatment of exposed carbon in the metal parts furnace should be limited to small quantities of exposed carbon—from, for example, agent collection system filter units and M-40 protective mask canisters—because the time required to completely oxidize all of the exposed carbon generated at a chemical agent disposal facility would seriously extend the disposal operations schedule of the metal parts furnace and closure of the disposal facility as a whole.

Treatment in Autoclaves

The Tooele Chemical Agent Disposal Facility (TOCDF) is planning to treat agent-exposed carbon in an autoclave at 305°F. The autoclave will use a high-pressure steam atmosphere to reduce agent concentrations on the carbon to levels suitable for shipment off-site to a permitted hazardous waste landfill. The steam also prevents the carbon from smoldering. Offgas from the autoclave will pass through an offgas treatment system to ensure that agent released during autoclave treatment will be destroyed before offgas is released to the atmosphere. The optimum autoclave operating conditions will be determined by demonstration testing. Results of any such testing were unavailable at the time this report was being prepared because the details of the autoclave process had not been completely developed. TOCDF has requested that its permit be modified to allow disposal of the treated carbon from the autoclave in a permitted hazardous waste landfill.

The operating principles for the autoclave are similar to those incorporated into the metal parts treater that will be used in the Blue Grass Chemical Agent Destruction Pilot Plant. The metal parts treater will use a steam atmosphere, but the temperature will be above 1000°F for more than 15 minutes to achieve an agent-free condition.

Finding 7-5. Autoclaving may be a satisfactory method of decontaminating exposed carbon, but its efficacy has not been demonstrated and the treated carbon may still contain agent in low concentrations.

Recommendation 7-5a. The use of dedicated autoclaves should be considered as an alternative means for treating large amounts of exposed used carbon to ready it for off-site shipment to a permitted hazardous waste disposal facility.

Recommendation 7-5b. The Chemical Materials Agency should review the planned sampling and analysis procedures for carbon that will be treated in the autoclave. This would ensure that they are appropriate for achieving the postautoclave processing condition of the carbon and that they can reliably measure agent concentrations at levels required by the permit for off-site shipment to a hazardous waste disposal facility.

CURRENT CMA CARBON MANAGEMENT STRATEGY

The CMA has proposed a carbon management strategy that uses on-site disposal of highly contaminated carbon in ACS vent filter trays and M-40 gas mask canisters. The strategy also states that all other exposed and unexposed carbon will be disposed of at a qualified TSDF, either by incineration or in a landfill. The feasibility of off-site disposal is decided by using approved sampling methods to determine the amount of agent contamination that is present on the carbon in each polyethylene shipping drum and comparing that amount to the amount allowed by a bounding TRA. A bounding TRA has been prepared and approved by the CMA for use on all agent-contaminated secondary waste shipments, including used carbon, having agent concentrations of >1 VSL. The committee did not assess the basis used for the bounding TRA since it was reviewed in prior National Research Council studies on secondary waste disposal and regulatory requirements (NRC, 2007, 2008). An addendum for carbon shipment is under development.

As noted earlier, CMA used a TRA to obtain state approval for the shipment of HD-exposed carbon from ABCDF and VX-exposed carbon from NECDF to the Veolia facility in Port Arthur, Texas. Use of a bounding TRA for carbon at other sites is expected to require acceptance by the state regulators for those sites and for each of the states through which the materials are proposed to be moved. However, the committee considers the use of a TRA to be an appropriate approach.

The bounding TRA specifies the maximum mass of a specific agent that may be held in a shipping container, the number of containers per shipment, and the total number of shipments in a given time. These values are set to limit general population risk to 1 acute exposure guideline level (AEGL).[6] Table 7-1 summarizes the limits of agent mass per drum determined by CMA using this approach. The maximum concentration allowed on the exposed carbon can be calculated by accounting for the expected mass of carbon per drum (~50 lb). The values are given in the third column of Table 7-1. The last column provides the anticipated actual concentration on the carbon based on analyses that have already been performed at ANCDF and NECDF. Clearly, the nerve agent GB presents the highest risk for off-site transportation to a TSDF. GB at greater than 20 ppb could be transported off-site if the TRA is approved by state regulators and procedures are implemented to satisfy the risk assessment values. These values are a function of accidental release scenarios assumed in the assessment and the frequency established for such release scenarios.

TABLE 7-1 Agent Mass Limits per Drum for Off-site Shipment of Secondary Waste

Agent	Maximum Agent Mass per Drum[a] Allowable to Meet GPL of 1 AEGL (g)	Maximum Concentration of Agent on Carbon[b] per Drum to Meet 1 AEGL (ppb)	Anticipated Actual Concentration of Agent on Exposed Carbon per Drum (ppb)
GB	0.008	400	130[c]
VX	0.29	13,000	17[c]
HD	6.5	290,000	80[d]

[a] Applies to both 55-gallon and 95-gallon drums. Amounts based on analyses for residual agent on decontaminated secondary waste. GPL, general population limit.

[b] Assumes 48 lb of carbon per 95-gallon drum.

[c] Based on analysis of Bank 1 carbon at ANCDF.

[d] Based on NECDF carbon.

SOURCE: Adapted from Michael McNaughton, Southwest Research Institute "Analytical procedures for GB/VX carbon," Presentation to the committee, July 23, 2008; Brian O'Donnell, Chief, Secondary Waste, Closure Compliance and Assessments, CMA, "Transportation risk assessment," Presentation to the committee, July 24, 2008; site visit to Southwest Research Institute, January 14-15, 2009.

The application of the CMA's bounding TRA will necessitate sampling and analysis. Currently, CMA is working on an analytical method to clear exposed carbon for off-site shipment. There are at least two challenges to implementing this methodology:

- *Sampling.* CMA must validate a sampling technique to ensure that samples of exposed carbon are representative of the carbon in the shipping container. This includes representative sampling within a filter unit, selection of the filter tray(s) within a bank, and, for carbon previously placed in polyethylene drums, the selection of drums within a lot.
- *Analysis.* CMA must show that the extractive analysis procedure accurately measures the concentration of agent on the exposed carbon at the parts-per-billion level. The method must be acceptable to the state regulators.

All exposed carbon is contained in steel filter trays consisting of two layers of carbon, each held between metal screens (see Figures 2-3 and 2-4). Each layer

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[6] Acute exposure guideline levels (AEGLs) are a hazard communication measure developed by the National Advisory Committee to Establish Acute Exposure Guideline Levels for Hazardous Substances. The committee developed detailed guidelines for devising uniform, meaningful emergency response standards for the general public. The guidelines define three tiers of AEGLs as follows:

- *AEGL-1.* The airborne concentration of a substance above which it is predicted that the general population, including susceptible individuals, could experience notable discomfort, irritation, or certain asymptomatic nonsensory effects. However, the effects are not disabling and are transient and reversible upon cessation of exposure.
- *AEGL-2.* The airborne concentration of a substance above which it is predicted that the general population, including susceptible individuals, could experience irreversible or other serious, long-lasting adverse health effects or an impaired ability to escape.
- *AEGL-3.* The airborne concentration of a substance above which it is predicted that the general population, including susceptible individuals, could experience life-threatening health effects or death.

The guidelines for each level consider five exposure periods: 10 minutes, 30 minutes, 1 hour, 4 hours, and 8 hours (NRC, 2001).

is approximately 2 inches thick. Upon removal from service, these filter trays are double bagged in plastic and placed in a polyethylene drum, one tray per drum. The drums are then moved to a safe storage location awaiting final disposition either on-site or off-site.

Sampling for agent on the carbon in filter trays requires that the sampling personnel don DPE suits and open the drums in a Level A area.[7] The double-bagged filter tray must be pulled from the drum and removed from the plastic bags. The workers in DPE suits must then cut open the metal screen on one side of a carbon layer to obtain representative samples. The sharp edges that result from cutting the screen to access exposed carbon for sampling pose a threat to the integrity of the DPE suits worn by workers.

Finding 7-6. The sampling of used carbon in filter trays involves a number of steps that increase the risk that workers in demilitarization protective ensemble suits will be exposed to agent.

Recommendation 7-6a. A protocol that uses statistical sampling methods to minimize the number of filter trays to be sampled and analyzed should be developed to ensure that the samples obtained are representative and accurately satisfy the criteria of the transportation risk for off-site shipment of exposed carbon while also minimizing the risk of personnel being exposed to agent.

Recommendation 7-6b. To minimize the risk of sampling personnel exposure to agent, sampling methods should be developed that minimize the number of polyethylene drums that must be opened while accurately determining agent concentrations on stored carbon.

Finding 7-7. The Chemical Materials Agency carbon management strategy includes treatment of all of the agent collection system filter unit carbon and carbon from the M-40 protective mask canisters on-site because treatment of the small quantities involved will not disrupt or delay overall facility operations or closure. The exposed carbon from the agent collection system filters is highly contaminated with agent, making off-site treatment and disposal undesirable. For all other carbon, the CMA's strategy is to seek regulatory approval for off-site shipment to a qualified treatment, storage, and disposal facility.

Recommendation 7-7. A transportation risk assessment and a suitable sampling and analysis protocol for all exposed carbon other than that from the agent collection system filter units and the M-40 mask canisters should be used to allow the carbon to be sent off-site for disposal. This approach could expedite closure and minimize the number of operations required by workers in demilitarization protective ensemble suits, thereby reducing worker risk and adhering to the facility closure schedule.

ALTERNATIVE METHODS FOR DISPOSAL OF CARBON

This section describes alternative methods for treating and disposing of exposed and unexposed carbon.

Use of Decontamination Solution for Off-site Disposal of Exposed Carbon

The committee believes that adding caustic NaOH decontamination solution to drums containing exposed carbon offers an attractive method for safely shipping this material to a TSDF. Other agent-contaminated waste has been treated with caustic solution to decontaminate it before bagging and drumming for shipment to a qualified TSDF from ABCDF, ANCDF, and NECDF (NRC, 2007). The committee believes this method could also be used for off-site disposal of exposed carbon. However, there has been little experience with using caustic decontamination solution on exposed carbon.

A protocol and a procedure would have to be established to determine how much decontamination solution should be added and how to ensure adequate wetting of carbon surfaces to achieve decontamination to levels safe for shipment. While experimental data indicate that a pH of 7 completely hydrolyzes GB in solution, decontamination solution having a pH of 10 or more could compensate for any effect that the carbon may have on the reaction. One approach might be as follows: Inject sufficient decontamination solution into the double bags to cover and fully wet all of the carbon. The decontamination solution should be in direct contact with the carbon inside the bags. For the filters that have not yet been removed from the banks, addition of caustic solution directly into the bags would

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[7] A Level A area is one expected to be contaminated with agent and under engineering controls.

be a simple additional step in the bagging and storage operation.

This approach could eliminate the requirement for sampling and analysis to determine the mass of agent on the carbon and the risk of any agent being released during transportation. However, because it also increases the weight of the drums and reduces the heat content of the carbon, it would result in higher transportation and incineration costs.

Finding 7-8. The committee believes that decontamination solution could be applied to carbon that has been exposed to agent to enable shipment off-site to a treatment, storage, and disposal facility based on the precedent that other secondary waste, porous and nonporous, exposed to agent has been decontaminated by this procedure and shipped to a qualified treatment, storage, and disposal facility.

Recommendation 7-8. The Chemical Materials Agency should investigate adding decontamination solution to drums of carbon exposed to agent as a means to allow the carbon to be transported to a qualified treatment, storage, and disposal facility for final disposal. A protocol should be formulated for specifying the amount of decontamination solution to be added to the carbon. This would include determining whether the carbon must be fully immersed in the decontamination solution or only wetted by it, and whether using caustic solution with a pH at or above 10 will guarantee that the GB concentration is below the waste control limit. Such a method could eliminate the need to measure agent contamination on carbon before shipping it off-site.

Reactivation of Unexposed Carbon

Sending carbon to a vendor for reactivation, blending it with other sources of carbon, and reselling it offers a disposal alternative, possibly reducing disposal costs. As indicated in Chapter 2, approximately 80 percent of all of the used carbon that will be generated at the four incineration facilities will never have been exposed to agent.

As noted previously, Calgon Carbon Corporation has reactivated 220,000 lb of unexposed carbon from NECDF. This carbon was considered agent-free based on generator knowledge and is being resold on the open market by the vendor. Calgon representatives told committee members that the company's permits and policies would not allow it to accept for reactivation carbon that contains mercury or other chemical species in concentrations exceeding the company's acceptance criteria. Calgon will accept exposed carbon for reactivation provided that (1) agent concentrations are below current detection limits, (2) unexposed filter trays are separated from exposed filter trays, and (3) unexposed filter trays are accompanied by a letter stating there is no detectable agent present based on either generator knowledge or test results and identifying the filter trays that were tested. These constraints preclude reactivation of carbon with detectable levels of agent (see Chapter 4). Other carbon reactivation companies have similar criteria for agent and other chemical species.

While unexposed carbon from NECDF has been reactivated, experience reveals some remaining challenges for exposed carbon even if the agent has been completely degraded. First, the carbon must be shown to be free of agent prior to reactivation because these units are not currently permitted for processing carbon that contains detectable levels of agent. Second, there is no body of evidence on the fate of the decomposition products that remain on the carbon, although the reactivation process, carried out at approximately 850°C, will destroy them. The Army also does not want to retain liability for the reactivated carbon after it arrives at the vendor. The reactivation facility must assume liability for any issues resulting from reuse of the reactivated carbon.

Finding 7-9. Reactivation of unexposed carbon from chemical agent disposal facilities has been demonstrated by the experience at the Newport Chemical Agent Disposal Facility. The reactivation of exposed carbon may require some level of sampling and analysis that may not be cost-effective.

Recommendation 7-9. The Chemical Materials Agency should consider reactivation and resale as an option for the disposal of unexposed carbon. However, it should evaluate the costs and liabilities associated with reactivation and compare them with those for other disposal options.

GENERAL FINDINGS AND RECOMMENDATIONS

The committee concludes this report with the following general findings and recommendations, which summarize the specific findings and recommendations set forth throughout this report.

General Finding 1. About 80 percent of all the used activated carbon that has been or will be generated at the chemical agent disposal facilities operating under the Chemical Materials Agency has never been exposed to agent and can be treated as ordinary hazardous waste. This includes the carbon from Banks 3 to 6 of the heating, ventilation, and air conditioning filter units and the bulk carbon from the filter beds of the pollution abatement system filtration system.

General Recommendation 1. All unexposed carbon (as determined by generator knowledge) should be disposed of off-site as a hazardous waste without further chemical analysis for agent or sent for reactivation if a contractor will accept it and assume ownership and liability. The choice of disposal method and treatment, storage, and disposal facility will be dictated by whatever other contaminants are present on the carbon.

General Finding 2. Unless there is an unexpected upset resulting in contamination with agent, all of the sulfur-impregnated carbon that is to be used in the pollution abatement system filtration systems will not have been exposed to agent. Thus, based on generator knowledge, the carbon can be sent off-site without further analysis for chemical agents. This carbon can be treated as a hazardous waste contaminated with mercury.

General Recommendation 2. All of the sulfur-impregnated carbon used in the pollution abatement system filtration systems and not involved in an unexpected upset condition at a chemical agent disposal facility should be sent off-site. This carbon should be treated as a hazardous waste that is contaminated with mercury.

General Finding 3. Treatment of all of the exposed carbon on-site in the metal parts furnace would seriously delay the closure of the currently operating Chemical Materials Agency chemical agent disposal facilities.

General Recommendation 3. Only the carbon filter trays from the agent collection system tank vent lines and the canisters from the M-40 protective masks should be treated on-site in the metal parts furnace when the metal parts furnace is not performing its primary function of treating metal parts or other wastes.

General Finding 4. Nerve agents GB and VX and mustard agent HD have been shown to degrade on activated carbon to their usual hydrolysis products by reacting with the moisture adsorbed on the carbon. This occurs both while the carbon is in use and after, during storage. Of the known analytical results, the concentrations of VX that remain on carbon samples from heating, ventilation, and air conditioning Bank 1 at the Anniston Chemical Agent Disposal Facility appear to be below the waste control limits of 20 parts per billion. However, the remaining concentration of GB appears to be about 130 parts per billion, well above the waste control limit of 20 parts per billion. Thus, the carbon that has been exposed to GB cannot be sent off-site based on the waste control limits. The concentration of HD that remains on carbon filters had not been measured at the time this report was prepared.

General Recommendation 4. Carbon that has been exposed to agent should be sent off-site under one of the following arrangements:

- *Use of waste control limits or permit compliance concentrations.* If the agent concentrations on the exposed carbon are below the waste control limits or the permit compliance concentrations, the carbon can be shipped off-site for proper disposal at a waste treatment facility licensed to receive and treat this waste under existing regulations. For this arrangement it will be necessary to develop and validate analytical methods that accurately measure agent concentration for both GB and HD. The methods must be capable of analyzing the agents on carbon that has been exposed to all three agents and that will have both the agents and their respective degradation products from hydrolysis adsorbed on the carbon.
- *Use of a transportation risk assessment.* If the mass of the agent on the carbon in a drum is less than specified by the Chemical Materials Agency transportation risk assessment (see Table 7-1), the drum can be transported to a treatment, storage, and disposal facility. The transportation risk assessment requires determining the mass of each agent on the carbon by a validated analytical method. In addition, each chemical agent disposal facility will have to negotiate with the appropriate regulatory authorities and apply for a permit change to ship exposed carbon off-site

based on the transportation risk assessment and the validated analytical methods.

- *Adding caustic solution to the drums.* If the addition of caustic (NaOH) decontamination solution to a drum of exposed carbon completely wets the carbon, the caustic will hydrolyze the agents remaining on the exposed carbon to below the waste control limit (WCL) or permit compliance concentration (PCC). The drum containing the decontaminated carbon and decontamination solution can then be shipped off-site. The method of applying the decontamination solution must be negotiated and approved by the facility's regulatory authority. Analysis for agent on the carbon should not be necessary with this arrangement.

General Finding 5. Environmental Protection Agency Method 3571 appears to have provided an improved method detection limit for extractive analysis of VX on the Bank 1 carbon sample from the Anniston Chemical Agent Disposal Facility, but it must still be validated. Neither Environmental Protection Agency Method 3571 for HD nor modified Method 3571 for GB, which appears to minimize re-formation of GB during extraction and analysis, had been validated at the time this report was being prepared.

General Recommendation 5. Both the original Environmental Protection Agency Method 3571 and the modified Method 3571 must be validated for use on carbon exposed to all three agents (GB, VX, and mustard) since the chemical agent disposal facilities expect to operate without changing out the heating, ventilation, and air conditioning filter units before closure.

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Appendixes

Appendix A

Calgon Carbon Corporation General Carbon Acceptance Criteria for Reactivation

The following tabular material provided by Calgon Carbon Corporation shows criteria for determining whether nonhazardous or RCRA-regulated granular activated carbon is suitable to accept for return for reactivation. Note the following definitions for acronyms used:

BSP	Big Sandy Plant
BLP	Blue Lake Plant
NIP	Neville Island Plant
TEQ	toxic equivalency (amount of 2,3,7,8-TCDD [2,3,7,8-tetrachlorodibenzo-p-dioxin] with toxicity equivalent to a complex mixture of 210 dioxin and furan isomers with four to nine chlorine atoms found in flue gases.)
RTM-10	Research Test Method (in-house designation for Determination of Ignitability Characteristic under RCRA for Spent Activated Carbon Test Method)

CALGON CARBON CORPORATION ACCEPTANCE CRITERIA

Criteria for Return for Reactivation of Non-Hazardous Granular Activated Carbon (GAC), which must be met:

Characteristic/Property	Limits of Acceptability
Size	Greater than or equal to 12 × 40 Mesh
pH Range	Greater than 2.0 and less than 12.5
Ignitable (per RTM-10)	Not Acceptable (Although BSP is permitted to receive D001 manifested material, they may not receive any spent carbon which exhibits the characteristic of ignitability.)
Instantaneously Ignitable (per RTM-10)	Not Acceptable
Dioxins	Not Acceptable at BSP or BLP < 20 ug/kg TEQs at NIP
Polychlorinated Biphenyls (PCB's)	< 50 mg/kg at NIP Not Acceptable at BSP
1,2-Dibromo-3-chloropropane (DBCP)	Not Acceptable at Neville Island Plant or Big Sandy.
Radioactivity	Not to Exceed Background Level

Note 1: Spent Granular Activated carbon to be returned for reactivation shall be free of any foreign debris (rock, wood, metal, etc.) or extraneous impurities, free of oil and grease, easily wetted by water, and free-flowing.

Note 2: Acceptance for reactivation of spent carbon which has not been supplied by Calgon Carbon Corporation must be investigated on a case-by-case basis.

The following are GENERAL GUIDELINES for acceptability of spent carbon for reactivation. Spent carbons which do not meet these guidelines can usually be processed using special handling and/or blending techniques. Greater than 98% of the projects submitted for reactivation acceptance are approved. However, due to the special handling required, return of these carbons may be approved with limitations as to choice of reactivation facility, method, volume and/or frequency of return.

The criteria listed below are guidelines. Because the regulations governing the operation of our reactivation facilities are complex and subject to change, Calgon Carbon Corporation must reserve the final right to reject the return of spent carbon to our facilities.

Characteristic/Property	Limits of Acceptability
Volatile Sulfur	1.0 % Maximum
Volatile Chloride	1.7 % Maximum—Neville Island 4.0 % Maximum—Big Sandy
Volatile Bromide	0.3% Maximum
Volatile Fluoride	0.4 % Maximum
High Exotherm During Reactivation	Require Case-by-Case Approval
Potassium	Maximum of 0.1 wt. %
Sodium	Maximum of 1.0 wt. %
Trace Metals	Require Case-by-Case Approval (See Metals Guidelines below)
Acutely Toxic, Odorous, or OSHA Regulated Adsorbates	Case-by-Case Approval

CALGON CARBON CORPORATION
ACCEPTANCE CRITERIA

Criteria for Return for Reactivation of RCRA Regulated Granular Activated Carbon (GAC), which must be met:

Characteristic/Property	Limits of Acceptability
Size	Greater than or equal to 12 × 40 Mesh
pH Range	Greater than 2.0 and less than 12.5
Ignitable (per RTM-10)	Not Acceptable (Although BSP is permitted to receive D001 manifested material, they may not receive any spent carbon which exhibits the characteristic of ignitability.)
Instantaneously Ignitable (per RTM-10)	Not Acceptable
Dioxins	Not Acceptable at BSP or BLP < 20 ug/kg TEQs at NIP
Polychlorinated Biphenyls (PCB's)	< 50 mg/kg at NIP Not Acceptable at BSP or BLP
1,2-Dibromo-3-chloropropane (DBCP)	Not Acceptable
Mercury	Not Acceptable
RCRA Waste Codes *Not Acceptable*	D001 (NIP), D002, D003, F020, F021, F022, F023, F026, F027, F028, F032
Reactive Cyanide > 250 mg/kg	Not Acceptable
Reactive Sulfide > 500 mg/kg	Not Acceptable
Radioactivity	Not to Exceed Background Level

Note 1: Spent Granular Activated carbon to be returned for reactivation shall be free of any foreign debris (rock, wood, metal, etc.) or extraneous impurities, free of oil and grease, easily wetted by water, and free-flowing.

Note 2: Acceptance for reactivation of spent carbon which has not been supplied by Calgon Carbon Corporation must be investigated on a case-by-case basis.

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Potassium	Maximum of 0.1 wt. %
Sodium	Maximum of 1.0 wt. %
Trace Metals	Require Case-by-Case Approval (See metals guidelines below)
Acutely Toxic, Odorous, or OSHA Regulated Adsorbates	Case-by-Case Approval

CARBON ACCEPTANCE METALS GUIDELINES FOR NEW CARBON ACCEPTANCE PROJECTS

This table lists the metals limitations which are used to evaluate carbon acceptance projects. Spent carbons with metals concentrations above these guidelines will not be approved for reactivation whether non-hazardous or RCRA hazardous.

Metal	Concentration, mg/kg
Antimony	< 1000
Arsenic	< 50
Beryllium	< 63.75
Barium	< 350
Cadmium	< 2.5
Total Chromium	< 200
Hexavalent Chromium	< 3.75
Copper	< 500
Iron	< 10,000
Lead	< 50
Manganese	< 5000
Nickel	< 5000
Selenium	< 200
Silver	< 200
Thallium	< 200
Zinc	< 500
Mercury	Not acceptable

Appendix B

Committee Meetings, Site Visits, and Virtual Meetings

FIRST COMMITTEE MEETING
JUNE 4-6, 2008
ANNISTON, ALABAMA

Objectives: National Research Council introduction (administrative actions, including committee introductions and composition/balance/bias discussions for committee members), committee statement of task and background review with sponsor, receive detailed process and equipment presentations, review preliminary report outline and report writing process, confirm committee writing assignments, and decide future meeting dates and next steps.

U.S. Army Chemical Weapon Demilitarization 101: Timothy Garrett, Site Project Manager, Anniston Chemical Agent Disposal Facility (ANCDF) Field Office
Consideration of Statement of Task: Robert A. Beaudet, Committee Chairman, and Timothy Garrett, Site Project Manager, ANCDF Field Office

Tour of Anniston Chemical Agent Disposal Facility

Use of Carbon at ANCDF: Robie Jackson, Waste Management Manager, and Traci Smith, Trial Burn Manager, ANCDF Field Office
Chemistry of Carbon Involving Carbon and Agents: Susan Ankrom, SAIC Task Manager, and Robert Kelly, Laboratory Manager, ANCDF
Program History of Carbon: Brian O'Donnell, Chief, Secondary Waste, Closure Compliance, and Assessments, Chemical Materials Agency (CMA)
Regulation and Permitting Issues: Timothy Garrett, Site Project Manager, ANCDF Field Office
Discussion with Committee onAlternatives for Disposal/Treatment: Timothy Garrett, Site Project Manager, ANCDF Field Office

SECOND COMMITTEE MEETING
JULY 23-25, 2008
ABERDEEN, MARYLAND

Objectives: National Research Council introduction and composition/balance/bias discussions for committee members, continue data gathering, review concept draft report, confirm additional committee writing assignments, determine requirement for site visits, and confirm next steps forward.

Repeat Presentation of U.S. Army Chemical Weapon Demilitarization 101: Timothy Garrett, Site Project Manager, ANCDF Field Office
Analytical Procedures for GB/VX Carbon: Michael McNaughton, Southwest Research Institute
Carbon Studies Sponsored by Umatilla Chemical Agent Disposal Facility (UMCDF), Thomas Sackett, UMCDF Field Office
Carbon Studies Sponsored by ANCDF–NMR Work: Leonard Buettner, Research Chemist, Edgewood Chemical and Biological Center
Open Discussion with Sponsor: Robert A. Beaudet, Committee Chairman, and Timothy Garrett, Site Project Manager, ANCDF Field Office

THIRD COMMITTEE MEETING
AUGUST 18-20, 2008
IRVINE, CALIFORNIA

Objectives: Review first full-message draft, produce preliminary concurrence draft, determine what is not yet known and how to learn it, and determine path forward.

SITE VISIT
SEPTEMBER 4, 2008
TOOELE, UTAH

Objective: Allow committee members who were not present in Anniston to visit an operating chemical agent disposal facility and discuss challenges entailed in disposing of chemical agent that might contain mercury.

SITE VISIT
SEPTEMBER 9, 2008
COLUMBUS, OHIO

Objectives: Receive briefing on Calgon Carbon Corporation operations and facilities and tour facility; determine which types of spent activated carbon (AC) cannot be regenerated (probe for presence of mercury and agent); determine what the split is between regeneration, landfill, and incineration for all spent activated carbon and whether the split is different for spent powdered activated carbon and spent granular activated carbon; determine what fraction of the AC that is used in liquid-phase applications and/or gas-phase applications is regenerated; determine whether spent AC is hazardous waste under RCRA, which landfills will accept it, and which incinerators will accept it; determine how the AC filters in motor vehicles are handled at the end of their useful lives; determine what percentage of AC sold is granular and what percentage is powdered; determine whether Calgon would buy back regenerated AC; and determine whether Calgon ever disposes of AC and, if so, whether it ever has to incinerate it.

FOURTH COMMITTEE MEETING
SEPTEMBER 29-OCTOBER 1, 2008
IRVINE, CALIFORNIA

Objectives: Review preliminary concurrence draft, produce next version of concurrence draft, determine what is not yet known and how to learn it, and determine path forward.

SITE VISIT
JANUARY 13-14, 2009
SAN ANTONIO, TEXAS

Objective: Visit Southwest Research Institute to review newly developed analytical procedures for determining any residual GB/VX on carbon.

VIRTUAL MEETINGS

February 12, 2009

Objectives: Share what was learned at the Southwest Research Institute site visit; examine Chapters 1-3 of the preconcurrence draft.

February 17, 2009

Objective: Examine Chapter 4 of the preconcurrence draft.

February 19, 2009

Objective: Examine Chapter 5 of the preconcurrence draft.

February 25, 2009

Objective: Examine Chapter 6 of the preconcurrence draft.

February 27, 2009

Objective: Examine Chapter 7 of the preconcurrence draft.

March 10, 2009

Objective: Examine general findings and recommendations of the pre-concurrence draft.

March 13, 2009

Objective: Examine general clarifications in the pre-concurrence draft.

March 16, 2009

Objective: Examine wrap-up of the pre-concurrence draft.

Appendix C

Biographical Sketches of Committee Members

Robert A. Beaudet, *Chair*, is professor emeritus of chemistry at the University of Southern California. He received his Ph.D. in physical chemistry from Harvard University in 1962. From 1961 to 1962, he was a U.S. Army officer and served at the Jet Propulsion Laboratory as a research scientist. He joined the faculty of the University of Southern California in 1962 and has served continuously in the Department of Chemistry since that time. He also has served on Department of Defense committees addressing both offensive and defensive considerations surrounding chemical warfare agents. He was chair of an Army Science Board committee that addressed chemical detection and trace gas analysis. He also was the chair of an Air Force technical conference on chemical warfare decontamination and protection. He has participated in two NRC studies on chemical and biological sensor technologies and energetic materials and technologies. Most of his career has been devoted to research in molecular structure and molecular spectroscopy. Previously, Dr. Beaudet served as a member of the NRC's Board on Army Science and Technology (BAST), as a member of the NRC Committee on Review of the Non-Stockpile Chemical Materiel Disposal Program, as a BAST liaison to the Committee on Review and Evaluation of the Army Chemical Stockpile Disposal Program (Stockpile Committee), and as chair of the Committee on Assembled Chemical Weapons Alternative Program.

Teresa J. Bandosz is a full professor in the Chemistry Department of the City College of New York of the City University of New York. She was awarded a Ph.D. in chemical engineering from the Technical University of Krakow, Poland, in 1989 and a D.Sc. in physical chemistry/analytical chemistry from the Marie Curie University in Poland in 1998. Dr. Bandosz has been a faculty member of the Chemistry Department of CCNY/CUNY since 1996 and guest professor at Dalian University of Technology in China since 2006. Her research, which has been reported in over 190 peer-reviewed papers, 5 book chapters, and more than 100 conference presentations, focuses on the application of adsorption to environmental problems and includes the development of new adsorbents based on activated carbons, clays, and industrial waste; desulfurization of air, fuel gases, and liquid fuel; and removal of toxic industrial gases. Dr. Bandosz has vast experience in the study of the surface chemistry of nanoporous carbons using infrared spectroscopy, titration, and TPD among other methods and relating this surface chemistry to the performance of these materials in the environmental context. She holds four patents, is a consultant for companies such as Dupont, Synagro, and Fuel Cell Energy, is responsible for controlling or removing odor from the water pollution control plants of New York City, has been a member of the scientific committees of various international conferences, serves on the editorial boards of *Adsorption Science and Technology* and the *Journal of Colloid and Interface Science,* and recently edited the book *Activated Carbon Surface in Environmental Remediation*.

Joan B. Berkowitz is currently managing director of Farkas Berkowitz & Company. She graduated from the

University of Illinois with a Ph.D. in physical chemistry. Dr. Berkowitz has extensive experience in the area of environmental and hazardous waste management, a knowledge of the technologies available for the cleanup of contaminated soils and groundwater, and a background in physical and electrochemistry. She has contributed to several Environmental Protection Agency studies, been a consultant on remediation techniques, and assessed various destruction technologies. Dr. Berkowitz is the author of numerous publications on hazardous waste treatment and environmental subjects.

Herek L. Clack is an associate professor in the Mechanical, Materials, and Aerospace Engineering Department at the Illinois Institute of Technology. He received his B.S. in aeronautical and astronautical engineering from MIT (1987) and his M.S. (1997) and Ph.D. (1998) in mechanical engineering from the University of California, Berkeley. Prior to joining the IIT faculty, Dr. Clack was an NRC postdoctoral fellow in residence at the National Institute of Standards and Technology in Gaithersburg, Maryland (1998-1999) and a member of the technical staff at the Rocketdyne Division of Boeing Corporation (1987-1992). He is engaged in research and publication in the general area of transport phenomena within dispersions such as sprays and aerosols, as applied to such areas as trace and toxic gas adsorption from combustion flue gases and combustion of droplets and sprays.

Willard C. Gekler is currently an independent consultant working for his previous employer, ABS Consulting, Inc. He graduated from the Colorado School of Mines with a B.S. in petroleum refining engineering and pursued graduate study in nuclear engineering at the University of California at Los Angeles. His extensive experience includes membership on NRC's ACWA committee and on the Mitretek Systems expert panel reviewing the quantitative risk assessments and safety analyses of hazardous materials handling, storage, and waste treatment systems for the Army's Anniston, Umatilla, Pine Bluff, and Aberdeen chemical agent disposal facilities. He also participated in a consequence screening assessment for the Newport Chemical Destruction Facility. Previously he was project engineer for various nuclear test facility designs and for development of facility design criteria for the Johnston Atoll Chemical Agent Disposal System. Mr. Gekler is a certified reliability engineer and a member of the Society for Risk Analysis, the American Institute of Chemical Engineers (AIChE), and the American Nuclear Society (ANS).

Loren D. Koller is an independent consultant and former professor and dean of the College of Veterinary Medicine at Oregon State University. His areas of expertise include pathology, toxicology, immunotoxicology, carcinogenesis, and risk assessment. He is a former member of the NRC Committee on Toxicology and has participated on several of its subcommittees, primarily those involved in risk assessment. Dr. Koller has served on the Institute of Medicine's Committee on the Assessment of Wartime Exposure to Herbicides in Vietnam and has been invited to serve on committees for the CDC, EPA, Homeland Security, the Agency for Toxic Substances and Disease Registry, and the U.S. Army. He received his D.V.M. from Washington State University and his Ph.D. in pathology from the University of Wisconsin.

M. Douglas LeVan is currently the J. Lawrence Wilson Professor of Engineering and chair of the Department of Chemical Engineering at Vanderbilt University. He received a B.S. in chemical engineering from the University of Virginia in 1971 and a Ph.D. in chemical engineering from the University of California, Berkeley, in 1976. After receiving his Ph.D., he worked for 2 years at Amoco Production Company's Research Center in Tulsa, Oklahoma, after which he was on the faculty of the University of Virginia for 19 years. He has been at Vanderbilt as department chair for 11 years. Professor LeVan's research area is adsorption. His work covers the full range from materials development to adsorption equilibria/thermodynamics to rate behavior to processes.

John Pendergrass, senior attorney at the Environmental Law Institute (ELI), received his B.S. in environmental science from Michigan State University in 1976 and his J.D. from Case Western Reserve University in 1979. His expertise includes Superfund enforcement, brownfields cleanup and redevelopment, hazardous substances, nanotechnology, national pollutant discharge elimination system permits, climate change as it relates to state programs to reduce greenhouse gas emissions, environmental management systems and conformity assessment, judicial education, and state programs. He was among the first to address improving legal and administrative mechanisms for protecting public health and the environment from the risks at contaminated sites where some hazardous substances are left in place. His research and writing on such institutional controls and long-term stewardship have led to changes in national policy and in the laws of many states. He also writes regularly about innovative state environmental and natural resource programs as well as federal preemption of state laws. He leads ELI's Judicial Education Program to educate judges in the United States and throughout the world about environmental law. Since 1997, Mr. Pendergrass has been a member of the accreditation council overseeing ISO 14001 (environmental management systems) certification bodies in the United States.

Krista S. Walton is the Tim and Sharon Taylor Assistant Professor in the Department of Chemical Engineering at Kansas State University. Her research activities focus on various aspects of the design and synthesis of functional porous materials for use in applications including adsorption separations, air purification, gas storage, chemical sensing, and catalysis. She has been recognized for her contributions to adsorption science and technology by the Graduate Research Award in Separations from AIChE in 2005 and by the Army Research Office Young Investigator Award in 2007. She has published over 15 research articles in peer-reviewed journals in the fields of novel porous materials, adsorption separations, and gas storage and has given more than 30 presentations at national and international research conferences. She is currently serving as a director in the Separations Division of AIChE and also serves on the AIChE Area 2e adsorption and ion exchange programming committee. She received a B.S.E. in chemical and materials engineering from the University of Alabama at Huntsville and a Ph.D. in chemical engineering from Vanderbilt University.

Walter Weber, Jr., NAE, has been the Gordon M. Fair and Earnest Boyce Distinguished University Professor of Environmental Engineering at the University of Michigan since 1994. He is also founding director of ConsEnSus, the university's program Concentrations in Environmental Sustainability; founding director of the Great Lakes and Mid-Atlantic Center for Hazardous Substance Research; founding director of the Institute for Environmental Sciences, Engineering and Technology; and founding director of the National Center for Integrated Bioremediation Research and Development. Dr. Weber has been recognized by the International Science Index as one of the most highly cited and quoted scientists in the world. He has served on the National Academies Engineering Review Panel as well as on its Board on Environmental Studies and Toxicology. Dr. Weber received an Sc.B. in chemical engineering from Brown University, an M.S.E. in civil engineering from Rutgers University, and a Ph.D. in water resources engineering from Harvard University. He was elected to the National Academy of Engineering in 1985 and chosen by the American Institute of Chemical Engineering's 2008 Centennial Celebration as one of the 100 most influential individuals of the New Era of Engineering: post-World War II.

Yu Chu Yang is a consultant to both government and industrial organizations and a former employee of the U.S. Army Edgewood Chemical and Biological Center (ECBC) at Aberdeen Proving Ground, Maryland. She has a B.S. in chemical engineering from Taiwan National University and a Ph.D. in physical chemistry from Tulane University. She worked for Exxon Corporation for over 5 years. In 1986, she joined ECBC and spent the following 10 years working as a research chemist. Her research focused on the reaction chemistry of chemical agents with applications to decontamination and neutralization. She has published in the fields of reaction kinetics and mechanisms, analytical chemistry, and the chemical detoxification reactions of chemical warfare agents. In 1997-2000, Dr. Yang served as chief of chemistry and biological sciences at the U.S. Army Research Laboratory-European Research Office in London, where she interacted with European researchers engaged in U.S.-Army-sponsored research. She later worked for the Program Manager for Assembled Chemical Weapons Alternatives (PMACWA), an organization responsible for the disposal of chemical weapons stored in Pueblo, Colorado, and Blue Grass, Kentucky. As chief scientist of PMACWA, she directed and advised on a number of laboratory-scale testing projects, which supported the plant designs at both sites. She retired from government service in February 2007.