

Evaluation of Alternative Technologies for Disposal of Liquid Wastes from the Explosive Destruction

SystemCommittee on Review and Evaluation of the Army
Non-Stockpile Chemical Materiel Disposal Program,
National Research Council

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Evaluation of Alternative Technologies for Disposal of Liquid Wastes from the Explosive Destruction System

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

Board on Army Science and Technology Division on Engineering and Physical Sciences National Research Council

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Preface

The Committee on Review and Evaluation of the Army Non-Stockpile Chemical Materiel Disposal Program (see Appendix A for biographies of committee members) was appointed by the National Research Council (NRC) to conduct studies on technical aspects of the U.S. Army Non-Stockpile Chemical Materiel Disposal Program. During its first year, the committee evaluated the Army's plans to dispose of chemical agent identification sets (CAIS)—test kits used for soldier training (NRC, 1999d). During the second year, the committee recommended nonincineration technologies that might be used for the posttreatment of neutralization wastes from Army nonstockpile materiel disposal systems. For this third year, the Army asked the committee to supplement its report on neutralent wastes to include wastes produced by the Army's newest mobile system, the explosive destruction system (EDS) (NRC, 2001a). In addition, in a report to be published in the spring of 2002, the committee is assessing the operational concepts for mobile and semipermanent facilities being developed by the product manager.

At its meetings, the committee was given a number of briefings (see Appendix B) and held subsequent deliberations. The committee is grateful to the many individuals, particularly Lt. Col. Christopher Ross, Product Manager for Non-Stockpile Chemical Materiel, and his staff, who provided technical information and insights during these briefings. This information provided a sound foundation for the committee's deliberations.

This study was conducted under the auspices of the NRC's Board on Army Science and Technology. The committee acknowledges the continued superb support of the director, Bruce A. Braun, associate director Michael A. Clarke, NRC staff, committee members, the study director, support staff, and the publication staff, who all worked diligently on a demanding schedule to produce this report. In addition, I would like to particularly recognize the extra leadership and effort by committee member Douglas Medville in the preparation of this specific report.

John B. Carberry, *Chair* Committee on Review and Evaluation of the Non-Stockpile Chemical Materiel Disposal Program

Acknowledgments

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

Joseph Bozelli, New Jersey Institute of Technology, Elisabeth M. Drake, Massachusetts Institute of Technology,

Gene Dyer, consultant,

Gary Lage, ToxiLogics, Inc., Alvin Mushkatel, Arizona State University, Carmo Pereira, DuPont Engineering, William R. Rhyne, consultant, Chandra M. Roy, ABS Consulting, and William Tumas, Los Alamos National Laboratory.

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 Bailar. Appointed by the NRC's Report Review Committee, 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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Acronyms and Abbreviations

ACWA	Assembled Chemical Weapons Assessment	HL	mustard-lewisite mixture
71C W 71	(Program)	HN-1, H-3	nitrogen mustard
ATAP	Alternative Technology Approach Program	HT	mustard agent T mixture
711711	Themative Teemology Tipprouch Trogram	111	mustare agent 1 mixture
BAA	broad agency announcement	L	lewisite
		LDR	land disposal restrictions
CAIS	chemical agent identification sets	LSC	linear shaped charge
CAMDS	chemical agent munitions disposal system		
CDU	capacitor discharge unit	MEA	monoethanolamine
CERCLA	Comprehensive Environmental Response,	MEK	methyl ethyl ketone
	Compensation and Liability Act	MMD	munitions management device
CFR	U.S. Code of Federal Regulations		
CG	phosgene	NATO	North Atlantic Treaty Organization
CSC	conical shaped charge	NPL	national priorities list
CSDP	Chemical Stockpile Disposal Program	NRC	National Research Council
CWA	Clean Water Act	NSCMP	Non-Stockpile Chemical Materiel Product
CWC	Chemical Weapons Convention	NSCWCC	Non-Stockpile Chemical Weapons Citizens
CWM	chemical warfare materiel	NG CHINA	Coalition
D.4		NSCWM	Non-Stockpile Chemical Warfare Materiel
DA	diphenylchloroarsine	0.100	.1 1
DM	adamsite	O/SS	oxidant/solvent system
DOT	U.S. Department of Transportation	D.C.D.	
DPG	Dugway Proving Ground	PCB	polychlorinated biphenyl
EDIII		PD	Porton Down (United Kingdom)
EBW	exploding bridge-wire	PINS	portable isotopic neutron spectroscopy
EDS	explosive destruction system	PMCD	Program Manager for Chemical
EPA	Environmental Protection Agency	D) D IG G) (Demilitarization
FOTW	federally owned treatment works	PMNSCM	Product Manager for Non-Stockpile Chemical Materiel
FSS	fragment suppression system	POP	persistent organic pollutants
	g	POTW	publicly owned treatment works
GA	tabun (nerve agent)	ppb	parts per billion (µg/L)
GB	sarin (nerve agent)	ppm	parts per million (mg/L)
GPCR	gas-phase chemical reduction	rr	
-		RAP	regulatory approval/permitting
Н	sulfur mustard	RCRA	Resource Conservation and Recovery Act
HD	sulfur mustard (distilled)	RD&D	research, development, and demonstration
_			,, ,, ,, ,, ,, ,

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RDX	cyclotrimethylenetrinitramine	TNT	trinitrotoluene
RMA RRS	Rocky Mountain Arsenal rapid response system	TSDF	treatment, storage, and disposal facility
CONTO		UXO	unexploded ordnance
SCWO SET	supercritical water oxidation solvated-electron technology	VOC	volatile organic compound
SVOC	semivolatile organic compound	VX	a nerve agent
TCLP	toxicity characteristic leaching procedure	WAO	wet-air oxidation

Executive Summary

Chemical warfare materiel (CWM) encompasses diverse items that were used during 60 years of efforts by the United States to develop a capability for conducting chemical warfare. Non-Stockpile CWM (NSCWM) is materiel not included in the current U.S. inventory of chemical munitions and includes buried materiel, recovered materiel, components of binary chemical weapons, former production facilities, and miscellaneous materiel. NSCWM that had been buried on former military sites is increasingly being dug up as the land is developed for other purposes. Other NSCWM may be found on or near the surface at former research facilities or test and firing ranges.

Through its Chemical Stockpile Disposal Program (CSDP), the U.S. Army is the designated executive agent for destroying CWM under the terms of the 1997 international Chemical Weapons Convention (CWC). Disposal of nonstockpile CWM is being handled by the Non-Stockpile Chemical Materiel Product (NSCMP), under the Program Manager for Chemical Demilitarization (PMCD). Because NSCWM is stored or buried at many locations, the Army is developing transportable treatment systems that can be moved from site to site as needed. Originally, the Army planned to develop three transportable treatment systems for

¹Formally known as the Convention on the Prohibition of the Development, Production, Stockpiling and Use of Chemical Weapons and on Their Destruction, the CWC requires the destruction of the chemical weapons in the stockpile by 2007 and any nonstockpile weapons in storage at the time of the treaty ratification (1997) within 2, 5, or 10 years of the ratification date, depending on the type of chemical weapon or on the type of chemical with which an item is filled. Any chemical weapons "discovered... after the initial declaration of chemical weapons shall be reported, secured and destroyed in accordance with Part IV (A) of the Verification Annex" (CWC Article IV, Paragraph 9). Thus, NSCWM buried before January 1, 1997, is excluded from the treaty requirements as long as it remains buried. However, once this CWM is dug up and removed from the ground, the recovered CWM must be identified, declared under the CWC, inspected, and destroyed as soon as possible (U.S. Army Final Programmatic Environmental Impact Statement, 2001, volume 1, pp. 1-3).

nonstockpile chemical materiel: the rapid response system (RRS), the munitions management device (MMD), and the explosive destruction system (EDS).

The RRS was designed to treat recovered chemical agent identification sets (CAIS), which contain small amounts of chemical agents and a variety of toxic industrial chemicals. These sets were developed as training aids, and, unlike chemical munitions, they were not designed with lethal intent. The MMD systems were conceived to dispose of nonstockpile chemical munitions and sample containers deemed stable enough for transport and long-term storage. The EDS was originally developed to destroy nonstockpile items that were deemed to be too unstable for transport or long-term storage; however, it can also be used to treat limited numbers of stable chemical munitions, with or without explosive components. The MMD systems proved to be complex, expensive, and difficult to permit, so their development was discontinued. The EDS, which is smaller and less complex than the MMD, is now considered the Army's primary transportable system for treatment of small quantities of nonstockpile items.²

This report is a supplement to an earlier report (NRC, 2001a), which evaluated eight alternative technologies³ for destruction of the liquid waste streams from the RRS and the MMD. This report evaluates the same technologies for the

²The EDS Phase 1 (EDS-1) can treat munitions containing up to one pound equivalent TNT; the larger EDS Phase 2 (EDS-2), under design and development, will treat munitions containing up to three pounds equivalent TNT. All EDS testing to date has been with the EDS-1. The EDS-1 is intended for use with World War I and World War II vintage chemical warfare materiel produced prior to 1945. Post-World-War II projectiles have larger bursters that exceed the capacity of the system.

³The technologies were chemical oxidation, wet-air oxidation, electrochemical oxidation using Ag(II) or Ce(IV), supercritical water oxidation, solvated electrons, biodegradation, gas-phase chemical reduction, and plasma arc.

destruction of liquid waste streams produced by the EDS. Although it focuses on the destruction of EDS neutralent, it also takes into consideration the ability of posttreatment technologies to process the more dilute water rinses that are used in the EDS following treatment with a reagent.

Between November 1999 and November 2000, the EDS Phase 1 (EDS-1) was tested at a military installation at Porton Down in the United Kingdom. In early 2001, it was used in an emergency action to dispose of six bomblets containing the nerve agent sarin at Rocky Mountain Arsenal (RMA) in Colorado. Subsequently, four more bomblets were discovered during remediation of the same area at RMA. At this writing, the EDS-1 had been dispatched to dispose of these also. As a result of the success of these operations, the decision was made to discontinue development of the MMD,⁴ another mobile system that used the same process chemistry as the EDS to destroy chemical agent but that was both more complex and less versatile than the EDS.

The EDS produces four types of liquid waste streams for which treatment options are being evaluated: (1) a neutralent resulting from treatment of the chemical agent with an alkaline chemical reagent, (2) rinsates resulting from washing the EDS vessel with clean water to remove any residues of reagent and reaction products remaining after treatment, (3) cleaning solution consisting of washes (water and detergent) that are made between processing of each munition, and (4) final washes (using, for example, water and acetic acid) carried out after completing a munitions campaign.

Neutralent wastes from the EDS are expected to be classified as hazardous wastes under the Resource Conservation and Recovery Act (RCRA)⁵ (U.S. Army, 2001g). The Army's current plan is to send them to a permitted hazardous waste incinerator for final disposal. Rinsates and cleaning solution from the EDS generally have much lower concentrations of hazardous chemicals and are more likely to be classified as nonhazardous wastes.⁶ Assuming rinsates and cleaning solution meet the pretreatment standards specified by the Clean Water Act, these waste streams may be eligible for

discharge to a publicly owned treatment works (POTW) or an equivalent federally owned treatment works (FOTW).

The incineration of chemical agents has generated opposition among some public interest groups, and this opposition may be extended to the incineration of EDS neutralents, even though the concentration of any remaining agent in the neutralents will be miniscule, ranging from undetectable to a few parts per million (ppm). As a result of this public concern, the Army is investigating alternative (nonincineration) technologies for disposing of EDS neutralents and has asked the National Research Council (NRC) for advice.

The committee wishes to stress that this report is a supplemental evaluation that is focused on the destruction of EDS liquid waste streams. Nothing discussed here should be interpreted as the committee's evaluation of the EDS as a complete operating system. Such an evaluation would examine issues such as the structural integrity of the EDS with repeated use, operational procedures, the process chemistry, and whether a secondary vapor containment structure is needed. A summary of NSCWM that has been destroyed to date by the EDS, as well as the main constituents of the liquid waste streams, is given in Table ES-1. The principal agent fills of nonstockpile munitions encountered are expected to be phosgene (CG), sulfur mustard (H, HD), and sarin (GB). In addition to these fills, it is possible that some nonstockpile items containing VX⁷ as well as arsenicderived chemical agents such as lewisite, an organoarsenic

TABLE ES-1 EDS-1 Liquid Waste Streams Considered in This Study

Agent Fill	Items Destroyed to Date	Key Constituents of Liquid Waste Streams
Phosgene (CG)	4 cylinders, 7 mortar rounds	Water, NaOH, NaCl, metals
Sulfur mustard (HD)	2 cylinders, 12 mortar rounds or projectiles	Water, MEA, volatile and semivolatile organics, metals, HD degradation products
Sarin (GB)	1 cylinder, 10 bomblets	Water, MEA, GB degradation products, volatile and semivolatile organics, metals

SOURCE: Compiled by the NRC from Army sources.

⁴Lt. Col. Chistopher Ross, Product Manager, Non-Stockpile Chemical Materiel Project, "U.S. Army Non-Stockpile Chemical Materiel Product (NSCMP) Project Overview/Status," presentation to the committee, March 15, 2001.

⁵Under RCRA, a substance is determined to be a hazardous waste either because it is listed as such in the federal or state regulation (a listed hazardous waste) or because it exhibits one or more characteristics of hazardous waste, as defined in the hazardous waste regulations (e.g., corrosivity), or because it is derived from a listed waste.

⁶High levels of chloroform—a listed hazardous waste under RCRA—were observed in EDS cleaning solutions from the RMA tests (Appendix C, Table C-1). The source appears to be the particular type of lubricant/sealant used to seal joints. The chloroform is therefore not a necessary constituent of the waste stream and could be eliminated by using a different formulation of sealant/lubricant.

⁷Although there are no known nonstockpile munitions containing the nerve agent VX, there are about 100 VX-filled containers in the nonstockpile inventory. Some of these—for example, glass bottles and vials—can be disposed of in the RRS, while others—for example, steel Department of Transportation (DOT) bottles and cylinders—are potential candidates for disposal in the EDS should the Army decide to do so.

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blister agent, may also be processed in the EDS. If this processing does take place, arsenic compounds such as sodium arsenite (from treatment with sodium hydroxide) will be produced, and these compounds will require conversion to relatively insoluble arsenate salts as part of the posttreatment of the EDS neutralent.

STATEMENT OF TASK

On March 16, 2001, the Army Product Manager for the NSCMP requested that the NRC undertake a supplemental assessment of alternative technologies for destruction of EDS liquid waste streams. The statement of task is as follows:

The NRC will:

- Examine alternative destruction technologies for liquid waste streams generated from the Explosive Destruction System (EDS).
- Discuss the regulatory approval issues and obstacles for the combined use of the EDS and the alternative technologies that treat the EDS secondary waste streams.

COMMITTEE APPROACH

As in the previous study (NRC, 2001a), the committee began by establishing some boundary conditions. Only liquid neutralent wastes from the EDS were considered, in accordance with the statement of task. Treatment of solid wastes, such as metal munition bodies, packing materials, and carbon air filters, was not considered. Waste solids from the EDS include metal fragments (from the munition bodies and the fragmentation suppression system), dunnage, used carbon filters, and disposable personnel protective equipment. These solids will be bagged, placed in waste containers, and disposed of in a hazardous waste landfill. The treatment goals for the neutralent destruction technologies considered were taken to be solids that could be disposed of in an approved (i.e., permitted) landfill and liquids that could be released to a POTW or FOTW.8 Air discharges from the neutralent treatment technologies should contain primarily carbon dioxide, water vapor, and nitrogen.

The primary analytical approach in this report was to evaluate the ability of alternative technologies to process EDS liquid waste streams, taking note of any differences between these waste streams and those generated by the MMD considered previously (NRC, 2001a). The committee then examined the extent to which any differences between the EDS and MMD liquid waste streams might alter its earlier recommendations on alternative technologies for destruction of these wastes. However, the committee notes that several important developments have occurred since the publication of the earlier report, *Disposal of Neutralent Wastes* (NRC, 2001a):

- The MMD program has been suspended; this means that the liquid waste streams generated by nonstockpile mobile treatment systems will be primarily from the EDS, with a small volume from the RRS.
- New data have become available regarding the performance of several of the alternative technologies, both from the Army's Technology Testing Program (see Chapter 3) and from its Assembled Chemical Weapons Assessment (ACWA) program, which was reviewed by another NRC committee (NRC, 1999a, 2000).

The committee's earlier recommendations are also reconsidered in light of recent test results from both the Army's Technology Testing Program and its ACWA program.

The committee also considered the criteria for public and regulatory acceptability that are likely to affect the selection of alternative destruction technologies. It identified several regulatory approval/permitting (RAP) issues associated with EDS liquid waste disposal, discussed the regulatory status of these wastes, and developed several findings and recommendations on regulatory and public acceptability issues.

FINDINGS AND RECOMMENDATIONS

Technical Issues

Finding: Neutralents from the EDS are similar to those from the MMD owing to similar treatment chemistries. However, there could be three differences:

- The potential presence of residual explosives or explosive-derived organic compounds in the EDS neutralents and rinsates. The MMD and the EDS produce different liquid wastes because of the different ways that munitions are processed. The MMD does not process items containing explosives, while the EDS can handle munitions containing bursters and/or fuzes. The EDS also uses explosives to open the munition and detonate any explosives contained therein.
- Potentially higher concentrations of dissolved or suspended metals (e.g., Hg, Pb, Cu, and Al) in EDS neutralents and rinsates owing to explosive accessing of the munition and/or the presence of fuzes or bursters. The fragmentation of the munition bodies may expose more metal surface to the

⁸The committee felt that, on the one hand, a technology need not be excluded if it did not completely mineralize the neutralents, as long as the resulting liquids could be sent for final treatment at a POTW/FOTW. On the other hand, it felt that multiple treatment technologies should not be necessary; the selected technology should be able to destroy neutralent such that the residuals could be either released to a POTW/FOTW or sent to a permitted landfill.

ALTERNATIVE TECHNOLOGIES FOR DISPOSAL OF LIQUID WASTES FROM THE EXPLOSIVE DESTRUCTION SYSTEM

monoethanolamine (MEA) reagent,⁹ which is a good extractant for some of these metal ions. In addition, the detonator materials in fuzes, such as lead azide and mercury fulminate, may introduce some highly toxic metal ions.

• The potential presence of arsenic compounds in the EDS neutralent from a small number of munition fills (the MMD was not intended to treat agents containing arsenic).

Finding: The fills expected to be processed most frequently in the EDS are sulfur mustard (H, HD), phosgene (CG), and—to a lesser extent—sarin (GB). Items filled with other agents—such as lewisite (L), which contains arsenic, or the nerve agent VX—are expected to be encountered much less often, but they do exist in the nonstockpile inventory.

The Army has conducted operational testing of the EDS only for munitions containing H, CG, and GB. Thus, the committee's analysis focused mainly on liquid waste streams resulting from EDS treatment of these three types of agent. However, because lewisite munitions are known to exist in the inventory and may be treated in the EDS, the committee also considered in its analysis the effect of high concentrations of arsenic compounds.

Finding: If agents containing arsenic (such as lewisite) are processed in the EDS, additional treatment steps will be needed to remove the arsenic from the EDS neutralent or reduce its mobility in treated solids. In these rare cases, however, suitable treatment chemistries are known and have been demonstrated to be effective.

Finding: The EDS neutralization process and subsequent water rinses produce four liquid waste streams in two categories: (1) organic-rich liquids consisting of the neutralent and a reagent-based rinse and (2) cleaning solutions and final washes containing relatively low concentrations of organics.

Recommendation: The committee recommends that the Army consider separate treatment strategies for organic-rich liquids and these other aqueous liquids, since their chemical properties and regulatory status are different.

Finding: Chemical analyses of EDS neutralents and rinsates obtained from testing of HD, CG, and GB in the EDS may not have accounted for some species, such as energetic compound decomposition products, that may be encountered during operations.

Recommendation: The Army should review the sampling and analytical techniques employed at Porton Down and at RMA to ensure they are sufficiently sensitive and complete to detect any species of agent, energetics, and other components that could be in concentrations high enough to be of concern to human health or the environment.

Finding: The two-track approach¹⁰ recommended for selecting treatment technologies for RRS and MMD neutralents in the committee's previous report (NRC, 2001a) remains valid for EDS liquid waste streams. However, based on new and preliminary results from NSCMP's Technology Test Program, as well as test results on some of the technologies obtained in the Army's Assembled Chemical Weapons Assessment (ACWA) Program, the preferential ranking of technologies in the resource investment track has changed, as described in the following recommendation.

Recommendation: The NSCMP should pursue a two-track strategy to identify a suitable treatment technology for EDS liquid waste streams. As part of the first track, the NSCMP should take advantage of available equipment that would require little or no investment (that is, it should piggyback on alternative technologies from the ACWA Program or on existing commercial technologies, such as chemical oxidation, wet-air/O₂ oxidation, or plasma arc¹¹ technology). The committee judged that if any of these existing and available technologies can accomplish the task safely, this would be a relatively rapid and inexpensive course of action.

If, on the other hand, none of the existing and available technologies can be used as is—for example, if substantial research and development resources would be needed to adapt them to the destruction of nonstockpile neutralents—the committee recommends that NSCMP, as part of track two, should invest first in chemical oxidation and wet-air/ O_2 oxidation. Only if these technologies cannot be adapted eas-

⁹The choice of MEA as a reagent was based on extensive previous experience with it in other CWM programs, its ability to dissolve the agents, miscibility with water, low corrosivity with stainless steel, and low flammability.

¹⁰In the report on disposal of neutralent wastes (NRC, 2001a), the first track of the two-track approach contained technologies that did not need any Army development investment. The second track consisted of alternative technologies requiring investment. The earlier report recommended investigating the track one technologies before turning to track two.

¹¹One commercial plasma arc technology (the PLASMOX process) has treated a chemical warfare agent in Switzerland. Although it has not yet been permitted for use on any hazardous waste in the United States, it has also been used for the commercial treatment of hazardous waste in Switzerland. The Army has represented to the committee that there are a number of plasma arc facilities permitted in the United States, primarily for treatment of medical wastes, and that it intends to test some of these plasma arc designs. The committee has not reviewed the emissions data from the PLASMOX treatment of chemical agent or from these commercial facilities. Plasma arc technologies may emit low levels of polychlorinated dibenzodioxins. Since PLASMOX uses oxygen, it may be considered by some regulators and some members of the public as a more sophisticated incinerator.

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ily does the committee recommend that the Army consider investing R&D resources in supercritical water oxidation (batch mode).¹²

The committee recommends that no further resources be spent on development of electrochemical oxidation, supercritical water oxidation (continuous mode), gas-phase chemical reduction, biotreatment (by itself), or solvated electron technology for this purpose.

Finding: The Army has an ongoing program to test several alternative technologies for their ability to destroy EDS neutralents. Based on information provided to it regarding this test program, the committee has several concerns:

- The tests are often being conducted with simulated EDS neutralents mixed from laboratory chemicals rather than with actual EDS neutralents.
- The Army does not appear to have identified key tracking compounds¹³ that are the most difficult to destroy and whose disposition can serve as indicators for the performance of the treatment technologies.
- The test program does not appear to be designed to provide basic data on the kinetics and thermodynamics of the oxidation of key waste stream components under process conditions.

Recommendation: The test program could be improved if the following steps are taken:

- To the extent feasible, the Army should use a representative range¹⁴ of actual EDS neutralents obtained from munition destruction in its tests of alternative treatment technologies.
- A limited number of tracking compounds chosen for their ability to gauge process performance and issues of regulatory concern should be identified and analyzed for in the treatment effluent.
- To supplement tests on EDS neutralents, the Army should collect information about the kinetics and thermody-

namics of the destruction of these tracking compounds by the preferred destruction technology.

• Physical properties of neutralents such as phase behavior (including suspended solids) and flash point should be determined on neutralent samples obtained from EDS-1 and EDS-2 treatment of actual chemical munitions.

Regulatory Issues

Finding: EDS neutralent may be treated off-site or on-site. If the EDS liquid waste is treated off-site, the Army must obtain a permit for a new facility or find a permitted hazardous waste treatment facility or a FOTW or POTW that can treat the EDS liquid wastes. If a facility with an existing permit is used for treatment, that existing permit may require modification.

Finding: Based on available data and the experience of the members of the committee, the chemical constituents most likely to be of concern in the RAP process for EDS liquid wastes are chlorinated organics, possible degradation products of energetic compounds, metals, suspended solids, ¹⁵ and monoethanolamine (MEA). These constituents were chosen based on their abundance in the neutralent, their inherent toxicity, their resistance to treatment, or overall regulatory and public concern.

Recommendation: The Army's RAP strategy should ensure that sufficient information is obtained about the chemical constituents of greatest concern in the RAP process for the EDS liquid wastes: chlorinated organics, degradation products of energetic compounds, metals, suspended solids, and MEA.

Finding: RAP options associated with treatment of EDS neutralents, rinsates, and cleaning solutions depend on whether the waste is regulated as hazardous within the state where it is generated and, if it is, whether it is a "listed" hazardous waste, a "characteristic" hazardous waste, or both.

If EDS liquid wastes are determined to be hazardous under the federal RCRA program (via the RCRA characteristics), RCRA's land disposal restrictions (LDRs) apply, and the wastes must be treated to meet specific requirements.

Note that the remainder of the findings and recommendations in this section are based on the premise that neutralent (but not necessarily rinsate or residue) will be defined as hazardous waste. This may not always be the case, although the Army's policy to date has been to treat the neutralent as hazardous waste.

¹²If any of the technologies in track one can be demonstrated to work and be cost effective, then the committee recommends that research and development on track two technologies be terminated. However, the strict time constraints imposed by the CWC—i.e., that all NSCWM recovered prior to 1997 must be destroyed by 2007—in effect require that the two tracks be pursued at the same time.

¹³One example of a tracking compound for destruction of nerve agents might be methylphosphonic acid, which is very stable and difficult to destroy. Further discussion of tracking compounds may be found in Appendix D.

¹⁴As noted in Chapter 2, the compositions of EDS neutralents from destruction of separate NSCWM will not necessarily be consistent, even for munitions of the same type.

¹⁵Suspended solids are a concern only if they are determined to contain residual chemical agent in microscopic cracks and crevices. See discussion in Chapter 2.

ALTERNATIVE TECHNOLOGIES FOR DISPOSAL OF LIQUID WASTES FROM THE EXPLOSIVE DESTRUCTION SYSTEM

Finding: In the near term, the Army is likely to continue to use permitted hazardous waste incinerators to dispose of EDS liquid wastes (especially neutralents), because of their proven effectiveness. Many commercial hazardous waste facilities use nonincineration technologies to treat wastes similar to EDS liquids and might also be available.

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Finding: Dilute aqueous rinsates from the EDS and wastes resulting from treatment of neutralent may be classified as listed hazardous wastes either as a result of the "derived from" rule or because the state explicitly lists the rinsate. However, these solutions are primarily water with much lower concentrations of hazardous constituents than the initial neutralent. As a result, they pose relatively little risk and could probably be safely managed as nonhazardous wastes, thereby lowering disposal costs without causing any meaningful change in the degree of protection.

Finding: The EDS treatment process also generates spent cleaning solutions that are distinct from the rinses. The cleaning solutions are a mixture of aqueous detergent solutions and a dilute acetic acid wash. The detergent apparently has a tendency to leach chloroform out of the solvent-based sealant used on the EDS seals. While the acetic acid may also leach metals from the walls of the EDS, the levels of these metals appear not to be high enough to warrant considering the resulting waste as hazardous. The chloroform may be of concern, however. Except for the higher amounts of chloroform, these solutions are also primarily water, generally with much lower concentrations of hazardous chemicals than the initial neutralent. As a result, if chloroform is not generated in the EDS cleaning process, even the aqueous cleaning solutions could probably be safely managed as nonhazardous waste.

Finding: The Army has suggested that the chloroform found in the rinsate is leaching from a sealant utilized in the EDS. There may be other equivalent sealants that do not contain chloroform and that could be substituted for these sealants.

Recommendation: The Army should expeditiously substitute a sealant that does not contain chloroform in the existing EDS systems and all future EDS units.

Recommendation: In states where rinsates, cleaning solutions, or wastes resulting from treatment of neutralent are listed as hazardous wastes or are considered hazardous waste because they are derived from treatment of a listed hazardous waste, the Army should work with the state regulators toward the designation of these wastes as nonlisted hazardous waste. For spent cleaning solutions, this recommendation assumes that the source of chloroform in the rinses can be eliminated. The Army should collect all data on the EDS rinsates and cleaning solutions for presentation to the state

regulators in support of a hazardous waste listing determination. If it is found that these wastes do not meet the hazardous waste listing criteria, they should be designated nonlisted hazardous waste by modifying the state regulations or the permit or equivalent documentation. While the state regulators could require the Army to submit RCRA delisting petitions, the committee believes that a modification in the state regulations or in the permit or equivalent documentation would be the more cost-effective option.

Recommendation: The Product Manager for Non-Stockpile Chemical Materiel (PMNSCM) should work with regulators and the concerned public to resolve RAP issues surrounding the EDS waste streams well in advance of EDS deployment to a particular site.

Finding: Regulatory issues related to the posttreatment of liquid wastes (neutralents, rinsates, and cleaning solutions) produced by the EDS are distinct and different from the regulatory issues related to use of the EDS itself. There are a number of RAP mechanisms that could be used for management of EDS liquid wastes.

With the proper approvals or permits, treatment of EDS liquid wastes may be conducted on-site or at off-site facilities. In some cases, treatment may be conducted under a facility's existing treatment, storage, and disposal facility (TSDF) permit, if that permit is written sufficiently broadly to allow acceptance of EDS liquid wastes. Other options include obtaining a hazardous waste permit for treatment, modifying an existing hazardous waste treatment permit, using emergency exemptions available under most state hazardous waste regulations, obtaining an emergency permit under the state hazardous waste regulations, using a RCRA compliance order (RCRA §§ 3008(a), 3008(h) or 7003), or using the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) removal authority. In some cases, the wastes could be managed under a waste management plan established under a CERCLA record of decision. RCRA research, development, and demonstration (RD&D) permits and treatability studies may also be appropriate in certain cases.

Recommendation: The Army should develop RAP guidance for field personnel (e.g., base commanders) on the disposition of EDS neutralent and rinsate waste streams, taking into consideration the nature of the NSCWM and the specific regulatory environment at locations where the EDS might be sited. This guidance should cover all aspects of RAP for the EDS and treatment (as necessary) of neutralents and rinsates, including setup, operation, and closure. Development of this guidance should be coordinated with the states, and a jointly issued guidance document should be considered.

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Public Acceptability Issues

Finding: The committee's earlier conclusions (NRC, 2001a) concerning public acceptability for RRS and MMD neutralent treatment processes also apply to treatment of EDS neutralents and rinsates. The committee's discussion with citizen groups indicated a need for—and the value of—public involvement in the Army's decisions on the selection and deployment of technologies for disposing of neutralents and, indeed, all nonstockpile chemical materiel.

Recommendation: The Army should continue to expand its program for public involvement in the disposal of nonstockpile chemical materiel. Enough time should be scheduled and enough resources allocated to ensure that the decision-making process is open and that members of the public are involved in making the trade-offs among the selection, siting, deployment, and employment of disposal technologies.

1

Background and Overview

This report supplements an earlier report (NRC, 2001a) that evaluated eight alternative technologies¹ for destruction of the liquid waste streams from two of the U.S. Army's transportable treatment systems for nonstockpile chemical materiel:² the rapid response system (RRS)³ and the munitions management device (MMD).⁴ This report evaluates the same technologies for the destruction of liquid waste streams produced by a third transportable treatment system, the explosive destruction system (EDS).

The EDS is a trailer-mounted system (a schematic is shown in Figure 1-1) that can be driven or flown to a site where nonstockpile chemical materiel is discovered or where recovered materiel has been stored. In the EDS, the nonstockpile munition or container of chemical agent to be destroyed is first enclosed in a sealed chamber. The munition is then opened by detonating shaped explosive charges that are also intended to detonate any explosives present inside the munition. The chemical fill thus accessed is then neutralized by appropriate reagents that are pumped into the chamber. After the concentration of chemical agent falls

below the treatment goal (see Chapter 2), the liquid waste solution is transferred out of the chamber into a waste drum.

The EDS is capable of treating both nonexplosively configured munitions and explosively configured munitions. EDS Phase 1 (EDS-1) handles munitions with up to one pound TNT-equivalent weight of explosives; EDS Phase 2 (EDS-2), under development, is designed to handle munitions with up to three pounds TNT-equivalent weight of explosives. The EDS is intended for use with World War I and World War II vintage chemical warfare material produced prior to 1945. Post-World War II munitions have larger bursters, which exceed the capacity of the system.

The Army's baseline plan for destruction of the drummed EDS liquid waste is to incinerate it in a commercial treatment, storage, and disposal facility (TSDF). However, concerns raised by some public interest groups have prompted greater interest in evaluating alternative, nonincineration technologies for liquid waste destruction.

The EDS was originally developed to destroy nonstock-pile items that were judged to be too unstable for transport or long-term storage. As such, it was intended to complement the MMD systems, which were designed to be the mobile systems of choice for the treatment of nonstockpile items deemed stable enough for recovery operations. However, the prototype MMD system to dispose of nonexplosively configured munitions proved to be complex, expensive, and difficult to permit. A system that would dispose of explosively configured munitions was designed but never built. The EDS is a smaller and less complex system than these MMD systems, and it is now considered the Army's transportable system of choice for treatment of small quantities of nonstockpile munitions.

¹The technologies were chemical oxidation, wet-air oxidation, electrochemical oxidation using Ag(II) or Ce(IV), supercritical water oxidation, solvated electrons, biodegradation, gas-phase chemical reduction, and plasma arc.

²Nonstockpile chemical materiel includes all materiel not part of the chemical weapons stockpile, such as buried chemical weapons, recovered chemical weapons, binary chemical weapons, former production facilities and miscellaneous chemical materiel.

³The RRS is a mobile glove box designed to dispose of chemical agent identification sets (CAIS). CAIS are test kits used from 1928 to 1969 to train soldiers in chemical warfare. The sets contain small amounts of mustard and lewisite and a variety of highly toxic industrial chemicals.

⁴The MMD systems were conceived to dispose of nonstockpile chemical munitions. MMD Version 1 was designed to dispose of nonexplosively configured chemical munitions. A second version, never constructed, was designed to dispose of munitions containing both agent and explosives.

⁵The process of obtaining a RCRA permit for initial testing of the MMD-1 in the state of Utah has taken over 5 years.

⁶Sites with a large number (that is, hundreds or thousands) of nonstockpile items are expected to be served by semipermanent treatment facilities.

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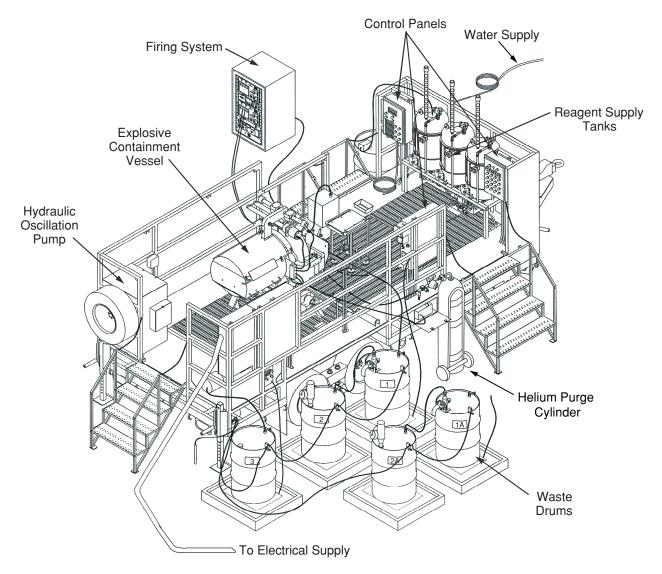


FIGURE 1-1 Diagram of the EDS-1 vessel on its trailer. SOURCE: U.S. Army (2001b).

Recently, the Army collected data on the performance of the prototype EDS-1 during two disposal campaigns. One campaign involved interim testing of the EDS-1 on a variety of containers of chemical agent and nonstockpile munitions; it was carried out in Porton Down, United Kingdom, from November 1999 to November 2000 (U.S. Army, 2000). The other campaign involved the destruction of six bomblets containing the agent sarin (GB) at Rocky Mountain Arsenal (RMA) in January and February 2001 (U.S. Army, 2001b). The Army provided the committee with preliminary data on the neutralization processes and the composition of the EDS liquid waste streams resulting from those campaigns.

STATEMENT OF TASK

On March 16, 2001, the Army Non-Stockpile Chemical Materiel Program (NSCMP) requested that the NRC undertake a brief supplemental assessment of alternative technologies for the destruction of EDS liquid waste streams. The statement of task is as follows:

The NRC will:

- Examine alternative destruction technologies for liquid waste streams generated from the Explosive Destruction System (EDS).
- Discuss the regulatory approval issues and obstacles for the combined use of the EDS and the alternative technologies that treat the EDS secondary waste streams.

⁷Subsequently, four more bomblets were discovered during remediation of the same area at RMA. At this writing, the EDS-1 had been dispatched to dispose of these also.

COMMITTEE APPROACH

In its earlier report (NRC, 2001a), the committee evaluated eight of the most promising alternative technology candidates for destruction of liquid waste streams from the RRS and MMD. The purpose of the present report is to evaluate these same eight technologies for destruction of EDS liquid waste streams. However, the committee notes that there have been several important developments since the publication of its last report:

- The MMD program has been suspended; this means that the liquid waste streams generated by nonstockpile mobile treatment systems will be primarily from the EDS, with a small volume from the RRS.
- New data have become available from the Army's Technology Testing Program (see Chapter 3) and from its Assembled Chemical Weapons Assessment (ACWA) program on the performance of several of the alternative technologies.⁸

The primary approach used in this report is to evaluate the ability of alternative technologies to process EDS liquid waste streams and to examine the extent to which the different compositions of the MMD and EDS liquid waste streams might alter the committee's earlier recommendations on technologies for their destruction. These recommendations are also reconsidered in light of the most recent technology testing results.

Because data on the composition of EDS liquid waste streams are still incomplete, the committee found it necessary to make conservative assumptions or to assume the worst case in order to ensure that the recommendations are protective of health, safety, and the environment. Where such assumptions were made, they are duly noted. The committee also highlighted those areas where additional EDS test data are needed to resolve key issues.

REPORT SCOPE

The committee wishes to stress that this report is a supplemental evaluation that is focused on the destruction of EDS liquid waste streams. Nothing discussed here should be interpreted as the committee's evaluation of the EDS as a complete operating system. Such an evaluation would have to examine issues such as the structural integrity of the EDS with repeated use, operational procedures, and the EDS's process chemistry, and would have to assess whether a secondary vapor containment structure is needed. A broader discussion of the system itself could be considered in a future report on systems for the destruction of nonstockpile materiel.

The scope of this report is in almost all respects parallel to that of the committee's earlier report on the treatment of liquid waste (NRC, 2001a). Only the liquid waste streams of the EDS are considered; no consideration is given to the treatment of solid waste streams. Similarly, no consideration is given to gaseous emissions that may escape through the carbon filter of the waste drum or from the containment chamber as it is opened. In this report, the neutralizing reagents (e.g., monoethanolamine (MEA)) chosen by the Army for use in the EDS-1 are taken as a given; no effort is made to examine how changes in the neutralizing reagents might affect the composition of the liquid waste streams and the applicability of posttreatment technologies.

One difference from the earlier report arises from a difference in the procedures used in the EDS and the MMD. Because the EDS is opened after destruction of each individual CWM item, it must be rinsed several times to remove residuals following the initial agent neutralization step. These dilute aqueous rinsates are considered in this report as a separate EDS liquid waste stream. MMD rinsates were not considered separately in the earlier report.

As was the case for RRS and MMD wastes covered in the earlier report, the treatment goals for the EDS neutralent destruction technologies considered are that the chemical species and their concentrations in the treatment residuals are such that the residuals could be released directly into the environment or to a publicly owned (or federally owned) treatment works (POTW or FOTW). Because this is a supplemental report, only the eight treatment technologies considered previously are considered here; the same criteria used previously to evaluate these technologies are also applied here (see Appendix E).

While the focus of this report is on the liquid waste streams from the EDS, the committee notes that it is not always possible to separate the regulatory approval and permitting (RAP) process for EDS liquid waste destruction technologies from the regulatory approval process for the EDS system as a whole. RAP issues for the overall EDS system are to be explored in greater detail in a subsequent report.

STRUCTURE OF THIS REPORT

Chapter 2 provides a brief description of the EDS, its operational history, the data available on the composition of EDS liquid waste streams, and a comparison with the composition of the MMD liquid waste streams. In Chapter 3, the

⁸The ACWA program was reviewed in several studies by another NRC committee (NRC, 1999a, 2000).

⁹The committee felt that, on the one hand, a technology need not be excluded if it did not completely mineralize the neutralents, so long as the resulting liquids could be sent for final treatment at a POTW/FOTW. On the other hand, the committee felt that multiple treatment technologies should not be necessary; the selected technology should be able to destroy neutralent such that the residuals could either be released to a POTW/FOTW or sent to a permitted landfill.

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committee examines the applicability of the technologies examined previously to the destruction of EDS liquid waste streams and ranks them in order of preference. Technology-specific findings and recommendations are also presented in Chapter 3.

In Chapter 4, RAP issues associated with the treatment and disposal of EDS liquid wastes, as well as issues relating to public acceptance of disposal processes for EDS liquid wastes, are discussed and appropriate findings and recommendations are presented.

2

Description of EDS Treatment Processes and Liquid Waste Streams

DESCRIPTION OF THE EXPLOSIVE DESTRUCTION SYSTEM

The Explosive Destruction System Phase 1 (EDS-1) is a trailer-mounted mobile system that is intended to destroy explosively configured chemical warfare munitions deemed unsafe to transport or store. The EDS-1 can also be used to destroy small quantities¹ of recovered chemical munitions, with or without explosive components. A schematic view of the EDS-1 appears at Figure 1-1; a detailed description of the system and its operation is found in Appendix F.

The heart of the EDS-1 is a 6.5-cubic foot (189-liter) explosion containment vessel mounted on a 20-foot-long flatbed trailer. The vessel body and door are made of forged 316 stainless steel and are designed to contain detonations of up to one pound (0.45 kg) of TNT equivalent. The vessel has an inside diameter of 51 cm and is designed to handle three commonly found chemical munitions: a 75-mm artillery shell, a 4.2-inch mortar, and a Livens projectile.

The explosion containment vessel contains the explosive shock, fragments, and chemical agents during the explosive opening of the munition and also serves as a processing vessel for subsequent treatment of the chemical agent that was contained in the munition.

The Army expects to fabricate three EDS-1 units. The EDS developer, Sandia National Laboratories, is also designing and fabricating an EDS Phase 2 (EDS-2), capable of handling nonstockpile items having up to three pounds of TNT-equivalent explosives. This larger version of the EDS will be able to destroy munitions as large as 155-mm projectiles. The Army plans to construct four EDS-2 units, two for operations and two for replacement units.

EXPERIENCE WITH THE EDS-1

At this writing, there have been two campaigns in which the EDS-1 was used to destroy actual chemical munitions: one at Porton Down, United Kingdom, and one at Rocky Mountain Arsenal, Colorado.

Porton Down

The EDS-1 was shipped to a United Kingdom testing facility at Porton Down on October 11, 1999. Following setup and personnel training, pretrial activities took place in November 1999 to test the explosive accessing methods and the introduction of reagents into the EDS-1.

After completion of the preliminary testing, tests of the EDS-1 with containers and munitions filled with the chemical agents phosgene (CG), sulfur mustard (HD), and sarin (GB) took place between late November 1999 and November 9, 2000. For phosgene, 11 items were tested: four cylinders and seven 4-inch Stokes mortars. For mustard, 14 items were tested: two cylinders, seven 4.2-inch mortar rounds, and five 4.5-inch projectiles. For sarin, one steel cylinder containing 1.3 pounds of agent was tested (U.S. Army, 2000).

Following the disposal of each munition and container at Porton Down, neutralents, rinsates, and vapors were tested by the Defence Evaluation and Research Agency of the U.K. Ministry of Defence. Using gas chromatography/mass spectrometry, tests were conducted for residual GB and HD, metals, and volatile and semivolatile organic compounds. Test results and analytical procedures used were provided to the committee (U.S. Army, 2001h). The compositions of the neutralents produced from EDS disposal of two representative mustard-filled munitions are presented in columns 3 and 4 of Table 2-1; the composition of the neutralent produced from the disposal of the single GB-filled container is shown in column 3 of Table 2-2, and the neutralent compositions from a representative munition and container containing

¹The processing rate of the EDS-1 is currently about one item every two days. Thus, it may be most appropriate for treatment of a few tens of items, rather than hundreds or thousands of items.

TABLE 2-1 Composition of Mustard (HD) Neutralent Derived from Treatment with 90 Percent MEA

Compound/Element	MMD at DPG, HD Sample (NRC, 2001a), Bench-Scale Test	EDS at PD, HD Projectile (U.S. Army, 2000a), Munition 92703	EDS at PD, HD Mortar (U.S. Army, 2000a), Munition 92704
Sulfur mustard ^a	<50 μg/L	<200 μg/L ^b	<200 μg/L ^b
1,4-Dithiane	80-1,600 mg/L ^b	113 mg/L ^b	$170~\mathrm{mg/L}^b$
Explosives	N/A	N/D	N/D
Semivolatile organics detected			
1,4-Dichlorobenzene	N/R	<0.6 mg/L	4.9 mg/L
Pentachlorophenol	N/R	<0.8 mg/L	4.9 mg/L
Pyridine	N/R	<0.7 mg/L	2.2 mg/L
Volatile organics detected			
Benzene	N/R	6.1 mg/L	11.4 mg/L
Chlorobenzene	N/R	178.4 mg/L	152.4 mg/L
Chloroform	0.14-0.2 mg/L	<1 mg/L	<1 mg/L
Vinyl chloride	5.8-6.9 mg/L	<1 mg/L	<1 mg/L
Metals detected			
Lead	N/R	9,600 μg/L	2,300 μg/L
Silver	N/R	15 μg/L	3.6 µg/L
Selenium	3.0-3.6 ppm	<0.15 ppm ^c	<0.15 ppm ^c
Arsenic	0.14-0.23 ppm	<0.05 ppm ^c	<0.05 ppm ^c
Calcium	N/R	12 mg/L	11 mg/L
Mercury	N/R	2.1 μg/L	0.6 µg/L
Chromium	0.53-0.62 ppm	0.34 ppm^c	0.32 ppm ^c
Barium	N/R	3.0 mg/L	4.4 mg/L

NOTE: N/A, not applicable; N/R, not reported; and N/D, not detected. Explosives detection limits at Porton Down: 50 mg/L for HMX, RDX, TNT, tetryl; 65 mg/L for nitrocellulose; 30 mg/L for nitroglycerin. Semivolatile organics (SVOCs) analyzed at Porton Down: 1,4-dichlorobenzene, 2,4- and 2,6-dinitrotoluene, hexachlorobutadiene, nitrobenzene, o-cresol, pentachlorophenol, pyridine, 1,2,4-trichlorobenzene, 2,4,5- and 2,4,6-trichlorophenol. Detection limit on all SVOCs except pyridine was 0.6 mg/L; that for pyridine was 0.7 mg/L. Volatile organics (VOCs) analyzed at Porton Down: benzene, carbon tetrachloride, chlorobenzene, chloroform, 1,4-dichlorobenzene, 1,2-dichloroethane, 1,1-dichloroethylene, 1,1,1,2- and 1,1,2,2-tetrachloroethane, trichloroethylene, 2-butanone (methyl ethyl ketone (MEK)), and vinyl chloride. Detection limit was 1 mg/L on all VOCs.

phosgene are shown in columns 3 and 4 of Table 2-3. These analytical results are based on samples of each neutralent.

Rocky Mountain Arsenal

After the completion of testing at Porton Down, the EDS-1 was shipped to the Edgewood Area of the Aberdeen Proving Ground, Maryland, on November 24, 2000, to prepare it for operational testing. Before this could take place, however, the EDS-1 was sent to Rocky Mountain Arsenal (RMA) near Denver, Colorado, on December 17, 2000, to support the emergency destruction of six M139 bomblets, each of which contained about 1.3 pounds of the nerve agent GB. These bomblets had been recovered from a scrap pile in a former parking lot and, based on their fuze design, were considered to be unsafe for transport to a storage area.

Following a preoperational survey, the EDS destroyed the bomblets without incident between January 28 and February 9, 2001. The EDS was then decontaminated and returned to Aberdeen Proving Ground on March 3, 2001.

Following the destruction of each bomblet at RMA, neutralent and rinsate samples were tested by the on-site Environmental Analytical Laboratory for residual GB, metals, GB decomposition products, residual explosives, and volatile and semivolatile organic compounds. Test results and analytical procedures were provided to the committee (Foster Wheeler, 2001). The composition of the neutralent for a representative munition (bomblet 3) is shown in column 4 of Table 2-2. These data are based on a single analytical sample of the neutralent. For all six bomblets, the ranges of both neutralent and water rinse components are presented in Appendix C, Table C-1.

[&]quot;The higher detection limits for sulfur mustard in the EDS tests at Porton Down reflect the GC/MS analytical procedure used by the Defence Evaluation and Research Agency in the United Kingdom, which, along with contracted commercial laboratories, performed the neutralent analyses.

 $^{^{\}textit{b}}\text{For ease}$ of comparison, the original units of $\mu\text{g/ml}$ and % are converted to mg/L or $\mu\text{/L}.$

^cFor ease of comparison, the original units of μg/L and mg/L have been converted to ppm (mg/kg).

14 ALTERNATIVE TECHNOLOGIES FOR DISPOSAL OF LIQUID WASTES FROM THE EXPLOSIVE DESTRUCTION SYSTEM

TABLE 2-2 Composition of Sarin (GB) Neutralent Derived from Treatment with 45 Percent MEA in Water

Compound/Element	MMD at DPG, GB Sample (NRC, 2001a), Bench-Scale Test	EDS at PD, GB Cylinder (U.S. Army, 2000), Sample GB-DOT-01	EDS at RMA, Bomblet 3 (U.S. Army, 2001e), Munition MEAB31
Monoethanolamine (MEA)	33.9-40.3%	N/R	44.9%
Water	49.0-49.4%	N/R	55.1%
GB degradation products MEA IMPA salt (O-isopropyl methylphosphonate)	0.7-8.5%	N/R	4,300 ppm on 4-hr sample
Diisopropyl methylphosphonate (DIMP)	0.03-0.36%	DIMP detected	22,100 μg/L
Sarin (GB)	<25 ppb	<100 ppb ^a	<103 ppb
рН	N/R	12.3	12
Explosives	N/A	N/D	<1 mg/L
Volatile organics detected			
Benzene	6.5-6.8 mg/L	3.3 mg/L	2.64 mg/L
Chlorobenzene	N/R	1.1 mg/L	N/R
Dichloromethane	N/R	N/R	97.1 μg/L
Toluene	N/R	N/R	810 µg/L
Metals detected			
Lead	550-1,300 ppb b	96 ppb ^a	237 ppb ^a
Silver	N/R	<2.0 μg/L	<174 μg/L
Selenium	N/R	<150 µg/L	N/R
Arsenic	660-760 ppb ^b	<50 ppb ^a	<200 ppb ^a
Calcium	N/R	1.6 mg/L	N/R
Mercury	N/R	0.4 μg/L	<0.5 µg/L
Chromium	410-1,080 ppb b	450 ppb ^a	703 ppb ^a
Barium	N/D-750 ppb ^b	$3,000 \text{ ppb}^a$	<44.7 ppb ^a
Aluminum	76-81.5 ppm	N/R	9.35 ppm ^c
Cadmium	N/R	N/R	<6.81 μg/L
Zinc	N/R	N/R	30,000 µg/L
Copper	N/R	N/R	18,200 μg/L

NOTE: The RMA results are on waste drum 1 (MEAB31) or, for the IMPA analysis, on the 4-hr sample from bomblet 3 (2001-02-02). Analyses for bomblet 3 wastes were chosen as being the most comprehensive. N/A, not applicable; N/R, not reported; and N/D, not detected. Explosives detection limits at Porton Down: 50 mg/L for HMX, RDX, TNT, tetryl; 65 mg/L for nitrocellulose; 30 mg/L for nitroglycerin. Semivolatile organics (SVOCs) analyzed at Porton Down: 1,4-dichlorobenzene, 2,4- and 2,6-dinitrotoluene, hexachlorobutadiene, nitrobenzene, o-cresol, pentachlorophenol, pyridine, 1,2,4-trichlorobenzene, 2,4,5- and 2,4,6-trichlorophenol. Detection limit on all SVOCs except pyridine was 0.6 mg/L; that for pyridine was 0.7 mg/L. Volatile organics (VOCs) analyzed at Porton Down: benzene, carbon tetrachloride, chlorobenzene, chloroform, 1,4-dichlorobenzene, 1,2-dichloroethane, 1,1-dichloroethylene, 1,1,1,2- and 1,1,2,2-tetrachloroethane, trichloroethylene, 2-butanone (methyl ethyl ketone (MEK)), and vinyl chloride. Detection limit was 1 mg/L on all VOCs.

[&]quot;For ease of comparison, the original units of g/ml, μ g/L, and mg/L have been converted to ppb (μ g/kg).

^bAs contained in the Utah MMD permit, available at http://www.eq.state.ut.us/eqshw/cds/ MMDPermit.htm>. RCRA toxicity-characteristic component concentration is less than TCLP regulatory limit.

^cFor ease of comparison, the original units of μg/L have been converted to ppm.

TABLE 2-3 Composition of Phosgene (CG) Neutralent Derived from Aqueous Caustic Treatment

Compound/Element	MMD at DPG CG Sample (NRC, 2001a), Bench-Scale Test	EDS at PD CG Mortar (U.S. Army, 2000), Munition 1051905	EDS at PD CG Cylinder (U.S. Army, 2000), Munition CG-MOCK-2
Sodium hydroxide content or pH	8-9%	pH 13-14	pH 13-14
Explosives	N/A	N/D	N/D
Semivolatile organics	N/R	N/D	N/D
Volatile organics	N/R	N/D	N/D
Metals detected			
Lead	N/R	2,100 μg/L	280 μg/L
Silver	N/R	19 μg/L	13 μg/L
Selenium	N/R	<150 µg/L	2,200 μg/L
Arsenic	N/R	0.42 mg/L	<150 mg/L
Calcium	N/R	7.2 mg/L	23 mg/L
Mercury	N/R	1.5 µg/L	0.9 µg/L
Chromium	N/R	<0.05 mg/L	5.3 mg/L
Barium	N/R	11.5 mg/L	8.5 mg/L

NOTE: N/A, not applicable; N/R, not reported; and N/D, not detected. Explosives detection limits at Porton Down: 50 mg/L for HMX, RDX, TNT, tetryl; 65 mg/L for nitrocellulose; 30 mg/L for nitroglycerin. Semivolatile organics (SVOCs) analyzed at Porton Down: 1,4-dichlorobenzene, 2,4- and 2,6-dinitrotoluene, hexachlorobutadiene, nitrobenzene, o-cresol, pentachlorophenol, pyridine, 1,2,4-trichlorobenzene, 2,4,5- and 2,4,6-trichlorophenol. Detection limit on all SVOCs except pyridine was 0.6 mg/L; that for pyridine was 0.7 mg/L. Volatile organics (VOCs) analyzed at Porton Down: benzene, carbon tetrachloride, chlorobenzene, chloroform, 1,4-dichlorobenzene, 1,2-dichloroethane, 1,1-dichloroethylene, 1,1,1,2- and 1,1,2,2-tetrachloroethane, trichloroethylene, 2-butanone (methyl ethyl ketone (MEK)), and vinyl chloride. Detection limit was 1 mg/L on all VOCs.

OPERATIONAL PROCESSES OF THE EDS-1

Predetonation Procedure

Before the munition is placed in the EDS containment vessel, it is surrounded by a fragment suppression system (FSS) (see Appendix F) to protect the walls of the EDS containment vessel from high-velocity fragments of the detonation. The FSS is also used to mount and properly locate the explosive charges used to access the chemical fill and detonate the fuze and burster of the munition. A linear shaped charge cuts open the munition and exposes its contents for chemical treatment, and conical shaped charges detonate the internal energetic compounds. The shaped charges are composed of RDX or Composition A, an RDX/polyethylene composite.

Following the preparation of the sealing surface of the EDS-1 vessel door and installation of a new o-ring, the door is closed and a leak test is conducted. If no leaks are detected, detonation is initiated. Although the detonation produces high temperature and pressure transients, the reactions with the neutralizing reagents take place at 25° to 60°C and pressures slightly above ambient.

The explosion of the RDX linear shaped charge and the Composition A-3 conical shaped charge was estimated by Army experts to be 99 percent complete (U.S. Army, 2001h, enclosure 1). In only one of the RMA tests was any intact

RDX found in a solid residue. In all the RMA tests, the liquid effluent contained less than 1,000 ppm of RDX or other explosives. Although the explosion may destroy some of the chemical agent contained in the munition, the agent destruction products appear to arise primarily from the subsequent neutralization process. The concentration of IMPA, the primary GB hydrolysis product, in the neutralent corresponds to between 70 and 90 percent of the agent originally present (U.S. Army, 2001c). Other hydrolysis products were also present, suggesting that, at least with GB, most of the agent survives the blast and is destroyed by the neutralizing reagent.

Postdetonation Treatments and Liquid Waste Streams

After the contents of the munition have been released into the EDS vessel, a neutralizing reagent is introduced to destroy the chemical agent and any remaining energetics. The reagents used in the EDS-1 to neutralize three of the most common chemical munition fills—sulfur mustard, phosgene, and sarin—are shown in Table 2-4.²

²A complete list of proposed reagents for various chemical agents is provided in U.S. Army, 2001e, table 3-1.

Chemical Fill	Solution and Waste Disposition	Chemical Treatment (Source of Neutralent) ^a	Second Treatment (Source of Rinsate) ^b	Rinses (Source of Rinsate) ^c	End-of-Run Cleaning Solution ^d	End-of-Campaigr Cleaning Solution ^e
Mustard (HD)	Composition	90% MEA/H ₂ O (60°C)	Water (100°C)	Water (ambient)	Water/detergent (ambient)	H ₂ O/vinegar
	Collection	Drum 1	Drum 2	Drum2	Drum 3	Drum 3
Phosgene (CG)	Composition	$20\text{-}22\% \text{ NaOH/H}_2\text{O}$ (ambient)	Not needed	Water (ambient)	H ₂ O/detergent	H ₂ O/vinegar
	Collection	Drum 1		Drum 2	Drum 3	Drum 3
Sarin (GB) ^c	Composition	45% MEA/H ₂ O (25°C)	Water (100°C)	Water (ambient)	H ₂ O/detergent	H ₂ O/vinegar
	Collection	Drum 1	Drum 2	Drum 2	Drum 3	Drum 3
Lewisite (L) ^f	Composition	20% NaOH (ambient)	NA	Water (ambient)	H ₂ O/detergent	H ₂ O/vinegar
	Collection	Drum 1	Drum 2	Drum 2	Drum 3	Drum 3

NOTE: There are no known nonstockpile munitions containing VX. Were such munitions to be found, the reagent is expected to be a combination of MEA and aqueous NaOH.

SOURCE: Michael L. Duggan, Group Leader, Mobile Systems Acquisition, "Explosive Destruction System (EDS)," presentation to the committee, June 15, 1999; U.S. Army 2001d; U.S. Army 2001e; U.S. Army 2001f.

Based on current and expected operation of the EDS, four types of liquid wastes are generated:

- *neutralent*, consisting of the initial treatment of agent with active reagent (e.g., MEA) and any subsequent chamber washes with chemical reagent (if used)
- *rinsates*, consisting of additional agent treatment with water and chamber washes with water after opening the EDS
- *cleaning solutions*, consisting of washes (water/detergent) that are made between processing of each munition, and final washes (e.g., water/vinegar) made after completing a munitions campaign
- *final washes*, using, for example, water and acetic acid, carried out after completing a munitions campaign

The expected source and handling scheme for these wastes is presented in Table 2-4. The term "treatment" is used to describe steps involving addition of reagent or water to the EDS and agitation for a certain period prior to opening

the chamber. Note that water treatment and rinse water wastes are combined (rinsate). To date, the Army has chosen to segregate the four types of waste, in order to keep open the option of a separate treatment strategy for the waste streams that are primarily water.³

For treatment of the residues from an HD-containing munition, a monoethanolamine (MEA) solution (90 percent MEA, 10 percent water) is heated to 60°C. The EDS chamber is at 50°C at the time of the addition. After the MEA is added, the mixture is agitated by rocking (EDS-1) the containment vessel (the EDS-2 design envisages rotating the containment vessel),⁴ and the temperature is maintained at

^aTemperatures shown in parentheses are vessel temperatures.

^bInitial tests at Porton Down included a second chemical treatment with reagent, but this was discontinued after munition 1061602.

^cInitial tests at RMA included rinses with MEA/water solution, but this was discontinued after bomblet 2.

^dDetergent is used periodically to remove lubricant from metal door seal.

^eUnited Kingdom only: denatured alcohol, potassium hydroxide, bleach, and water. RMA: vinegar (acetic acid) and water are used for line rinsing periodically. Water, bleach, and detergent are used for hardware cleaning.

fLewisite has not yet been treated in the EDS at this writing.

³The treatment neutralent is transferred to a 55-gallon drum. The subsequent water rinsates are transferred to a second drum, and cleanup wash water is discharged to a third drum (see also Figure 1-1).

⁴Rotation of the EDS-2 containment vessel should improve mixing of the released chemical agent with the neutralizing reagents and thus could reduce the munition processing time, compared with the EDS-1.

60°C for 4 hours. Samples of the liquid in the vessel are withdrawn periodically until the HD concentration is less than 50 ppm, the current detection limit in HD neutralent solutions that may contain compounds that interfere with the detection of HD. When the treatment is complete, the vessel liquid contents are drained from the vessel and transferred to a storage drum. The vessel is then treated with 100°C water to decompose small amounts of mustard occluded in solid residues as well as to remove residual MEA and reaction products. After repeated rinsing with water, the vessel is flushed with helium or other inert gas to remove residual HD vapor that may be present in the headspace. The helium and any agent vapor are passed through a carbon filter to capture the agent. The helium is then released to the atmosphere. Before the vessel is opened, a gas sample is bled off into a test bag and tested. If there is a positive reading for agent, additional treatment will take place. Several detectors are available that can be set to detect various agent types; the analysis takes about 6 minutes. The vessel is then opened to remove any solid residues. The neutralent, the 100°C posttreatment water/rinse water, and the solids are stored in separate waste drums.

Similar procedures are used to neutralize other chemical agents, but the treatment cycle and the neutralizing reagent are specific to each type of chemical agent. For treatment of the GB-containing bomblets at RMA, the EDS vessel was maintained at 25°C and oscillated during reaction with a 45 percent MEA solution in water. A neutralent sample was collected after 2 hours and was analyzed for agent concentration. Additional samples were taken every 2 hours until the GB concentration dropped below the detection limit of 1 mg/L (1 ppm). When this end point was reached, the neutralent was transferred to a container for liquid waste. The vessel was then rinsed with 65 L water at 40°C to 50°C (U.S. Army, 2001d). Appendix C describes the neutralent, rinsate, and cleaning solution waste streams that resulted from destruction of the GB bomblets in the EDS.

The reagents used to treat the postdetonation materials contained within the EDS chamber are essentially identical to those used in the MMD (NRC, 2001a). Like those used in the MMD, the EDS reagents produce neutralents and organic-contaminated water washes that require posttreatment before ultimate disposal. The aqueous EDS reagents, listed in Table 2-4, differ substantially from the nonaqueous reagents used in the RRS system to destroy CAIS items (see NRC, 2001a). RRS reagents and procedures are not appropriate for the munitions to be processed in the EDS and are not discussed in this report.

EDS LIQUID WASTE VOLUME AND COMPOSITION DATA

Useful data on the composition and quantity of EDS waste streams have come from the tests at Porton Down (PD) (U.S. Army, 2000) and the emergency destruction campaign at

TABLE 2-5 Summary of Liquid Wastes from EDS Tests to Date

		Liquid Wastes			
Test Site/Agent	Munitions Destroyed	Average Volume/Test (gal) ^a	Agent Content (μg/ml) ^b		
PD/CG	4 cylinders, 7 mortar rounds	53	<1°		
PD/HD	2 cylinders, 12 mortar rounds or projectiles	61	<0.2		
PD/GB	1 cylinder, 1.3 lb GB	67	<0.1		
RMA/GB	6 GB-filled bomblets, 1.3 lb GB in each	74	<0.1		

"The volume reported is an average and includes neutralent, a postreaction wash, and rinse liquid. The postreaction wash was either dilute reagent or water; subsequent rinses used water. The liquids were collected and stored separately. The volume reported does not include the cleaning solution to clean the EDS after test completion.

 b The concentration of CWM in the neutralent after 4 hours reaction was below the analytical detection limit. The detection limits of <1 ppm (1 µg/ml ~ 1 ppm for dilute aqueous solutions) for CG and <0.2 ppm for HD were safely lower than the treatment goal of <50 ppm for these two agents (U.S. Army, 2000a). Likewise, the detection limit of <0.1 ppm for GB was adequately lower than the treatment goal of <1 ppm (U.S. Army, 2001a).

^cThe liquid waste was analyzed for phosgene in only one test. The vapor phase often showed low levels of phosgene; original units of mg/L changed to μg/ml.

SOURCE: Compiled by the NRC from Army sources.

RMA (U.S. Army, 2001d). Table 2-5 summarizes the amount of liquid waste produced in test experiments and the effectiveness of the neutralization as judged by the amount of residual agent in the liquid effluents produced. More detail on the EDS-1 waste compositions is provided in Tables 2-1 to 2-3, along with the available data on the compositions of MMD neutralents.⁵ MMD and EDS neutralent component listings are not comparable because different sets of constituents were analyzed, the analysis detection limits were different, and the magnitude of operations/tests differed. As noted in Tables 2-1, 2-2, and 2-3, the analytical data are for neutralents from specific munition items. The ranges of analyses for neutralents from the six GB bomblets treated at RMA are shown in Table C-1. However, the data

⁵The MMD neutralent analysis data come from bench-scale tests conducted at Dugway Proving Ground (DPG), Utah, rather than from actual operation of the MMD.

in the tables permit concluding that EDS and MMD neutralents are similar and should be treatable by the same posttreatment technologies. This having been said, the difference in analytical methods means that this conclusion must be stated in a qualitative rather than a quantitative way.

In the destruction of the six bomblets at RMA, a total of 196 gallons of neutralent were produced along with 248 gallons of rinse water (U.S. Army, 2001f). The compositions of the GB neutralents, the water rinses, and the liquids resulting from cleaning the EDS transfer lines between operations are tabulated in Appendix C. It appears that the transfer lines were cleaned with aqueous acetic acid between campaigns and with aqueous detergent between treatment of individual rounds. The used cleaning solutions were combined for disposal.⁶ As noted in Table C-1 of Appendix C, surprisingly high levels of chloroform are noted in the used cleaning solutions from cleaning the EDS after a munition has been processed. The concentrations are sufficiently high to raise a question about the suitability of this aqueous waste stream for processing in a FOTW facility. (This waste stream from the RMA operation was sent to a commercial TSDF for disposal.) That the concentration of chloroform in the cleaning solution is higher than in the neutralent or rinsate suggests that it arises from the cleaning process rather than from the detonation or the neutralization processes. The Army supposes that it comes from the commercial lubricant Perma-Slik, which is used to lubricate and seal the door seals on the EDS.⁶ The lubricant may be washed off the door seal during the detergent rinse of the apparatus after treatment of each munition. This explanation seems likely because the lubricant was formulated from a mixture of organic solvents including trichloroethane. Newer formulations substitute ethyl acetate for the trichloroethane and may not present this prob-

Comparison of EDS and MMD Liquid Waste Compositions

The MMD and the EDS neutralents are similar. The phosgene neutralents, which are alkaline, aqueous solutions of inorganic salts (NaOH, NaCl, Na₂CO), are nonflammable, single-phase liquids containing small quantities of suspended solids. The MMD and EDS neutralents derived from HD and GB are also single-phase liquids over the range of 5:1 to 200:1 MEA reagent:CW agent (Lucille Forrest and James Horton, personal communication, October 1, 2001). However, most of the information on physical properties comes from studies on laboratory simulations of the neutralization process (U.S. Army, 1997). More data from actual EDS test neutralents would be valuable.

Differences may arise from the contrasting types of munitions processed in the two systems and the divergent ways they are processed. The MMD system does not process items containing explosives, while the EDS can handle munitions containing bursters and/or fuzes. The EDS system introduces the explosives RDX and Composition A to open the munition and to detonate any explosives contained therein.

The EDS waste analyses did not show residual explosives except for RMA bomblet 1. The solid residue from this device contained 18.3 ppm of RDX, which presumably resulted from incomplete detonation of the shaped charges used to open the bomblet. The absence of RDX (detection limit ca. 1 ppm) in the neutralent from other bomblets probably reflects the ability of MEA to destroy RDX. The Army has stated as follows: "Both MEA and aqueous alkali have been shown to efficiently destroy TNT and RDX" (U.S. Army, 2000). Apparently no analyses were performed to detect RDX-MEA reaction products, which may be complex organic amines.

The explosives present in the munition⁷ could also produce a variety of compounds in the EDS-1 liquid waste streams that may need to be removed or destroyed by a subsequent treatment technology.⁸ If the munition fuze and burster charges are successfully detonated by the shaped charges, there may be little residual explosive remaining after the blast. If, on the other hand, the fuze and burster charges in the munition are not successfully detonated by the shaped charges, as may occur especially in older munitions,⁹ the energetics are likely to be hydrolyzed to a considerable extent by the MEA-water or sodium hydroxide-water reagent (NRC, 1999a, Appendix E).¹⁰ Even if there is little residual explosive remaining in the neutralent, hydrolysis products from the energetics will still be present in the liquid waste streams.

Another difference between the MMD and EDS wastes may be the presence of higher levels of metal ions and metal oxides of Fe, Co, Ni, Pb, Al, Zn, Sn, and Cu in some EDS neutralents. The fragmentation of the munition bodies in the EDS, as well as the hours of rocking back and forth during the neutralization process, may expose more metal surface to the MEA reagent, which is a fairly good extractant for these metal ions. In addition, heavy metal constituents of the munition fuze (e.g., mercury from mercury fulminate) will

⁶Lucille Forrest, Office of the Project Manager, Non-Stockpile Chemical Materiel, "Re: Cleaning Solutions for EDS," memorandum to the committee, May 10, 2001.

⁷Fuzes were made from a variety of primary explosives, such as mercury fulminate. The most common explosives used in burster charges are tetryl, TNT, and Composition B (a mixture of TNT and RDX).

⁸Various compounds that may be present can be found in *Review and Evaluation of Alternative Technologies for Demilitarization of Assembled Chemical Weapons*, Appendix E (NRC, 1999a).

⁹In the Porton Down tests, the fuze or burster in the munition failed to detonate in several cases.

¹⁰The committee did not receive information on procedures that might be followed if detonation of the shaped charges results in cracking of the munitions casing but fails to expose the chemical agent fully to the neutralizing solution.

remain in the vessel and may well dissolve in the neutralizing reagents. Unfortunately, as indicated in Tables 2-1 to 2-2, an adequate comparative analysis for these metals, which are likely materials of construction in various munitions, is not currently available.

In general, the EDS and MMD neutralents are similar apart from the concentrations of metal ions and explosives-derived organic compounds. The latter are likely to be destroyed by posttreatments that destroy MEA, because they are less stable chemically. The metal components may require stabilization or solidification before final disposal, especially if toxic metals such as lead or mercury are involved. The toxicities of the MMD and EDS-1 neutralents are discussed and compared in Appendix D.

POTENTIAL FOR ENCOUNTERING UNUSUAL CHEMICAL SPECIES IN THE EDS

Munitions Containing Arsenic and Other Toxic Metals

The preceding discussion of munitions to be treated in the EDS covers those most likely to occur in Non-Stockpile Chemical Warfare Materiel (NSCWM) "finds." However, some munitions containing arsenic-derived chemical agents may also be encountered. Past experience indicates that there may be projectiles filled with lewisite, an organoarsenic blister agent. Some old German *traktör* rockets stored at Pine Bluff Arsenal appear to contain *Winterlost*, a mustard formulation containing phenylarsenic dichloride (PD) and diphenylarsenic chloride (DA) as freezing-point depressants (Martens, 1998). There may also be items containing adamsite (DM), an arsenic-containing vomiting agent intended for riot control.

It is uncertain whether the EDS will be used to destroy munitions containing arsenic. If so, the neutralizing reagent will need to be tailored to the anticipated chemical agent because their neutralization chemistry is quite diverse. The Army has proposed neutralizing agents and treatment conditions for the agents reasonably expected to be treated in the EDS (U.S. Army, 2001e).

Alkaline neutralization like that used for the destruction of phosgene is planned for the destruction of lewisite in the EDS (U.S. Army, 2001e). The agent from an opened munition is to be treated with 22 percent aqueous sodium hydroxide at ambient temperature for 1 hour. Hydrolysis with hot aqueous sodium hydroxide solution forms the basis for neutralization of bulk lewisite in a new process to be implemented at Gorny in the Saratov region of Russia (Petrov et al., 1998; N.N. Kovalyev, Monterey–Moscow Study Group on Russian Chemical Disarmament, personal communication to G.W. Parshall, member of the committee, February 25, 1997). The alkaline treatment destroys the lewisite, forming acetylene gas, sodium chloride, and sodium arsenite. The arsenite may be oxidized to arsenate to facilitate disposal.

In a related process, to be implemented at the Chemical

Agent Munitions Disposal System (CAMDS) in Utah (Utah, 1998), the lewisite is first oxidized with aqueous hydrogen peroxide, then hydrolyzed with sodium hydroxide solution. The resulting sodium arsenate solution will be solidified with cement for disposal in a hazardous waste landfill. The solidification process is being studied under an NSCMP test (Edward Doyle, Office of the Project Manager, Non-Stockpile Chemical Materiel, communication to the committee, March 16, 2001). As practiced in the United States and some European countries, the sodium arsenate could also be converted to ferric arsenate, a less soluble salt that is resistant to leaching by groundwater. The separation of arsenate can be accomplished by precipitation with ferric chloride to form ferric arsenate, which is insoluble in either cold or hot water (Hodgman, 1963). The CAMDS process is based on the process used to destroy Canada's stockpile of lewisite in Project Swiftsure (McAndless et al., 1992).

Based on the Draft Final Standard Operating Procedure for the EDS (U.S. Army, 2001e), the mixture of sulfur mustard and phenylarsenic chlorides contained in Winterlost is likely to be treated according to the same protocol as HD alone, i.e., 90 percent MEA, 10 percent water, at 60°C for 4 hours. While MEA will break the As-Cl bonds associated with the vesicant activity of DA and PD, it is unclear whether the treatment will break the phenyl-As bonds. Further posttreatment may be needed to prepare the neutralent for disposal. Much the same situation arises with the proposed neutralization of DA and PD in the absence of HD. The Army plans to treat the agent and munition residues in the EDS with denatured 95 percent ethanol (or possibly acetone for DA) at ambient temperature for 1 hour. While this treatment will dissolve the organoarsenic compounds and partially hydrolyze the As-Cl bonds, it will produce a neutralent requiring significant further treatment.

Adamsite and the phenylarsenic chlorides are customarily hydrolyzed with acid rather than alkali (Wertejuk et al., 1998). Treating these organoarsenic compounds with hot concentrated hydrochloric acid destroys the compounds, but this reagent may be too corrosive for use in the current EDS system. Alkaline reagents like aqueous sodium hydroxide hydrolyze the As-Cl chemical bonds in these compounds, thus reducing their toxicity, but do not necessarily destroy the organoarsenic structures. For the small number of munitions containing these agents, it may be most appropriate to treat the detonation products with aqueous sodium hydroxide reagent and then destroy the neutralent in a treatment unit or facility capable of substantially reducing the toxicity, mobility, and volume of the arsenic wastes. At present, the only commercial facilities available are commercial incineration facilities that are permitted to treat wastes containing arsenic.

The requirement that the initial arsenic-containing products be oxidized to arsenate salts gives an advantage to neutralent treatment processes that have an oxidative character. This class includes chemical oxidation, electrochemical oxidation, wet air oxidation, supercritical water oxidation, and plasma processes, which incorporate a secondary oxidizer (see Chapter 3). Reductive processes such as solvated electron technology and gas-phase chemical reduction can be adapted to produce arsenate via posttreatment oxidation, but at substantial additional cost and complexity. Biochemical processes are generally unsuitable for treating wastes containing arsenic, lead, and mercury because these elements deactivate the enzymes needed to degrade organic wastes.

POTENTIAL FOR ENCOUNTERING OTHER UNUSUAL CHEMICAL COMPOUNDS

To date, the Army has tested protocols for treating munitions containing only sulfur mustard, phosgene, and sarin in the EDS, but treatment regimes for all the anticipated arsenic-containing agents have been established based on known chemistry (U.S. Army, 2001e). Chemistry to stabilize and solidify arsenic-containing treatment wastes is being tested in a PMNSCM-funded R&D program (Edward Doyle, Office of the Project Manager, Non-Stockpile Chemical Materiel, communication to the committee, March 16, 2001). Given that many agents¹¹ and toxic industrial chemicals¹² have been used to fill chemical weapons over the years, it is possible that other fills, including the nerve agent VX, will be encountered. However, there appears to be little information with which to estimate the probability of encountering these other fills.

Apart from the variety of possible agent fills, there are several other reasons why unusual compounds might be present in recovered munitions. Special formulations of agents and industrial chemicals were sometimes used to achieve certain effects. For instance, tin tetrachloride was encountered in phosgene rounds treated in the Porton Down tests of the EDS-1. This chemical was added to facilitate the penetration of gas masks and to produce a smoke that aided in spotting where rounds had landed. Chlorobenzene, possibly used as a solvent or stabilizer, was found in the mustard rounds processed at Porton Down (Table 2-1). Chlorinated rubber was used as a thickener in some mustard formulations. In addition, unusual compounds or sludges may result from chemical reactions such as corrosion and polymerization that may occur among the components over a period of decades.

DATA GAPS AND UNCERTAINTIES

During the Porton Down and RMA experiences with the EDS-1, the Army was still refining its treatment procedures. For example, the number and composition of rinses following the initial neutralization step varied from munition to munition, even among munitions of the same type, as at RMA. This led not only to different volumes of neutralents and rinsates generated for each munition but also to different concentrations of organics and metals in the neutralents and rinsates. These variations could affect both the choice of treatment technology and the regulatory status of the liquid wastes (see Chapter 4). As more experience is gained with treatment of a variety of munitions and agents in the EDS-1, these variations should grow smaller.

Beyond the variations introduced before EDS treatment protocols become fully standardized, a number of factors will inevitably cause the composition of the neutralents and rinsates to vary from munition to munition. These include the exact composition of the chemical agents inside the munition, the age of the munition, and factors relating to the composition and status of the energetics in the munition. If, as discussed above, the fuze and/or burster in the munition are not successfully detonated by the conical shaped charges, hydrolysis products of energetics may be present in substantial concentrations in the neutralent. The neutralent chemical analysis data provided to the committee contained information on residual energetics (in general, they were not detected) but not on hydrolysis products of energetics.

A potential concern relates to the possibility that residual chemical agent may inhere in the microscopic cracks and crevices of suspended solids that are inaccessible to the neutralizing reagent. The presence of such occluded agent residues was observed in early efforts to develop chemical decontamination methods for large metal parts in the U.S. Chemical Stockpile Destruction Program (Richard Magee, former chairman of the NRC Stockpile Committee, personal communication, September 7, 2001).

The EDS neutralent is known to contain suspended solids, as evidenced by the fact that it is cloudy. To date, the Army has not done any tests to determine the quantity of suspended solids or whether any residual chemical agent might inhere in them, reasoning that these solids remain in contact with the neutralizing solution until the waste drums are processed through the incinerator and that any agent that might escape from a microscopic crack would immediately be neutralized. Nevertheless, if such residual agent is present in high enough concentrations in suspended solids, it is conceivable that exposures could occur to workers handling the waste drums or in the event of a spill. This potential concern could be easily resolved by a test involving filtration of the neutralent followed by heating the filtered solids and testing the off-gas for the presence of agent.

The foregoing discussion shows that the composition of the neutralents and rinsates derived from the processing of

¹¹These include tabun (GA), sarin (GB), Levinstein mustard (H/HS), distilled mustard (HD), HT, nitrogen mustard (HN), lewisite (L), VX, and adamsite (DM)

¹²These include hydrogen cyanide, bromoacetone, bromobenzyl cyanide, phosgene, cyanogen chloride, chlorine, chloroacetophenone, chloropicrin, and diphenylchloroarsine (DA).

DESCRIPTION OF EDS TREATMENT PROCESSES AND LIQUID WASTE STREAMS

by the Army to dispose of these liquid wastes must be able to destroy a wide variety of chemical species; i.e., they must be robust. This criterion, among others, is considered by the committee in its evaluation of the alternative secondary waste treatment technologies discussed in the next chapter.

nonstockpile items in the EDS is both highly variable and unpredictable. In the future, it will be important to analyze the neutralents for all chemical species that could be of health, safety, environmental, or regulatory concern. In addition, any nonincineration posttreatment technologies used

3

Applicability of Treatment Technologies to EDS Liquid Waste Streams

In its previous report (NRC, 2001a), the committee evaluated eight nonincineration technologies for their ability to process liquid wastes produced by the rapid response system (RRS) and the munitions management device (MMD). A technology was selected for evaluation if one or more of the following were true:

- A substantial amount of information about it was available.
- It was under serious consideration and/or evaluation for other demilitarization or waste treatment processes—for example, the Assembled Chemical Weapons Assessment (ACWA) Program—or used widely for commercial waste treatment
- It was likely to be safe, effective, easily permitted (relative to incineration technologies), and capable of passing the committee's pollution prevention criteria.

A complete list of the evaluation criteria used by the committee in this report and the previous report (NRC, 2001a) appears at Appendix E. The committee gave the "top priority" criteria more weight than the "important" criteria.

The eight technologies evaluated were the following:

- chemical oxidation using a variety of oxidants, such as hydrogen peroxide, ultraviolet-activated hydrogen peroxide, ozone, and peroxydisulfate
- wet-air oxidation, or a variation using pure oxygen instead of air
- electrochemical oxidation using silver (II) or cerium (IV) ions to oxidize organic compounds
 - supercritical water oxidation
 - solvated electron technology
 - biodegradation
 - · gas-phase chemical reduction
 - · plasma arc technology

Process descriptions and evaluations for each of these technologies were given in Chapter 4 of *Disposal of Neutralent Wastes* (NRC, 2001a).

PREVIOUS TECHNOLOGY RECOMMENDATIONS

In its previous report (NRC, 2001a), the committee recommended that the Non-Stockpile Chemical Materiel Product (NSCMP) should pursue a two-track strategy to identify a suitable treatment technology for MMD neutralents. As part of the track-one strategy, the committee recommended that NSCMP should take advantage of available equipment that would require little or no investment—that is, it would piggyback on alternative technologies from the ACWA Program or existing commercial technologies, such as chemical oxidation, wet-air/ O_2 oxidation, or existing plasma are technology. The committee judged that if any of these existing and available technologies can accomplish the task safely, this might be the most rapid and inexpensive course of action.

If, on the other hand, neither the ACWA nor the commercially mature technologies could be used as is—for example, if substantial process or permit documentation would be needed to dispose of nonstockpile neutralents—then as part of the track-two strategy, the committee recommended that the Army should invest research and development resources first in chemical oxidation and wet-air/O₂ oxidation.¹ Only if these technologies cannot be adapted easily did the committee recommend that the Army consider investing re-

¹The committee chose to include some technologies, such as chemical oxidation and wet-air/O₂ oxidation, in both track one and track two because although they are commercially mature, they nevertheless may require the investment of resources to optimize them for destruction of the EDS neutralents

sources in the adaptation of ACWA technologies listed below in order of preference:²

- 1. electrochemical oxidation with Ag(II) or Ce(IV)
- 2. supercritical water oxidation
- 3. gas-phase chemical reduction
- 4. plasma-arc technology.

Biodegradation was judged unsuitable for treatment of MMD and RRS neutralents. The committee recommended that the Army should not invest in further development of biodegradation for nonstockpile wastes.

ARMY TECHNOLOGY TESTING PROGRAMS

Since the publication of the committee's previous report (NRC, 2001a), technology test data have become available from two ongoing programs that bear on the committee's assessment of the technologies in track two. Although the data are preliminary and many of the tests are incomplete, the committee wished to incorporate the latest results (those available as of July 2001) into its recommendations for the EDS-1 liquid waste treatment technologies in this report. One data source is NSCMP's Technology Testing Program, in which several ACWA technologies are to be tested on MEA-based neutralents/rinsates or simulated neutralents/ rinsates. The status of this program is summarized in Table 3-1. The other data source is testing from the ACWA Program itself. The ACWA Program has been reviewed by another NRC committee (NRC, 1999a; NRC, 2000; NRC, 2001b).

RECONSIDERATION OF THE PREVIOUS TECHNOLOGIES FOR DESTRUCTION OF EDS LIQUID WASTE STREAMS

The EDS-1 uses the same MEA-based reagents for HD, GB, and VX as does the MMD, and it also uses the same aqueous sodium hydroxide reagent to treat CG (see Table 2-4). The EDS may, however, be called upon to dispose of munitions having fills that the MMD was not designed to process (e.g., lewisite), and for these munitions and fills, other reagents may be needed.

Although the neutralizing reagents used in the MMD and the EDS-1 are essentially identical, there are several operational process differences between these systems that give rise to differences in the compositions of the liquid waste streams. First, the MMD³ was not intended to process

TABLE 3-1 NSCMP Technology Test Program Status

Technology	Vendor/Test Site	Feed Streams
PLASMOX	Burns and Roe Enterprises/MGC Plasma in Muttenz, Switzerland	H neutralent simulant, GB neutralent simulant
Gas-phase chemical reduction	Eco Logic International, Inc./ Edgewood, Md.	GB neutralent, H neutralent simulant, RRS neutralent, DF simulant, vials of CHCl ₃
Supercritical water oxidation (continuous)	TBD/TBD	Binary chemicals, Rinsates, neutralents
Supercritical water oxidation (batch)	Sandia National Laboratories/ Livermore, Calif.	H neutralent simulant, GB neutralent simulant, vials of CHCl ₃
Persulfate oxidation	Southwest Research Institute/ San Antonio, Tex.	HD neutralent simulant, GB neutralent simulant, DF
Electrochemical oxidation	CerOx Corp./ University of Nevada at Reno	H neutralent simulant, GB neutralent simulant, DF simulant
UV oxidation	Purifics Inc./ Toronto, Canada	Rinsate
Wet-air oxidation	Zimpro Products/ Rothschild, Wisc.	Neutralent simulant, binary DF, and QL simulant

SOURCE: Lt. Col. Christopher Ross, Product Manager, Non-Stockpile Chemical Materiel Project, "U.S. Army Non-Stockpile Chemical Materiel Product (NSCMP) Update," presentation to the committee, July 10, 2001.

nonstockpile items containing energetics, whereas items processed in the EDS-1 may contain bursters and fuzes. Consequently, the potential exists for some energetics and their reaction products to be found in the EDS-1 neutralents.

Second, in the MMD the chemical agent is accessed by drilling into the item to be processed and draining the agent, while the EDS-1 uses explosives to open the munition and release the agent in its explosion containment vessel. The metal fragments of the munition body are then rocked back and forth with the neutralizing reagent for several hours, which may result in higher concentrations of metals being found in EDS-1 neutralents than in MMD neutralents.⁴ Metals such as lead and mercury may also be present in the mu-

²The neutralent report (NRC, 2001a) included solvated-electron technology in the ACWA technologies to be considered. However, this technology was viable only for RRS neutralents and not for MMD. Therefore, it is not considered here.

³A second version of the MMD, which would have processed explosively configured munitions, was designed but never built.

 $^{^4}For$ the six bomblets processed in the EDS-1 at RMA, the average quantities of metals in the neutralent in $\mu g/liter$ were Al, <9,235; Cr, 680; Cu, 13,840; Zn, 31,400; and Pb, 147. The quantities of these metals in the liquid neutralent generated from each bomblet were Al, <1.15 grams; Cr, 0.08 grams; Cu, 1.72 grams; Zn, 3.89 grams; and Pb, 0.02 grams (U.S. Army, 2001d).

nition fuze materials and become dissolved in the EDS neutralents.

Third, after the neutralent is drained from the EDS-1 containment vessel, operating procedures call for further treatment of the vessel contents with water at 100°C, followed by water rinses at about 50°C.⁵ Thus, EDS-1 produces additional aqueous waste streams that must be disposed of.

In evaluating the ability of each of these technologies to process liquid wastes produced by the EDS-1, the committee took account of the above differences in the compositions of the MMD and EDS-1 liquid waste streams and considered the results of ongoing tests of these technologies by the Army in processing simulated and actual liquid wastes. The committee's evaluation and its reranking of the technologies for application to the EDS-1, where appropriate, are described below.

Evaluation of Chemical Oxidation for Processing EDS Neutralents

The use of chemical oxidants, such as hydrogen peroxide, potassium permanganate, Oxone,6 and peroxydisulfate, is a promising candidate for treatment of EDS liquid waste streams because of its technical effectiveness for similar wastes, good pollution prevention qualities, robustness, and low cost. Emissions are minimal, and production of chlorodibenzodioxins and chlorodibenzofurans is precluded because of the low temperatures involved.⁷ The biggest potential disadvantage of chemical oxidation is that it may not fully mineralize all of the compounds in the neutralents or that it may not mineralize them rapidly enough to be practical. Additionally, many organics, particularly simple aliphatics and halogenated alkanes, are somewhat recalcitrant to simple chemical oxidation. Long reaction times, large amounts of oxidants, and significant dilution may be required.

Oxidation without UV enhancement is much preferred over treatment with UV enhancement. The problems associated with UV activation are discussed in NRC, 2001a. These include the need for special equipment, lack of effectiveness when the solution being treated is opaque, and fouling of the optical surface.

The potential presence of residual energetics or their hydrolysis products in the EDS neutralent should not pose any particular difficulty. These materials will probably also be oxidized, although this remains to be verified by testing. If additional metal ions/hydroxides are present in the EDS

neutralents, they may consume oxidant or catalyze its decomposition; appropriate testing could answer this question.

The dilute aqueous rinsates produced during EDS operation should be amenable to treatment by chemical oxidation. Typical oxidants such as those mentioned above are commonly employed in aqueous systems and do not react with water.

If arsenic is present, it will probably be oxidized to arsenate ion, which can be stabilized. Organic arsenicals will probably be mineralized, which would be serendipitous since they are difficult to stabilize (Conner, 1990).

The experimental evaluation of persulfate oxidation of EDS neutralents was under way as this report was being written (Table 3-1). The results of this work will be extremely helpful in evaluating the usefulness of chemical oxidation.

Evaluation of Wet-Air Oxidation for Processing EDS Neutralents

Wet air oxidation (WAO) is a hydrothermal process for the oxidative destruction of organic wastes that is carried out in liquid water at temperatures of 150° to 315°C and pressures of 150 to 3,000 psia. The oxidizing agent is dissolved oxygen, which may be derived from air, or pure oxygen may be supplied externally.

WAO operates at temperatures and pressures below the critical point of water (374°C; 3,204 psia). Most inorganic salts that would form during oxidation of EDS neutralents are soluble in subcritical water. Therefore, WAO, unlike supercritical water oxidation (see below), is not prone to plugging by precipitated salts.

WAO can treat any pumpable fluids provided that the chemical oxygen demand (COD) is less than 120,000 mg/L. To achieve this, one technology (William Copa, U.S. Filter Zimpro, personal communication, February 15, 2000) estimates that the MMD neutralent for GB would have to be diluted seven- to ninefold prior to wet air oxidation. The MMD neutralent for VX would have to be diluted 12- to 15-fold. Similar levels of dilution would be required for the EDS neutralents and could be achieved in whole or in part by combining the primary neutralent with the dilute aqueous rinsates. It should be noted that the dilution required to achieve the appropriate chemical oxygen demand ensures that the neutralents are aqueous-based and do not have low flash points.

The presence of small quantities of energetics or energetics reaction products in EDS neutralents may increase the COD above that for MMD neutralents, necessitating additional dilution, but otherwise, process applicability should be similar.

WAO is used routinely in commercial applications to treat sewage sludge containing 10 to 15 percent solids. Therefore, the higher levels of dissolved metal ions or suspended solids

⁵For two GB-filled bomblets at RMA, neutralization was followed by a reagent/water rinse and then a water rinse (U.S. Army, 2001d).

⁶Oxone, a registered trademark of DuPont Specialty Chemicals, is a triple salt (2KHSO₅·KHSO₄·K₂SO₄).

⁷See discussion of chlorodibenzodioxins in Appendix G.

in EDS neutralents compared with MMD neutralents are not likely to compromise the applicability of the process.

WAO does not fully mineralize organics but instead reduces them to short-chain molecules such as acetic acid (the primary component of vinegar). Thus, effluents would need to be treated further by biotreatment, possibly at a POTW. Prior to biotreatment, toxic heavy metals in the EDS neutralent would need to be precipitated, filtered out, and stabilized for disposal in a hazardous waste landfill. Arsenic, if present, would be converted to arsenate ion, a form that is readily stabilized. NSCMP plans for testing of WAO to be completed by the end of 2001.

Evaluation of Electrochemical Oxidation for Processing EDS Neutralents

In the electrochemical oxidation process, a strong oxidizing agent—in this case Ag(II) or Ce(IV)—is generated in concentrated nitric acid in an electrochemical cell. Ideally, the oxidizing agent then reacts with the introduced organic waste material to produce carbon dioxide and inorganic salts. After it has been reduced by the reaction with the waste, the oxidizing agent is regenerated in the electrochemical cell.

The Ag(II) process is being tested extensively by the ACWA program as a primary treatment to destroy neat chemical agents and a variety of energetic materials found in stockpiled assembled chemical weapons. Chemical agents can be destroyed to destruction removal efficiencies of 99.9999 percent; however, the treatment of energetic materials is still very immature (NRC, 1999b; NRC, 2000).

This committee found that the major disadvantage of using Ag(II) is that large quantities of silver salts and chlorides are generated, which could lead to problems with corrosion and precipitation. Recent test data from the ACWA Program indicate that silver salts containing polynitroaromatic compounds (e.g., trinitrobenzene, trinitrobenzoic acid) precipitate on the walls of the vessels and piping during the treatment of liquid wastes containing explosive residues (Winkler, 2001). These solids were difficult to oxidize any further. Another disadvantage is that large quantities of silver and nitric acid (a corrosive) are required for the operation of this technology, which could increase toxic emissions, effluents, and cost. To correct all of these problems, numerous unit operations have been added, making the system extremely complex and immature.

The Ag(II) process has never been tested as a secondary treatment for neutralents. Because neutralents contain a high percentage of water, the concentrated nitric acid solutions will be diluted. This could alter the chemistry and necessitate the removal of water.

Electrochemical oxidation with Ce(IV) avoids some of the deficiencies of the Ag(II) process; for example, unlike Ag, Ce does not form an insoluble salt with chloride ions. Nevertheless, like the Ag(II) process, the Ce(IV) process requires large quantities of corrosive nitric acid and generates large quantities of nitrogen oxides at the cathode, which must be reformed and the waste gases scrubbed.

The committee found that the most serious disadvantage of Ce(IV) is that the technology is not mature enough for immediate use (NRC, 2001a). The electrochemical cells were designed specially by the vendor and are not commercially available. Furthermore, there is no mechanism for removing salts produced in the reaction from the anolyte solution; the solution must be drained periodically and replaced as the salt concentrations increase. The University of Nevada is using a small Ce(IV) unit to process small quantities of organic waste, including chlorine-containing compounds. Testing of this unit on mustard and sarin neutralent as part of the NSCMP's Technology Test Program is scheduled to begin in mid-2001.8

Evaluation of Supercritical Water Oxidation for Processing EDS Neutralents

Supercritical water oxidation (SCWO) is a hydrothermal process for the oxidative destruction of organic wastes. An oxidant and the wastes to be disposed are fed to a reactor in the presence of high concentrations of water heated above the critical temperature and pressure of pure water (374°C, 3,204 psia). These wastes can be fed continuously into the SCWO reactor (continuous SCWO) or, in an alternative design, a small volume of waste is mixed with water and an oxidizer (H₂O₂) in a pressure vessel, heated to reaction temperature above the critical point of water, and then cooled (batch SCWO). The committee evaluated continuous SCWO in its previous report (NRC, 2001a), but did not evaluate batch SCWO, which was still at a very early stage of development.

Although the committee found that continuous SCWO would effectively mineralize agent neutralents, it concluded that issues related to the mechanisms and locations of salt buildup, the chemical composition of the salts produced, and the effectiveness of the flushing of salts are unresolved. Corrosion and plugging of SCWO reactors, erosion of valve seats and nozzles, and pressure containment are other issues to be addressed. As a result, the committee ranked continuous SCWO fairly low as a process for mineralizing MMD neutralents.

Constituents of the EDS-1 neutralent from the GB bomblet operation include small quantities of explosive solids (a maximum of between 0.77 and 1.3 ppm) and liquids possibly containing explosives (<1,000 µg per liter of each constituent). These small quantities of energetics should, if anything, assist the temperature-sustaining exothermic reac-

⁸Lt. Col. Christopher Ross, Product Manager, Non-Stockpile Chemical Materiel Project, "U.S. Army Non-Stockpile Chemical Materiel Product (NSCMP) Update," presentation to the committee, July 10, 2001.

tion in the SCWO reactor (NRC, 2001a). Other components of the EDS-1 neutralent, e.g., volatile and semivolatile organics, should be readily destroyed in the SCWO chamber.

One area of concern with regard to continuous SCWO, however, is the presence of metal ions in the EDS-1 neutralent. Ten different metal ions were detected in the analysis of EDS-1 neutralent obtained from destruction of the sarin bomblets at RMA. Although the quantities detected were small, these metals add to the potential for accumulation of salts in the SCWO reactor.

The batch SCWO concept, currently being developed and tested at Sandia National Laboratories, could help address the salt buildup problem, because salts accumulated in the batch SCWO reactor can be flushed out after each batch is processed. The batch SCWO could also help to address the problems of pressure letdown and corrosion (by better control of the pH). However, relatively small quantities of neutralents can be processed per batch. The size of the transportable batch SCWO reactor currently being tested would have to be scaled up to process the volumes of neutralent produced by the EDS.⁹

Although it shows promise as a technology for mineralizing EDS neutralent wastes, batch SCWO is still in the early stages of development. Additional testing at both the laboratory and pilot scales is needed to determine whether corrosion and salt buildup are less problematic with batch SCWO than with continuous SCWO.

It should be noted that the EDS-1 has yet to be tested with munitions containing VX, arsenicals, and other miscellaneous chemical fills, and that the composition of the resulting neutralents is not yet known. SCWO has destroyed hydrolysates from VX neuralization with aqueous sodium hydroxide, but to the committee's knowledge, it has not yet destroyed MEA-based VX neutralents.

Evaluation of Gas-Phase Chemical Reduction for Processing EDS Neutralents

Gas-phase chemical reduction (GPCR) is a thermal treatment technology (850°C, atmospheric pressure) that reduces organic chemicals to water, methane, carbon soot, and other by-products in a hydrogen-rich atmosphere. The by-products include acid gases, phosphorus-containing products from VX and GB neutralents, and arsenic-containing products from lewisite neutralent. These products, as well as the carbon soot, require scrubbing or further treatment, adding to the complexity of the process.

Although GPCR is a well-established thermal treatment technology, it can generate large volumes of effluent gases and is a complex process that requires the management of hot hydrogen gas in the reactor, the scrubbing of effluent gases, and the control of carbon soot buildup. For these reasons, as well as a lack of regulatory experience in the United States, the committee gave GPCR a low rating as a posttreatment process for MMD neutralent.

These same challenges are likely to be faced in the application of GPCR to EDS-1 neutralents. Although small concentrations of residual energetics or energetics decomposition products in the EDS-1 neutralents are not expected to pose a problem, the potential presence of additional metal ions—particularly toxic heavy metals such as mercury and arsenic—is of concern since these must be captured and disposed of.

As indicated in Table 3-1, NSCMP has completed testing of a GPCR system with a variety of actual and simulated neutralent wastes. Initial tests encountered partial plugging in a pipe between the thermal reduction batch processor and the GPCR reactor due to the buildup of a green glassy material and a tarry substance. In tests on DF simulant, hydrofluoric acid was formed, which attacked the metal reactor seals, severely corroding them.¹¹ The suitability of GPCR for treating phosphorus- and arsenic-containing wastes has not been fully demonstrated. Phosphorus-containing wastes have the potential to produce the toxic gas phosphine (PH₃), although a previous NRC report (NRC, 1996) presented theoretical calculations suggesting that phosphine is a less likely product than P(III) oxides. Arsenic-containing wastes have the potential to form the toxic gas arsine (AsH₂), although elemental arsenic may be a more likely product. Russian work on the high-temperature, gas-phase hydrogenolysis of lewisite showed the production of elemental arsenic and As(III) compounds (Petrov, 1998).

Evaluation of Plasma Arc for Processing EDS Neutralents

Plasma arc technology utilizes electrical discharges to produce a field of intense radiant energy and high-temperature ions and electrons that cause dissociation of chemical compounds in a containment vessel. Operating at electron temperatures as high as 20,000°C, material exposed to the plasma environment is transformed into atoms, ions, and electrons.

In its previous analysis, the committee recognized that plasma arc systems can achieve very high destruction efficiencies, but it noted that they are most efficient when used

⁹The volume of the SCWO reactor required to process a batch of waste varies linearly with the volume of waste.

¹⁰The EDS-1 was tested at Porton Down, with British munitions and cylinders containing phosgene (CG) and sulfur mustard (HD) as well as a GB-filled container.

¹¹William Brankowitz, Office of the Project Manager, Non-Stockpile Chemical Materiel, "U.S. Army Non-Stockpile Chemical Materiel Product (NSCMP) Project," presentation to the committee, May 23, 2001; Edward Doyle, Office of the Project Manager, Non-Stockpile Chemical Materiel, communication to the committee, July 10, 2001.

to treat low-volume, highly concentrated feed streams (e.g., neat chemical agents) rather than dilute neutralent solutions. Recently a variant of this technology¹² was successful in destroying adamsite (DM), CG, L, H, and HL in tests conducted in Spietz, Switzerland, with a destruction and removal efficiency greater than 99.9999 percent.

Nevertheless, the committee gave plasma arc technology a low rating for treatment of MMD neutralent solutions compared with the other alternative technologies it considered. This rating was based on its reduced efficiency for treatment of dilute neutralent streams, its very high operating temperature (with consequent potential to produce hazardous byproducts such as chlorodibenzodioxins and chlorodibenzofurans) and the need for treatment of the off-gases produced.

To provide data on the effectiveness of plasma arc technology on EDS-1-type neutralent, the Army tasked Stone & Webster, Inc., to conduct tests with MGC Plasma AG in Switzerland using that company's PLASMOX technology to destroy H and GB neutralent simulants (Table 3-1). The preliminary results indicate that the PLASMOX system successfully destroyed a simulated neutralent containing 52 percent water. The initial review of the gaseous effluents indicated that even though low concentrations of dioxins and furans were detected, the system should not have any difficulty in satisfying environmental regulations (Stone & Webster, 2001).

The high temperatures in the reactor vessel are expected to destroy the residual energetics or energetic hydrolysis products in the neutralent. PLASMOX technology has been successful in removing metal ions (including heavy metals such as arsenic) and having them reform into a slag that can be readily disposed of. The data on the fate of the phosphorus during the test are still being evaluated. The unit that was tested was not a commercial unit and needs to have some safety features added to meet U.S. health and safety criteria.

Some reviews of destruction technologies for CWM suggest a greater degree of public acceptance for plasma arc technology as a viable alternative to incineration than the committee had previously perceived. Plasma arc was accepted as an alternative by the ACWA Dialogue group (NRC, 1999b), and the Stone & Webster citizen panel indicated that plasma arc technology might be accepted in some locations and not in others (Stone & Webster, 2001). At least one commercial plasma arc unit has been permitted, according to information provided by the Army (Edward Doyle, Office of the Project Manager, Non-Stockpile Chemical Materiel, communication to the committee, July 10, 2001). These observations, combined with the promising test results discussed above, suggest that PLASMOX may be a technically effective treatment technology for nonstockpile

neutralents and a publicly acceptable alternative to incineration in some locations.

Evaluation of Biotreatment for Processing EDS Neutralents

The committee concluded in its previous report that biological treatment is a doubtful candidate for treatment of MMD neutralent. Reasons included the relatively low destruction efficiency (typically around 90 percent for most compounds, as opposed to the five or six "nines" usually sought in destroying hazardous materials), the presence of compounds that are known to be difficult to destroy by biotreatment (e.g., chloroform, hexachlorobenzene, and hexachlorobutadiene), the fact that the process yields large volumes of off-gas that must be treated, and that the equipment is bulky and not easily transported. A previous test of biotreatment for GB and VX hydrolysate was unsuccessful (NRC, 2000).

These same disadvantages are expected to pertain to the biotreatment of liquid waste streams of the EDS-1. Although the presence of residual energetics or energetics hydrolysis products in the EDS neutralent should not be a problem (they are biodegradable), the presence of additional metal ions, especially toxic heavy metals such as arsenic, may be detrimental to the microorganisms. The presence of dichlorobenzene, pentachlorophenol, and chlorobenzene (Tables 2-1 to 2-3) in some test samples presents a problem, because all of these compounds are difficult to treat biologically. Overall, it is the committee's conclusion that biological treatment is of doubtful use for the treatment of EDS neutralent.

Evaluation of Solvated Electron Technology for Processing EDS Neutralents

As stated in NRC (2001a), solvated electron technology (SET) would not be an appropriate technology for treatment of MMD neutralents because of their high water content. The first step of the SET process is reduction of organic compounds with solutions of metallic sodium in anhydrous liquid ammonia. If used to treat EDS neutralents, the sodium would react violently with the aqueous component of the neutralent, causing a release of hydrogen gas, before reacting with any of the organic components. The large quantities of metallic sodium that would be needed, and the safety problems associated with the hydrogen, preclude the use of SET for EDS neutralents.

RECONSIDERATION OF THE COMMITTEE'S EARLIER RECOMMENDATION ON NEUTRALENT TREATMENT TECHNOLOGIES FOR APPLICATION TO LIQUID WASTE STREAMS

Table 3-2 summarizes the earlier evaluations of alternative technologies for processing EDS neutralents (NRC,

¹²The plasma arc technology being evaluated is the PLASMOX system offered by MCG Plasma AG, a Swiss firm that has licensed the technology to Burns and Roe in the United States (Stone & Webster, 2001).

Technology	Advantages	Disadvantages	Conclusions
Chemical oxidation	Simplicity, pollution prevention, low cost	Not proven for neutralents	Promising candidate for targeted R&D program
Wet-air/O ₂ oxidation (WAO)	Simplicity; subcritical water conditions avoid salt precipitation	Not proven for neutralents; further treatment of effluents may be necessary; neutralents would have to be diluted	Promising candidate for targeted R&D program
Electrochemical oxidation	Strong oxidizing capability	Large quantities of toxic and hazardous materials required; pollution control systems immature	Disadvantages outweigh advantages
Supercritical water oxidation (SCWO)	Strong oxidizing capability; pollution prevention	High temperatures and pressures make system complex and prone to failures; corrosion and plugging due to precipitated salts are problems	Batch SCWO could address problems of continuous SCWO but requires significant further development
Gas-phase chemical reduction	Good destruction efficiencies for larger organic molecules	Produces significant amount of carbon soot as well as a large vapor stream requiring sophisticated treatment	Disadvantages outweigh advantages
Plasma arc	Good destruction efficiency, robust, promising test results on simulated neutralent	Large vapor stream requiring treatment; may not be perceived as true alternative to incineration	Promising candidate if acceptable to public interest groups
Biotreatment	Effective on some biodegradable molecules; benign process conditions	Low destruction efficiency for some components of EDS neutralent	Not appropriate for this application
Solvated electron technology	Effective on some organic waste streams	Ineffective for EDS neutralents because of their high water content	Not appropriate for this application

SOURCE: NRC (2001a).

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2001a). Based on the discussion above and the preliminary results of technology testing, the committee believes that the two-track approach it recommended for selecting treatment technologies for RRS and MMD neutralents remains valid for EDS liquid waste streams. However, the preferential ranking of technologies in the resource investment track (track two above) is modified as follows.

If neither the ACWA nor the commercially mature technologies can be used as is—if, for example, substantial process or permit modifications would be needed to dispose of nonstockpile neutralents—then the committee recommends that NSCMP should invest R&D resources first in further improvements in chemical oxidation and wet-air/O₂ oxidation. Only if these technologies cannot be adapted easily does the committee recommend that the Army consider investing resources in supercritical water oxidation (batch mode).¹³

In summary, the committee retains chemical oxidation and wet air/O₂ oxidation at the top of its preference list on the resource investment track (track two). Based on promising test results of plasma arc technology on simulated EDS neutralents and the possibility of public acceptance, the committee judges that advancements in plasma arc technology confirm its position on track one (existing commercial technology), thus removing it from track two (requiring R&D investment).¹⁴ SCWO (batch mode) is retained in track two, since it promises to address many of the problems associated with continuous SCWO.

Electrochemical oxidation with Ag(II) is dropped from the second track because it seems a poor choice for posttreating the chloride-rich neutralents derived from HD, CG, and L agents, which are likely to be involved in most

¹³If any of the technologies in track one can be demonstrated to work and to be cost-effective, then the committee recommends that R&D on track two technologies be terminated. However, the strict time constraints imposed by the CWC—i.e., that all NSCWM recovered prior to 1997 must be destroyed by 2007—effectively require that the two tracks be pursued at the same time.

¹⁴Plasma arc technology is a mature commercial hazardous waste treatment technology that is used in the United States and Europe. At least one design also has been tested using some CWM. However, as with any commercial treatment technology, additional tests and refinements in the design are necessary to ensure that the treatment technology in operation on specific wastes meets all applicable regulatory requirements and protects human health and the environment on a site-specific and design-specific basis.

EDS applications. In addition, new test data from the ACWA Program indicate that polynitroaromatic compounds (e.g., trinitrobenzoic acid and trinitrobenzene) precipitate during treatment of liquid wastes containing explosive residues, which may be present in EDS neutralents (Winkler, 2001). Electrochemical oxidation with Ce(IV) is also dropped from track two, owing to its relative immaturity and the possibility of corrosion and plugging of the electrochemical cells as a result of higher levels of metal ions in the EDS neutralents.

Supercritical water oxidation (continuous mode) is dropped from track two because the characteristics of the EDS neutralents (high chloride content, higher metal concentrations) are likely to exacerbate ongoing problems with corrosion and plugging. The committee found no reason to change its low ranking of gas-phase chemical reduction (GPCR), because initial testing showed that a variety of undesirable by-products were formed and because the addition of equipment to capture toxic heavy metals such as arsenic and mercury would add significant cost and complexity. Biotreatment and solvated-electron technology (SET), which were judged inappropriate for treatment of MMD liquid wastes, are similarly inappropriate for EDS liquid wastes.

To summarize, the committee recommends that available R&D resources be focused on development of chemical oxidation, wet-air oxidation, and supercritical water oxidation (batch mode). Similarly, it recommends that no further resources be spent on development of electrochemical oxidation, supercritical water oxidation (continuous mode), GPCR, biotreatment, or SET for this purpose.

Data Gaps and Uncertainties

The biggest data gap relates to the fact that, at this writing, only GPCR had been tested for its ability to destroy actual EDS neutralent. Through its alternative technology testing program, the Army plans to use actual neutralent in some of its tests, but for most tests it will use simulated neutralent. The committee recognizes that there may be a number of good reasons for using simulated neutralent in technology testing, particularly for early testing trials. Actual EDS neutralent may not be readily available, and there may be regulatory issues associated with using actual neutralent during testing (see Chapter 4). However, the committee feels that the credibility of such testing would be significantly enhanced if actual EDS neutralent were to be used.

A complementary approach that could increase confidence in the technology test results would involve the use of tracking compounds.¹⁵ A key factor in the evaluation of any

alternative treatment technology is its ability to either destroy the chemical compounds of greatest concern or to change them into a form that allows them to be easily removed or immobilized. Typically, a number of tracking compounds are identified and their fate is examined. Tracking compounds are chosen based on regulatory concerns as well as their resistance to destruction, with the understanding that if the tracking compounds are adequately destroyed or immobilized, the compounds of concern will also be destroyed or immobilized. Some potential tracking compounds—one example might be methylphosphonic acid (MPA), which is stable and difficult to destroy—are identified in Appendix G, along with a discussion of the concept.

Tracking compounds are used to evaluate incinerator performance, and a similar approach would be desired in the regulatory approval process of any alternative treatment technology (see Chapter 4). In addition, an understanding of the thermodynamics and kinetics of the destruction of the tracking compounds is highly desirable, in order to optimize process conditions.

As the Army proceeds with its Technology Testing Program, it would be desirable for it to identify and collect information on the fate of appropriate tracking compounds to better evaluate the performance of the technologies.

FINDINGS AND RECOMMENDATIONS

Finding: Neutralents from the EDS are similar to those from the MMD owing to similar treatment chemistries. However, there could be three differences:

- The potential presence of residual explosives or explosive-derived organic compounds in the EDS neutralents and rinsates. The MMD and the EDS produce different liquid wastes because of the different ways that munitions are processed. The MMD does not process items containing explosives, while the EDS can handle munitions containing bursters and/or fuzes. The EDS also uses explosives to open the munition and detonate any explosives contained therein.
- Potentially higher concentrations of dissolved or suspended metals (e.g., Hg, Pb, Cu, and Al) in EDS neutralents and rinsates owing to explosive accessing of the munition and/or the presence of fuzes or bursters. The fragmentation of the munition bodies may expose more metal surface to the monoethanolamine (MEA) reagent, ¹⁶ which is a good extractant for some of these metal ions. In addition, the detonator materials in fuzes, such as lead azide and mercury fulminate, may introduce these highly toxic metal ions.

¹⁵Tracking compounds have long been used by the chemical industry to evaluate the performance of chemical processes. A similar concept is involved in EPA's requirement that the trial burn data accompanying permit applications for hazardous waste incinerators must contain information on the destruction and removal efficiency of thermally stable "principal organic hazardous constituents" in the waste feed. See 40 CFR, Parts 270.19 and 270.62.

¹⁶The choice of MEA as a reagent was based on extensive previous experience with it in other CWM programs, its ability to dissolve the agents, miscibility with water, low corrosivity with stainless steel, and low flammability.

• The potential presence of arsenic compounds in the EDS neutralent from a small number of munition fills (the MMD was not intended to treat agents containing arsenic).

Finding: The fills expected to be processed most frequently in the EDS are sulfur mustard (H, HD), phosgene (CG), and—to a lesser extent—sarin (GB). Items filled with other agents—such as lewisite (L), which contains arsenic, or the nerve agent VX—are expected to be encountered much less often, but they do exist in the nonstockpile inventory.

The Army has conducted operational testing of the EDS only for munitions containing H, CG, and GB. Thus, the committee's analysis focused mainly on the liquid waste streams resulting from EDS treatment of these three types of agent. However, because lewisite munitions are known to exist in the inventory and may be treated in the EDS, the committee also considered in its analysis the effect of high concentrations of arsenic compounds.

Finding: If agents containing arsenic (such as lewisite) are processed in the EDS, additional treatment steps will be needed to remove arsenic from the EDS neutralent or reduce its mobility in treated solids. In these rare cases, however, suitable treatment chemistries are known and have been demonstrated to be effective (Utah, 1998; McAndless et al., 1992).

Finding: The EDS neutralization process and subsequent water rinses produce four liquid waste streams in two categories: (1) organic-rich liquids consisting of the neutralent and a reagent-based rinse and (2) cleaning solutions and final washes containing relatively low concentrations of organics.

Recommendation: The committee recommends that the Army consider separate treatment strategies for organic-rich liquids and these other aqueous liquids, since their chemical properties and regulatory status are different.

Finding: Chemical analyses of EDS neutralents and rinsates obtained from testing of HD, CG, and GB in the EDS may not have accounted for some species, such as energetic compound decomposition products, that may be encountered during operations.

Recommendation: The Army should review the sampling and analytical techniques employed at Porton Down and at RMA to ensure they are sufficiently sensitive and complete to detect any species of agent, energetics, and other components that could be in concentrations high enough to be of concern to human health or the environment.

Finding: The two-track approach¹⁷ recommended for selecting treatment technologies for RRS and MMD neutralents in

the committee's previous report (NRC, 2001a) remains valid for EDS liquid waste streams. However, based on new and preliminary results of NSCMP's Technology Test Program, as well as results of tests on some of the technologies obtained in the Army's Assembled Chemical Weapons Assessment (ACWA) Program, the preferential ranking of technologies in the resource investment track has changed, as described in the following recommendation.

Recommendation: The NSCMP should pursue a two-track strategy to identify a suitable treatment technology for EDS liquid waste streams. As part of the first track, the NSCMP should take advantage of available equipment that would require little or no investment, that is, it should piggyback on alternative technologies from the ACWA Program or on existing commercial technologies, such as chemical oxidation, wet-air/O₂ oxidation, or plasma arc¹⁸ technology. The committee judged that if any of these existing and available technologies can accomplish the task safely, it should provide a relatively rapid and inexpensive course of action.

If, on the other hand, none of the existing and available technologies can be used as is—for example, if substantial research and development resources would be needed to adapt them to the destruction of nonstockpile neutralents—the committee recommends that NSCMP, as part of track two, should invest first in chemical oxidation and wet-air/O₂ oxidation. Only if these technologies cannot be adapted easily does the committee recommend that the Army consider investing R&D resources in supercritical water oxidation (batch mode). ¹⁹

¹⁹If any of the technologies in track one can be demonstrated to work and be cost effective, then the committee recommends that R&D on track two technologies be terminated. However, the strict time constraints imposed by the CWC—i.e., that all NSCWM recovered prior to 1997 must be destroyed by 2007—in effect require that the two tracks be pursued at the same time.

¹⁷In the report on disposal of neutralent wastes (NRC, 2001a), the first track of the two-track approach contained technologies that did not need Army development investment. The second track consisted of alternative technologies requiring investment. The earlier report recommended investigating track one technologies before turning to track two.

¹⁸One commercial plasma arc technology (the PLASMOX process) has treated a chemical warfare agent in Switzerland. Although it has not yet been permitted for use on any hazardous waste in the United States, it has also been used for the commercial treatment of hazardous waste in Switzerland. The Army has represented to the committee that there are a number of plasma arc facilities permitted in the United States, primarily for treatment of medical wastes, and that it intends to test some of these plasma arc designs. The committee has not reviewed the emissions data from the PLASMOX treatment of chemical agent or from these commercial facilities. Plasma arc technologies may emit low levels of polychlorinated dibenzodioxins. Since PLASMOX uses oxygen, it may be considered by some regulators and some members of the public as a more sophisticated incinerator.

The committee recommends that no further resources be spent on development of electrochemical oxidation, supercritical water oxidation (continuous mode), gas-phase chemical reduction, biotreatment (by itself), or solvated electron technology for this purpose.

Finding: The Army has an ongoing program to test several alternative technologies for their ability to destroy EDS neutralents. Based on information provided to the committee regarding this test program, the committee has several concerns:

- The tests are often conducted with simulated EDS neutralents mixed from laboratory chemicals rather than with actual EDS neutralents.
- The Army does not appear to have identified key tracking compounds²⁰ that are the most difficult to destroy and whose disposition can serve as indicators for the performance of the treatment technologies.
- The test program does not appear to be designed to provide basic data on the kinetics and thermodynamics of the

oxidation of key waste stream components under process conditions.

Recommendation: The test program could be improved if the following steps are taken:

- To the extent feasible, the Army should use a representative range²¹ of actual EDS neutralents obtained from munition destruction in its tests of alternative treatment technologies.
- A limited number of tracking compounds chosen for their ability to gauge process performance and issues of regulatory concern should be identified and analyzed for in the treatment effluent.
- To supplement tests on EDS neutralents, the Army should collect information about the kinetics and thermodynamics of the destruction of these tracking compounds by the preferred destruction technology.
- Physical properties of neutralents such as phase behavior (including suspended solids) and flash point should be determined on neutralent samples obtained from EDS-1 and EDS-2 treatment of actual chemical munitions.

²⁰One example of a tracking compound for destruction of nerve agents might be methylphosphonic acid, which is very stable and difficult to destroy. Further discussion of tracking compounds may be found in Appendix D.

²¹As noted in Chapter 2, the compositions of EDS neutralents from destruction of separate NSCWM will not necessarily be consistent, even for munitions of the same type.

4

Regulatory and Public Involvement Issues

This chapter explores regulatory approval and permitting (RAP) issues associated with the treatment and disposal of EDS liquid waste streams, as well as some of the concerns expressed by public interest groups about such treatment and disposal. As happened with the RRS and MMD, unresolved RAP issues and the concerns of some public interest groups can dramatically increase the cost and time associated with disposal of nonstockpile CWM with mobile treatment systems such as the EDS. It took 3¹/₂ years for the RRS prototype, located at Deseret Chemical Depot, Utah, to obtain a RCRA permit. The MMD RCRA Research, Development and Demonstration (RD&D) permit at Dugway Proving Ground, Utah, required over 5 years. The considerable length of time required for the RD&D permit for the MMD contributed to the suspension of the program.¹

REGULATORY APPROVAL AND PERMITTING

Use of a mobile treatment system such as the EDS has two stages. The first stage involves the following:

- obtaining the regulatory approvals necessary to operate the mobile treatment system
 - transporting the system to the site
- actual neutralization of the nonstockpile chemical materials

The second stage involves the subsequent treatment and disposal of the EDS waste streams, whether at the site where they are generated or at an off-site facility.

Although the RAP mechanism used for operation of the EDS device itself will affect the choice of a RAP mechanism for treatment of the EDS liquid waste streams, the two

¹D. Lyle, U.S. Army PMCD, personal communication to the committee, March 15, 2000.

are nevertheless distinct. In many cases, different RAP mechanisms may be used for primary and secondary waste treatment, especially when secondary wastes are treated at facilities/sites other than those at which they are generated. This discussion focuses on RAP issues associated with the second stage and deals primarily with liquid EDS wastes; RAP issues associated with the EDS system as a whole, and other NSCM treatment systems, will be discussed in a subsequent report.

There are a number of RAP mechanisms that could be used for management of liquid EDS waste streams, including the following:

- obtaining a new hazardous waste permit for a treatment, storage, or disposal facility (TSDF) already at the site
- conducting the treatment activity under an existing TSDF permit (applicable if a TSDF already exists at the site and the permit is sufficiently broad to allow treatment without needing to modify the existing permit)
- modifying an existing hazardous waste TSDF permit available at the facility to allow treatment of the liquid wastes
- using emergency exemptions (to permitting) available under most state hazardous waste regulations
- using a Resource Conservation and Recovery Act (RCRA) order, including a compliance order (RCRA § 3008(a)), an imminent and substantial endangerment order (RCRA § 7003), a corrective action order (RCRA § 3008(h)), or state-specific counterparts to these orders
- obtaining an emergency permit under federal or state hazardous waste regulations, as applicable
- using a RCRA Research Development & Demonstration (RD&D) permit or a RCRA treatability study
- using Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) removal authority
- conducting the treatment activity pursuant to an existing waste management plan established under CERCLA authority

As discussed earlier, the EDS was used to destroy six sarin bomblets at RMA. Although the mustard agents are listed hazardous wastes in Colorado, sarin was not listed at the time.2 The first stage of the EDS operation was carried out through a state-issued emergency compliance order, which is the counterpart to the federal Imminent and Substantial Endangerment Order (RCRA §7003), with one order modification. RMA is federally listed on the CERCLA National Priorities List (NPL) and has an ongoing remediation program. The Army used the existing structure under RMA's CERCLA remediation program to destroy the sarin bomblets. In essence, the Army implemented the Colorado emergency compliance order as a CERCLA emergency removal action. This enabled it to use existing funding and waste management procedures established under the ongoing CERCLA remediation program to implement the effort, and allowed both the Army and the state to avoid the long RAP delays experienced in Utah with RCRA permitting of the RRS and MMD. The Army hopes that the approach used at RMA can be a model for the RAP process at future sites where the EDS might be employed.³

While the state of Colorado was also pleased with the outcome of the RMA situation, it initially had many concerns as the Army was evaluating means of destroying the bomblets. These concerns pertained to the Army's initial proposal to use open detonation to destroy the GB bomblets. This initial proposal, which was later dropped in favor of the EDS, was the primary impetus behind the state's issuance of the emergency compliance order. The EDS device was not the Army's first choice for destroying the bomblets. The RAP mechanism deployed at RMA pertained only to use of the EDS itself (the first stage, as discussed above). Management of secondary neutralent and rinsate waste, which is the focus of this report, was deferred to the RMA waste management plan (U.S. Army, 2001c).

If the EDS waste is to be treated in an off-site facility and is determined to be a hazardous waste, the Army must either find a permitted hazardous waste TSDF to accept the waste, or a new facility must be permitted. Considering the RRS and MMD experience, and the low volume of the EDS wastes that would be generated in most cases, the Army is likely to seek an existing TSDF that is willing to accept the waste.⁴ The TSDF would need to determine whether it can treat the EDS neutralent pursuant to its existing permit or

whether a permit modification is necessary. In the short term, off-site treatment means incinerating the neutralent, since the nonincineration treatment technologies discussed in this report have not yet been proven for the application. However, several available commercial facilities use chemical oxidation to treat wastes similar to neutralents. These facilities would probably require a permit modification before they could accept the neutralents.

For incineration, there are a number of well-defined environmental requirements in the existing federal and state regulations. For example, hazardous waste incinerators must demonstrate the ability to destroy or remove a minimum of 99.99 percent of the hazardous waste constituents entering the incinerator (40 CFR 264.343).⁵ In addition, there are procedures that allow the derivation of waste-specific or site-specific requirements, if necessary. Operating and closure requirements are similarly well established.

In contrast, no such well-established specific environmental requirements exist for nonincineration technologies relating to the treatment of nonstockpile hazardous wastes, although generic requirements may apply (e.g., 40 CFR 264 Subpart X). In its earlier report (NRC, 2001a), the committee recommended that the Army develop a RAP and public involvement implementation plan, and it reiterates that general recommendation in this report. Part of this plan would involve the establishment of treatment goals or standards for alternative technologies. Operating and closure standards must also be developed. However, because the establishment of treatment goals is an objective that applies to all technologies for treating the entire spectrum of nonstockpile CWM and waste streams, not just EDS liquid wastes, a more detailed discussion of this issue is beyond the scope of the current report and will be addressed in a subsequent NRC report dealing with all of the treatment technologies available to destroy nonstockpile materiel.

The regulatory issues involved in the nonstockpile program are complex and require detailed knowledge of the state and federal hazardous waste regulations (e.g., RCRA, CERCLA), other environmental laws such as the Clean Water Act, and the Chemical Weapons Convention. Given the number of regulatory options available to it and the variability from state to state and sometimes from site to site, it is recommended that the Army develop guidance for field personnel who may be involved in managing nonstockpile chemical warfare materials. The guidance should detail how to determine whether these materials are hazardous wastes; at present, such guidance varies from state to state (see below), as do the legal mechanisms that are appropriate for

² The state of Colorado has since proposed and finalized a rule that does list sarin as a hazardous waste, as well as additional agent-related waste streams (Colorado, 2001).

³William Brankowitz, Office of the Product Manager, Non-Stockpile Chemical Materiel, "U.S. Army Non-Stockpile Chemical Materiel Product (NSCMP) Project Overview/Status," presentation to the committee, May 23, 2001.

⁴In the case of EDS neutralent generated at RMA, the Army contracted with a TSDF out-of-state to incinerate the waste.

⁵The RCRA requirement for most hazardous constituents is that a minimum of 99.99 percent of the hazardous constituent must be destroyed. EPA has established a more stringent standard of 99.9999 percent destruction, however, for certain types of constituents, such as dioxins and furans. The more stringent standard of 99.9999 percent has been applied for incineration of chemical agents in the stockpile program.

various site conditions. In addition, the guidance should be coordinated with applicable state regulatory programs.⁶

Regulatory Status of EDS Neutralents and Rinsates

As described in Chapter 2 and Appendix C, the operation of the EDS produces essentially two distinct types of liquid waste streams: (1) organic-rich liquids, for example, the neutralent and a reagent-based rinse, and (2) aqueous streams (rinsates, cleaning solutions, and wastes) containing nondetectable or very low concentrations of organic and inorganic constituents. These two waste streams have different physical and chemical properties and different toxicities, and Army protocols require that they be stored in separate waste drums. This suggests that it may be appropriate for neutralents and rinsates to be treated by different methods. The regulatory status of these waste streams strongly affects the treatment and disposal options, and this status may vary from state to state.

Although RCRA is a federal statute, the responsibility for implementing the statute and issuing permits under RCRA lies primarily with the states. While authorized states must implement the basic federal legislation, they have the option of being more stringent or broader in scope than the federal program. For example, chemical warfare agents are not listed in the federal regulations, but six individual states—Colorado, Indiana, Kentucky, Maryland, Oregon, and Utah—have listed them as hazardous wastes. In each state, the listed chemical agents are different, and the manner of listing differs as well.

If a waste is a listed hazardous waste, waste streams derived from treatment of that waste may also be deemed hazardous under RCRA's "derived from" rule. This is important because if CW agents treated in the EDS are listed hazardous wastes in a given state, then both neutralents and rinsates, which are "derived from" the treatment of the agents, may also be deemed hazardous wastes. In some states, regulations or permit language may, however, be structured so as to classify some derived-from waste as nonlisted.⁷

In all states, the EDS neutralents could be considered characteristic hazardous wastes under RCRA. With some exceptions, a hazardous waste may only be treated, stored, or disposed of in a RCRA-permitted TSDF. In addition, any treatment technology must meet RCRA requirements, such as the Land Disposal Restrictions (LDRs) (40 CFR 268). In accordance with the LDRs, wastes must meet certain treatment standards prior to land disposal. These restrictions provide for additional protection of human health and the environment, but they add considerably to the cost and time required to treat and dispose of the waste stream. Other standards must also be met, such as those associated with treatment facility operation and closure.

The EDS treatment process also generates cleaning solutions and washes that are distinct from the rinses. The rinses are done with hot water and are an integral part of the operating procedure for destroying each munition. The cleaning solutions are a mixture of aqueous detergent solutions resulting from cleaning the EDS after each campaign. They also include a wash with dilute acetic acid to clean the plumbing of the EDS. The acid has a tendency to leach metals from the walls of the EDS. The detergent washes out the solvent-based sealant used on the EDS seals.

As with the neutralents, EDS rinsates and spent cleaning solutions may be classified as listed hazardous wastes in some states. In states where the EDS rinsates are not listed as hazardous waste, given their dilute nature it is unlikely that they would meet any of the RCRA characteristics and would therefore not be designated as hazardous waste. Except for the anomalous high measurements of chloroform in the spent cleaning solutions, these solutions are also primarily water, with much lower concentrations of hazardous constituents than the initial neutralent. As a result, if chloroform were not generated in the EDS cleaning process, even the aqueous rinses and cleaning solutions would probably not have any of the RCRA characteristics and would therefore not be designated as hazardous waste. In states where these wastes are listed hazardous waste, however, they would of course be considered listed hazardous waste.

The Army has suggested that the chloroform found in the cleaning solutions is leaching from a sealant utilized in the EDS. There may be other equivalent sealants that do not contain chloroform that could be substituted for these sealants.

To ensure that these neutralents, rinsates, or spent cleaning solutions are classified properly for regulatory purposes, the Army should work with the regulators and the public. If

⁶The committee considered whether defining RAP mechanisms might be better incorporated into regulations rather than guidance. The RCRA regulations define requirements for all RAP mechanisms. In general, however, the regulations do not specify which RAP mechanisms must be used in particular situations. This is because the regulator and the regulated need the flexibility to decide which RAP mechanism is best under a given set of circumstances. This is especially the case for NSCWM, which may be found in varying configurations, in varying amounts, in varying states of deterioration, and at varying locations. Hence, it is inappropriate to define these types of requirements as part of the regulations. Guidance is not only sufficient in this case; it is preferred.

⁷ The Army could also pursue certain exemptions available under RCRA, such as a RCRA delisting petition (40 CFR 260.22). In accordance with this exemption, the waste would no longer be considered hazardous waste and may be disposed of in a nonhazardous waste landfill.

⁸Under RCRA, a waste is classified as hazardous if it is specifically listed and/or because it exhibits certain hazardous characteristics (ignitability, corrosivity, reactivity, and toxicity). The EDS neutralents may exhibit the corrosivity characteristic due to high pH (pH > 12). They may also exhibit the toxicity characteristic if they contain specific compounds (e.g., lead, arsenic, benzene) above leachable concentration levels.

a liquid waste stream is classified as nonhazardous under RCRA, the options for disposal expand considerably, and the time and cost of disposal are greatly reduced. Assuming rinsates meet the pretreatment standards specified by the Clean Water Act, the waste stream may be discharged to a publicly owned treatment works (POTW) or an equivalent federally owned treatment works (FOTW). In the state of Colorado, for instance, the EDS rinsates from the destruction of the sarin bomblets at RMA were eligible for disposal in a POTW or FOTW.

The Army's Plan for Disposal of EDS Neutralents and Rinsates

Given the current lack of permitted commercial treatment facilities utilizing nonincineration treatment technologies applicable to EDS waste streams, the Army is planning to utilize commercial incineration facilities to treat the EDS neutralent and is likely to continue to do so for any EDS neutralent generated in the near term. For example, at this writing the neutralents generated in the recent destruction of the six sarin bomblets at RMA, after having been temporarily stored on-site, were sent out of state to a permitted hazardous waste incinerator. Based on the Army's reported quantities of residual chemical agents in EDS neutralents, transportation of neutralent wastes from the EDS should not be subject to any restrictions beyond the applicable federal RCRA, DOT, and state regulatory requirements.¹⁰

Nevertheless, the incineration of CWM has been a controversial issue, and the Army is concerned that—at least at some sites—the opposition of some states and public interest groups to incineration of stockpile chemical agents could one day be extended to incineration of nonstockpile neutralents from mobile treatment systems. This concern is one of the primary reasons for the interest in the alternative treatment technologies that are the subject of this study.

While the Army has not specified a preferred method for disposing of EDS rinsates, where feasible it may seek to process them through a wastewater treatment plant. For example, EDS rinsates that were in temporary storage at RMA were sent to an on-site wastewater treatment facility.

To avoid having to obtain RCRA approvals to treat hazardous waste using an experimental nonincineration treatment technology, in its testing program for alternative technologies (see Chapter 3) the Army has often used simulated neutralents—laboratory chemicals mixed together in proportion to the results of actual neutralent analysis. The use of actual neutralents in tests would provide valuable additional information about the performance of the technologies. This might, of course, require regulatory approval, since the actual neutralents may be defined as hazardous waste. Approvals for treatment of hazardous waste with new technologies can be expedited through the mechanism of RCRA RD&D permits or treatability studies. However, it is important to note that these RAP mechanisms are intended for experimental or pilot-scale tests of a new technology and not as a routine mechanism for destroying neutralent.

Transportation Issues

Significant concerns have been raised about the transport of CWM. Indeed, concern about the movement of chemical agents has been a driving force behind the development of transportable treatment systems. As far back as 1969 (P.L. 91-121), Congress placed severe, almost insurmountable, restrictions on the transport of CWM, including a requirement for advance notification and coordination of shipments with the U.S. Department of Health and Human Services and Congress (except in cases of emergency). In 1995, Congress placed restrictions on moving nonstockpile CWM out of any state except to the closest permitted CWM storage facility, and then only under very strict conditions. Public concerns about transporting CWM have effectively foreclosed even this option except in extraordinary situations.

The neutralents generated by the EDS will primarily include hazardous waste and hazardous materials, which make them subject to RCRA and DOT requirements. If these are the only constituents, the neutralent could be transported as a routine hazardous waste or hazardous material under existing laws and regulations as long as it is packaged, marked, manifested, and shipped as required by those regulations.

However, the neutralent from the EDS may contain trace amounts of residual chemical agents, for example, GB (<1 ppm) or sulfur mustard (<50 ppm). At these levels, toxicity studies (see Appendix D) indicate that the concentration of residual agent would be too low to affect the overall toxicity of the waste streams. It is not known how much, if any, chemical agent would be present at concentrations lower than the treatment goal. Thus, based on the information provided by the Army, transporting neutralent wastes from the EDS should not be subject to any restrictions beyond the applicable federal RCRA, DOT, and state regulatory requirements. However, the public perception of "residual chemical agents" in the EDS waste streams may arouse concerns.

Although these residues will be present in extremely small amounts, the public could consider the overall neutralent waste mixture as "tainted" with chemical agent and, therefore, of special concern. The Army should address this potential problem proactively. This could be done in several

⁹Chloroform—a constituent that may cause wastes to be defined as hazardous, depending on concentration—was observed in EDS cleaning solutions from the RMA tests (Table C-1). The source appears to be the lubricant/sealant used to seal joints. The chloroform is therefore not a necessary constituent of the waste stream and could be eliminated by using a sealant/lubricant with a different formulation.

¹⁰This is the same conclusion reached by the committee in reference to transportation of neutralents generated by the RRS and MMD systems in NRC (2001a, p. 19).

ways. In a previous report, for example, the committee recommended that a comparative risk assessment be performed of the disposal of CWM in CAIS in an incinerator and the disposal of typical hazardous waste (NRC, 1999a). The Army could assess the comparative risk of transporting and disposing of neutralent and transporting and disposing of typical hazardous waste. Providing the public with this type of information would increase the transparency and credibility of the process.

Finding: EDS neutralent may be treated off-site or on-site. If the EDS liquid waste is treated off-site, the Army must obtain a permit for a new facility or find a permitted hazardous waste treatment facility or a FOTW or POTW that can treat the EDS liquid wastes. If a facility with an existing permit is used for treatment, that existing permit may require modification.

Finding: Based on available data and the experience of the members of the committee, the chemical constituents most likely to be of concern in the RAP process for EDS liquid wastes are chlorinated organics, possible degradation products of agent and energetic compounds, metals, suspended solids, ¹¹ and MEA. These constituents were chosen based on their abundance in the neutralent, their inherent toxicity, their resistance to treatment, or overall regulator and public concern.

Recommendation: The Army's RAP strategy should ensure that sufficient information is obtained about the chemical constituents of greatest concern in the RAP process for the EDS liquid wastes: chlorinated organics, degradation products of agent and energetic compounds, metals, suspended solids, and MEA.

Finding: RAP options associated with treatment of EDS neutralents, rinsates, and cleaning solutions depend on whether the waste is regulated as hazardous within the state where it is generated and, if it is, whether it is a "listed" hazardous waste, a "characteristic" hazardous waste, or both.

If EDS liquid wastes are determined to be hazardous under the federal RCRA program (via the RCRA characteristics), RCRA's land disposal restrictions (LDRs) apply, and the wastes must be treated to meet specific requirements.

Note that the remainder of these findings and recommendations in this section are based on the premise that neutralent will be defined as hazardous waste. This may not always be the case, although the Army's practice to date has been to treat the neutralent as hazardous waste.

Finding: In the near term, the Army is likely to continue to use permitted hazardous waste incinerators to dispose of EDS liquid wastes (especially neutralents), because of their proven effectiveness. Many commercial hazardous waste facilities use nonincineration technologies to treat wastes similar to EDS liquids and might also be available.

Finding: Dilute aqueous rinsates from the EDS and wastes resulting from treatment of neutralent may be classified as listed hazardous wastes either as a result of the "derived from" rule or because the state explicitly lists the rinsate. However, these solutions are primarily water with much lower concentrations of hazardous constituents than the initial neutralent. As a result, they pose relatively little risk and could probably be safely managed as nonhazardous wastes, thereby lowering disposal costs without causing any meaningful change in the degree of protection.

Finding: The EDS treatment process also generates spent cleaning solutions that are distinct from the rinses. The cleaning solutions are a mixture of aqueous detergent solutions and a dilute acetic acid wash. The detergent apparently has a tendency to leach chloroform out of the solvent-based sealant used on the EDS seals. While the acetic acid may also leach metals from the walls of the EDS, the levels of these metals appear not to be high enough to warrant considering the resulting waste as hazardous. The chloroform may be of concern, however. Except for the higher amounts of chloroform, these solutions are also primarily water, generally with much lower concentrations of hazardous chemicals than the initial neutralent. As a result, if the chloroform were not generated in the EDS cleaning process, even the aqueous cleaning solutions could probably be safely managed as nonhazardous waste.

Finding: The Army has suggested that the chloroform found in the rinsate is leaching from a sealant utilized in the EDS. There may be other equivalent sealants that do not contain chloroform and that could be substituted for these sealants.

Recommendation: The Army should expeditiously take action to substitute a sealant that does not contain chloroform in the existing EDS systems and all future EDS units.

Recommendation: In states where rinsates, cleaning solutions, or wastes resulting from treatment of neutralent are listed as hazardous wastes or are considered hazardous waste because they are derived from treatment of a listed hazardous waste, the Army should work with the state regulators toward the designation of these wastes as nonlisted hazardous waste. For spent cleaning solutions, this recommendation assumes that the source of chloroform in the rinses can be eliminated. The Army should collect all data on EDS rinsates and cleaning solutions for presentation to the state regulators in support of a hazardous waste listing determina-

¹¹Suspended solids are a concern only if they are determined to contain residual chemical agent in microscopic cracks and crevices. See discussion in Chapter 2.

tion. If it is found that these wastes do not meet the hazardous waste listing criteria, they should be designated nonlisted hazardous waste by modifying the state regulations or the permit or equivalent documentation. While the state regulators could require the Army to submit RCRA delisting petitions, the committee believes that a modification in the state regulations or in the permit or equivalent documentation would be the more cost-effective option.

Recommendation: The Product Manager for Non-Stockpile Chemical Materiel (PMNSCM) should work with regulators and the concerned public to resolve RAP issues surrounding the EDS waste streams well in advance of EDS deployment to a particular site.

Finding: Regulatory issues related to the posttreatment of liquid wastes (neutralents, rinsates, and cleaning solutions) produced by the EDS are distinct and different from the regulatory issues related to use of the EDS itself. There are a number of RAP mechanisms that could be used for management of EDS liquid wastes.

With the proper approvals or permits, treatment of EDS liquid wastes may be conducted on-site or at off-site facilities. In some cases, treatment may be conducted under a facility's existing treatment, storage, and disposal facility (TSDF) permit, if that permit is written sufficiently broadly to allow acceptance of EDS liquid wastes. Other options include obtaining a hazardous waste permit for treatment, modifying an existing hazardous waste treatment permit, using emergency exemptions available under most state hazardous waste regulations, obtaining an emergency permit under the state hazardous waste regulations, using a RCRA compliance order (RCRA §§ 3008(a), 3008(h) or 7003), or using the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) removal authority.

In some cases, the wastes could be managed under a waste management plan established under a CERCLA record of decision. RCRA research, development, and demonstration (RD&D) permits and treatability studies may also be appropriate in certain cases.

Recommendation: The Army should develop RAP guidance for field personnel (e.g., base commanders) on the disposition of EDS neutralent and rinsate waste streams, taking into consideration the nature of the NSCWM and the specific regulatory environment at locations where the EDS might be sited. This guidance should cover all aspects of RAP for the EDS and treatment (as necessary) of neutralents and rinsates, including setup, operation, and closure. Development of this guidance should be coordinated with the states, and a jointly issued guidance document should be considered.

PUBLIC INVOLVEMENT

As discussed in the earlier report on neutralent wastes (NRC, 2001a), the necessity, as well as the desirability, of proactively seeking public involvement in policy decisions that once were considered purely scientific has been well documented. Through previous research and case studies, and through the Army's recent experience with the ACWA Dialogue, productive ways of resolving contentious issues surrounding technology selection and disposal have been identified, the value of public involvement in general has been documented, and the issues of concern to the public in the selection of disposal technologies for chemical materiel have been clarified (NRC, 2001a).¹²

The public is not monolithic; rather it is composed of different "publics" whose interests, levels of awareness and information, and desired levels of involvement vary. As discussed in an earlier report on alternative technologies for disposing of secondary liquid wastes from the RRS and the MMD (NRC, 2001a), the committee focused on the views of citizen groups opposed to incineration that may be expected to continue as active participants in the decision to develop and deploy nonincineration technologies. In developing its report, the committee solicited the views of these citizen groups to gain a sense of what they considered would determine public acceptability of proposed technologies. These views apply to the treatment of EDS neutralent wastes, just as they apply to the treatment of other types of neutralent wastes.

The committee members sought information from various sources. They reviewed previous NRC studies (see especially NRC 1996 and 1996a); monitored the Non-Stockpile Chemical Weapons Coalition (NSCWC) and Chemical Weapons Working Group Web sites and publications that highlight public views of the non-stockpile program; and reviewed documents provided to them by the NSCWCC at the committee's request. The committee also solicited public opinion in both formal and informal discussions. These included a presentation to the committee in open session by two members of the NSCWCC and a citizen member of the ACWA/CATT group (the four-member Citizens' Advisory Technical Team that was established to work directly with the Army's technical team and report back to the citizens'

¹²The so-called ACWA Dialogue refers to the process established under the Assembled Chemical Weapons Assessment Program by which a broad range of participants was included in the selection and testing of alternative nonincineration technologies for destruction of assembled chemical weapons. Participants included representatives of all of the recognized parties of interest—e.g., Citizens Advisory Council members, public interest groups, and officials from state and federal regulatory agencies. The Dialogue is facilitated by the Keystone Center, a nonprofit association that specializes in resolving environmental and policy disputes.

interest groups as well as to members of the entire Dialogue); two committee members' observation of, and discussion with, participants in Core Group meetings (a national-level group sponsored by the NSCMP to exchange information among representatives of the public, regulators, and NSCMP personnel); and discussion with a member of the Core Group who accompanied the committee on a site visit to evaluate a treatment technology being considered.

In their discussions with the committee, citizen representatives affirmed their opposition to incineration and their preference for long-term storage rather than incineration of neutralent if an alternative does not become available in the near term. According to them, the primary criteria against which they evaluated the disposal technologies were the following:

- containment of by-products and effluents for analysis and further processing, if necessary
 - · identification of all by-products and effluents
 - low-temperature, low-pressure operation
 - · no emission of dioxins or furans
- pollution prevention (i.e., generation of as little secondary waste as possible)

The citizen representatives emphasized the need to consider not only technical criteria but also the broader social context of technology development and deployment and the value of early, direct public involvement. These additional factors affecting acceptability include the need for a fair and open decision-making process, including consultation with affected communities on their specific concerns; a desire for environmental justice; building a climate of trust with the Army and technology providers; and ensuring accountability and institutional safeguards.

Currently, NSCMP's public involvement program is focused on information distribution and outreach activities

with diverse groups, including minority populations and tribal governments. However, citizens group representatives cited the need for early, direct public involvement that goes beyond information and outreach activities to provide a formal mechanism for the public to be involved in the decision making (within the parameters set by an agency's legal mandate to make decisions). They praised the ACWA Dialogue process as a model for giving members of the public an opportunity to be engaged in establishing criteria for selecting and demonstrating technologies and in weighing the tradeoffs. Although the Core Group provides a valuable mechanism for information exchange and an opportunity to develop improved communication and effective working relationships between members of the public and Army personnel and contractors, unlike the ACWA Dialogue, it does not provide a formal mechanism, established by senior program management, for public involvement in the NSCMP's decision-making process.

Finding: The committee's earlier conclusions (NRC, 2001a) concerning public acceptability for RRS and MMD neutralent treatment processes also apply to treatment of EDS neutralents and rinsates. The committee's discussion with citizen groups indicated a need for—and the value of—public involvement in the Army's decisions on the selection and deployment of technologies for disposing of neutralents and, indeed, all nonstockpile chemical materiel.

Recommendation: The Army should continue to expand its program for public involvement in the disposal of nonstockpile chemical materiel. Enough time should be scheduled and enough resources allocated to ensure that the decision-making process is open and that members of the public are involved in making the trade-offs among to the selection, siting, deployment, and employment of disposal technologies.

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Appendixes



A

Biographical Sketches of Committee Members

John B. Carberry, chair, is director of environmental technology for E.I. duPont de Nemours and Company, where he has been employed since 1965. He is responsible for providing technical analysis of existing and emerging environmental issues. Since 1988, he has been involved with initiatives to advance DuPont's environmental excellence through changes in products, recycling of materials, and renewal of processes, with an emphasis on reducing waste and promoting affordable, publicly acceptable technologies for the abatement, treatment, and remediation of environmental pollution. Mr. Carberry is chairman of the Chemical Engineering Advisory Board at Cornell University, a fellow of the American Institute of Chemical Engineers, and a member of the Radioactive Waste Retrieval Technology Review Group for the U.S. Department of Energy. He was a member of the National Academy of Engineering (NAE) Committee on Industrial Environmental Performance Metrics. He holds an M.S. in chemical engineering from Cornell University and an M.B.A. from the University of Delaware.

John C. Allen is vice president of transportation at Battelle Memorial Institute. Prior to joining Battelle in 1983, he served as transportation economist and policy analyst with the U.S. Department of Transportation's Office of Hazardous Materiel Transportation. Mr. Allen has managed and participated in numerous studies involving the policy, regulatory, institutional, and safety aspects of transporting hazardous and nuclear materials. He has served on various National Research Council (NRC) advisory panels and has been chairman of the Transportation Research Board's Committee on Hazardous Materials Transportation for the past 4 years. He holds an M.B.A. in transportation from the University of Oregon and a B.A. in economics from Western Maryland College.

Richard J. Ayen, a member of the NRC Committee on Review and Evaluation of Alternative Technologies for Demilitarization of Assembled Chemical Weapons (I and II), received his Ph.D. in chemical engineering from the University of Illinois. Dr. Ayen, now retired, was director of technology for Waste Management, Inc. He has extensive experience in the evaluation and development of new technologies for the treatment of hazardous, radioactive, industrial, and municipal waste. Dr. Ayen managed all aspects of Waste Management's Clemson Technical Center, including treatability studies and technology demonstrations for the treatment of hazardous and radioactive waste. His experience includes 20 years at Stauffer Chemical Company, where he was manager of the Process Development Department at Stauffer's Eastern Research Center. Dr. Ayen has published extensively in his fields of interest.

Robert A. Beaudet is chair of the NRC Committee on Review and Evaluation of Alternative Technologies for Demilitarization of Assembled Chemical Weapons (I and II). He received his Ph.D. in physical chemistry from Harvard University and has served on U.S. Department of Defense committees that address offensive and defensive chemical warfare. Dr. Beaudet was chair of an Army Science Board committee that addressed chemical detection and trace gas analysis and for 2 years was chair of an Air Force technical conference on chemical warfare decontamination and protection. He also served on the NRC Committee on Chemical and Biological Sensor Technologies and the Committee on Energetic Materials and Science Technology. Most of his career has been devoted to research in molecular structure and molecular spectroscopy. Dr. Beaudet was a member of the Board on Army Science and Technology (BAST) and served as the BAST liaison to the Review and Evaluation of the Army Chemical Stockpile Disposal Program Committee during the development of nine reports. He is the author or coauthor of more than 100 technical reports and papers.

Lisa M. Bendixen is a principal in the environment and risk practice at Arthur D. Little, Inc. Since joining the company in 1980, Ms. Bendixen has been involved in risk manage-

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ment and risk assessment studies for numerous industries. She is the secretary of the NRC Transportation Research Board's Committee on Hazardous Materials and was the U.S. delegate to the International Electrotechnical Commission's working group on risk analysis until early 1999. She was a member of the NRC Committee on Fiber Drum Packaging for Transporting Hazardous Materials and is past chair of the Safety Engineering and Risk Analysis Division of the American Society of Mechanical Engineers (ASME). She has been involved in many studies on the chemical demilitarization of M55 rockets, including the identification and quantification of failure modes leading to agent release based on a generic disposal facility design; evaluations of sources of risk to separating agent from energetic components in the rocket; and preparation of criteria for evaluating storage, transportation, and on-site disposal options. Ms. Bendixen earned an M.S. in operations research at the Massachusetts Institute of Technology.

Joan B. Berkowitz, managing director of Farkas Berkowitz and Company, has extensive experience in environmental and hazardous waste management, technologies for the cleanup of contaminated soils and groundwater, and a strong background in physical and electrochemistry. She has contributed to several U.S. Environmental Protection Agency (EPA) studies, has been a consultant on remediation techniques, and has assessed various destruction technologies. Dr. Berkowitz is the author of numerous publications on hazardous waste treatment and environmental subjects. She was a member of the NRC Panel on Review and Evaluation of Alternative Chemical Disposal Technologies and is currently a member of the NRC Committee on Review and Evaluation of Alternative Technologies for Demilitarization of Assembled Chemical Weapons (I and II). She has a Ph.D. from the University of Illinois in physical chemistry.

Judith A. Bradbury, technical manager at Battelle Pacific Northwest National Laboratory, is currently evaluating public involvement programs across the U.S. Department of Energy (DOE) complex. She previously completed a series of evaluations of the effectiveness of DOE's 12 site-specific advisory boards and led an assessment of community concerns about incineration and perspectives on the U.S. Army Chemical Weapons Disposal Program. Dr. Bradbury is a member of the Risk Assessment and Policy Association. She earned a B.S. in sociology from the London School of Economics, an M.A. in public affairs from Indiana University of Pennsylvania, and a Ph.D. in public and international affairs from the University of Pittsburgh.

A. Stan Davis is a strategic planning consultant operating in Greenville, South Carolina. He recently held the position of Strategic Planning Officer at the University of South Carolina, Spartanburg. Mr. Davis was selected for membership on this committee for his extensive experience in a variety of

activities, including the engineering design of power generation components, the development of heat treatment and material vibration specifications, the deployment of statistical process control methods in a manufacturing environment, and the management of an environmental engineering organization that focused on environmental remediation. He also has extensive experience in strategic planning and leadership development. He graduated from Clemson University with a B.S. in mechanical engineering and from the Rensselaer Polytechnic Institute with a master's degree in mechanical engineering.

Martin C. Edelson has been a member of the staff at the Ames Laboratory since 1977 and is an adjunct associate professor of mechanical engineering at Iowa State University. His research interests include risk communication and the development of laser-based methods for materials processing and characterization. Dr. Edelson was a member of the Munitions Working Group and the DOE Laboratory Directors' Environmental and Occupational/Public Health Standards Steering Group. He currently represents the Ames Laboratory on the DOE Strategic Laboratory Council and the Subsurface Contamination Focus Area Lead Laboratory. Dr. Edelson is a technical editor of Risk Excellence Notes, a publication funded by the DOE Center for Risk Excellence. He earned a B.S. in chemistry and an M.A. in physical chemistry from City College of New York and a Ph.D. in physical chemistry from the University of Oregon.

Sidney J. Green, a member of NAE, is chairman and chief executive officer of TerraTek, a geotechnical research and services firm in Salt Lake City focused on natural resource recovery, civil engineering, and defense problems. Before that, he worked at General Motors and the Westinghouse Research Laboratory. He has an extensive background in mechanical engineering, applied mechanics, materials science, and geoscience applications and is a former member of the NRC Geotechnical Research Board. He was named Outstanding Professional Engineer of Utah and is the recipient of the ASME Gold Medallion Award and the Lazan Award from the Society of Experimental Mechanics. Mr. Green received a degree in engineering mechanics from Stanford University and an M.S. from the University of Pittsburgh and a B.S. from the University of Missouri at Rolla, both in mechanical engineering.

Paul F. Kavanaugh, an engineering management consultant, was the director of government programs for Rust International, Inc., and director of strategic planning for Waste Management Environmental Services. During his military service, he served with the U.S. Army Corps of Engineers, DOE, and the Defense Nuclear Agency and managed engineering projects supporting chemical demilitarization at Johnston Atoll. He earned a B.S. in civil engineering from Norwich University and an M.S. in civil engineering from

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Oklahoma State University. Brigadier General Kavanaugh is a fellow of the Society of American Military Engineers.

Todd A. Kimmell is principal investigator in the Environmental Assessment Division at Argonne National Laboratory. He is an environmental scientist and policy analyst. Mr. Kimmell was selected for membership on the committee for his expertise as an environmental regulatory and permitting specialist with more than 20 years of extensive experience in solid and hazardous waste management, program and policy development, chemical munitions, and explosives waste, as well as in many other activities related to regulatory and permitting issues. He graduated from the George Washington University with a master's degree in environmental science.

Douglas M. Medville recently retired from MITRE as program leader for chemical materiel disposal and remediation. He has led many analyses of risk, process engineering, transportation, and alternative disposal technologies and has briefed the public and senior military officials on the results. Mr. Medville led the evaluation of the operational performance of the Army's chemical weapon disposal facility on Johnson Atoll and directed an assessment of the risks, public perceptions, environmental aspects, and logistics of transporting recovered nonstockpile chemical warfare materiel to candidate storage and disposal destinations. Before that, he worked at Franklin Institute Research Laboratories and General Electric. Mr. Medville earned a B.S. in industrial engineering and an M.S. in operations research, both from New York University.

Winifred G. Palmer is a consultant in toxicology. She was a toxicologist for the U.S. Army between 1989 and 2000 at the Biological Research and Development Laboratory and the Center for Health Promotion and Preventive Medicine. Her work for the Army included assessment of health risks associated with chemical warfare agents, development of a military field water quality standard for the nerve agent BZ, development of the military standard for fog oil (an obscurant smoke), and studies of the mutagenicity of rifle emissions and the bioavailability of TNT in composts of TNT-contaminated soils. Dr. Palmer is a member of the Society of Toxicology, and her numerous publications span more than two decades of work in the field. She has a Ph.D. in biochemistry from the University of Connecticut and a B.S. in chemistry and biology from Brooklyn College.

George W. Parshall, a member of NAS, graduated from the University of Illinois with a Ph.D. in organic chemistry. After nearly 40 years of service, Dr. Parshall retired from E.I. duPont de Nemours and Company as director of chemical science in the Central Research and Development Division. He was selected for membership on this committee because of his experience in organic and inorganic chemistry and

catalysis and in conducting and supervising chemical research. Dr. Parshall is a past member of the NRC Board on Chemical Science and Technology and the NRC Committee on Review and Evaluation of the Army Chemical Stockpile Disposal Program.

James P. Pastorick is president of GEOPHEX UXO, Ltd., an unexploded ordnance (UXO) consulting firm based in Alexandria, Virginia, that specializes in UXO planning and management consulting to state and foreign governments. Since he retired from the U.S. Navy as an explosives ordnance disposal officer and diver in 1989, he has been working on civilian UXO clearance projects. Prior to starting his present company, he was the senior project manager for UXO projects at UXB International, Inc., and the IT Group.

R. Peter Stickles graduated from Northwestern University with a Master of Science in chemical engineering. He retired after 27 years of service from Arthur D. Little, Inc., as a Principal in Global Environmental and Risk Practice. Mr. Stickles was selected for membership on this committee for his more than 35 years of experience in a variety of activities in the area of chemical process engineering, including development and project activities that specified the design of petrochemical plants based on the thermal cracking of hydrocarbons, and participation in the design and startup of plants to produce ethylene and alpha olefins.

William J. Walsh is an attorney and partner in the Washington, D.C., office of Pepper Hamilton LLP. Prior to joining Pepper, he was as section chief in the EPA Office of Enforcement. His legal experience encompasses environmental advice and environmental injury litigation involving a broad spectrum of issues pursuant to a variety of environmental statutes, including the Resources Conservation and Recovery Act (RCRA) and the Toxic Substances Control Act (TSCA). He represents trade associations, including the Biotechnology Industry Organization, in rule-making and other public policy advocacy; represents individual companies in environmental actions (particularly in negotiating cost-effective remedies in pollution cases involving water, air, and hazardous waste); and advises technology developers and users on taking advantage of the incentives for, and eliminating the regulatory barriers to, the use of innovative environmental technologies. He has previously served on NRC committees concerned with Superfund and RCRA corrective action programs and the use of appropriate scientific groundwater models in environmental regulatory programs and related activities. Mr. Walsh holds a J.D. from George Washington University Law School and a B.S. in physics from Manhattan College.

Ronald L. Woodfin is a recently retired staff member of Sandia National Laboratories, where he coordinated work on mine countermeasures and demining, including sensor

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development. He is currently an adjunct professor of mathematics at Wayland Baptist University, Albuquerque Campus. Previously, he worked at the Naval Weapons Center, Naval Undersea Center, and Boeing Commercial Airplane Division. Dr. Woodfin has been an invited participant at several international conferences on demining and has served on an advisory task force on humanitarian demining for the General Board of Global Ministries of the United Methodist

Church. He also serves as pastor of Cedar Crest Baptist Church, Cedar Crest, New Mexico. Dr. Woodfin earned a B.S. in aerospace engineering from the University of Texas and an M.S. in aeronautics and astronautics and a Ph.D. in engineering mechanics from the University of Washington. He recently completed service on the Committee for Mine Warfare Assessment of the Naval Studies Board of the National Research Council.

Appendix B

Committee Meetings and Site Visit

MEETINGS

First committee meeting, January 22-24, 2001, National Research Council, Washington, D.C.

Presentations:

Opening Remarks

Jim Bacon, Program Manager, Chemical
Demilitarization

Margo Robinson, Budget Manager, ASAALT

Non-Stockpile Chemical Materiel Program Update and Status

William Brankowitz, Deputy for the Product Manager, Non-Stockpile Chemical Materiel Product

Second committee meeting, March 15-16, 2001, Edgewood, Maryland, and Aberdeen Proving Ground, Maryland.

Presentations:

Product Manager's Status Briefing

Lt. Col. Christopher M. Ross, Product Manager, NonStockpile Chemical Materiel Project

Committee Sub-group Meetings *John Nunn*, Maryland Citizens Advisory Council *Ken Stachew*, Remediation Advisory Board U.S. House of Representatives Armed Services Committee Concerns *Jean Reed*, House Armed Services Committee

Third committee meeting, May 23-24, 2001, Washington, D.C.

Presentation:

U.S. Army Non-Stockpile Chemical Materiel Product (NSCMP) Overview/StatusWilliam Brankowitz, Deputy for the Product Manager, Non-Stockpile Chemical Materiel Product

Fourth committee meeting, July 10-11, 2001, Aberdeen, Maryland

Presentations:

Opening Remarks

Jim Bacon, Program Manager for Chemical

Demilitarization

Remarks

Henry C. Dubin, Acting Deputy Assistant Secretary of the Army for Chemical Demilitarization

Non-Stockpile Chemical Materiel Product Update Lt. Col. Christopher M. Ross, Product Manager, Non-Stockpile Chemical Materiel Product

NOTE: The committee gathered additional information via telephone conference calls and by other means. Details are available online at http://www4nas.edu/deps/dmst.nsf/>.

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Committee Sub-group Meetings

Don Benton, Munitions Assessment and Processing
System

Jeff Harris, Rapid Response System

Dave Hoffman, Explosive Destruction System

Eric Kauffman, Pine Bluff Non-Stockpile Facility

Fifth committee meeting, September 25-26, 2001, Edgewood, Maryland

Presentations:

U.S. Army Non-Stockpile Chemical Materiel Product (NSCMP) UpdateLt. Col. Christopher M. Ross, Product Manager, Non-Stockpile Chemical Materiel Project

Destruction of Chemical Warfare Materials in Albania Using Plasmox[©] Technology *Joseph Sudol*, Burns and Roe Technology Test Program for Treatment of NSCMP Feeds

Joseph Cardito, Stone and Webster, and

Edward Doyle, Program Manager for Chemical

Demilitarization

SITE VISIT

Pine Bluff Arsenal, Arkansas, August 9, 2001

Site Team

Judith A. Bradbury, committee member Martin C. Edelson, committee member Nancy T. Schulte, study director

Appendix C

Composition of Liquid Waste Streams from Destruction of Sarin in the EDS

The destruction of sarin (GB) in the EDS using aqueous MEA (45 percent) as the treatment chemical produces an organic-rich neutralent stream, as described in Chapter 2. The posttreatment of this neutralent stream is the focus of this report, but there are also other liquid waste streams that must be dealt with. The other streams result from the rinsing of the EDS chamber with water after each use to remove residual MEA and solid residues and the cleaning to remove other solid and liquid residues. These waste streams must also be prepared for ultimate disposal unless their compositions meet the feed requirements for an on-site treatment works. The diverse nature of these waste streams is illustrated in Table C-1.

The data in Table C-1 indicate that there are two main types of liquid waste streams from the EDS treatment of GB as produced in the bomblet campaign at Rocky Mountain Arsenal: (1) organic-rich neutralent derived from the MEA treatment and from the MEA rinse step used with the first two bomblets and (2) aqueous streams resulting from water rinses of the EDS chamber and from aqueous acetic acid cleaning of the chamber.

Most of the MEA reagent and most of the GB and energetic degradation products appear in the organic-rich neutralent stream. The concentration of isopropyl methylphosphonic acid (IMPA), the major product of GB decomposition, approximates that expected from 70 to 90 percent hydrolysis of the 1.3 pounds of GB contained in each bomblet (Lucille Forrest, Office of the Product Manager, Non-Stockpile Chemical Materiel, communication to the committee, February 2001). It is clear that the neutralents are far too organic-rich for direct treatment in a water treatment works. Some further treatment such as oxidation is needed to mineralize the organic components for disposal through a treatment works or by deposition in a hazardous waste landfill. A further complication is the high concentrations of some metal ions such as aluminum, copper, and zinc. These metals presumably were present as materials of construction for the bomblets and were washed or extracted from the bomblet fragments by the MEA solutions.

The water rinsates contain small quantities of MEA and GB degradation products that clung to the bomblet fragments and to the interior surfaces of the EDS apparatus. The metal ion concentrations are generally much lower than in the neutralents. The rinsates may be suitable for disposal through FOTW or POTW, depending on the regulations and permit requirements applying to the particular treatment facility.

The spent cleaning solutions are primarily water-based and acidic. The acidity appears to have played a major role in extracting metal ions, of which mercury may be the most problematic. The protocol for cleaning liquid flow lines on the EDS appears to have been a work in progress during the RMA campaign. The concentrations of chloroform and dichloromethane in this waste stream appear to arise from a commercial lubricant used as a sealant on the EDS (Lucille Forrest, Office of the Product Manager, Non-Stockpile Chemical Materiel, memorandum to the committee, May 10, 2001). The appropriate disposal of the spent cleaning solutions requires careful analysis. It may be possible to combine them with the aqueous rinsates, but care must be taken to be sure that the mixture can be handled in accordance with regulatory standards for the treatment works.

There are no established treatment standards (e.g., RCRA land disposal restrictions) for the agent or degradation/hydrolysis products that may be of concern. Whether to establish numerical treatment standards for agents and degradation products has been the subject of intense discussions between the Army and the states.

The numerical pretreatment standards listed in EPA's Clean Water Act (CWA) are a minimum requirement. The sewerage agency must make a case-by-case determination to ensure that (1) the POTWs permit limits are not exceeded by the influent, (2) the water quality standards are not exceeded as a result of the discharge, (3) the toxic pollutants entering the POTW are adequately treated, and (4) the influent does not cause the POTW's sludge to exceed any applicable

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TABLE C-1 Composition of Liquid Waste Streams from the EDS Treatment of Sarin (GB) Bomblets at RMA

Waste Component from EDS Treatment of Sarin Bomblets at RMA	Neutralent ^{a,b}	Water Rinse ^b	Cleaning Solution ^c	POTW Feed Limit for Organic Chemical Industry	LDR Treatment Standards Goal of Treatment Prior to Disposal in Landfill
Monoethanolamine (MEA) (%)	43.8-48.3	0-4.7	0.8-1.1	None	None
Water (%)	51.7-56.2	95.3-100	98.9-99.2	NA	NA
Isopropyl methylphosphonic acid (IMPA) (ppm)	3,400-5,000	24-78			NA
Diisopropyl methylphosphonate (DIMP) ($\mu g/L$)	18,000-27,400	291-480	ND		NA
Explosives in liquids (µg/L)	<1,000	<1,000	<1,000		NA
Benzene (µg/L)	1,330-2,850	28.6-40.7	<100	137	140
Chloroform (µg/L)	ND-21.6	ND-4,380	8,360-10,500	325	46
Dichloromethane ($\mu g/L$)	ND-97.1	ND-71	377-968		NA
Toluene (µg/L)	369-810	ND-23.7	<2	74	80
Mercury (µg/L)	0.1-1	0.1-2.65	17.9-25		150
Aluminum (μg/L)	8,720 to 11,100	876 to 11,800	<876		
Arsenic (µg/L)	<200	<20	<20		1,400
Cadmium (µg/L)	6.81-10	<0.68	2.2-46		690
Chromium (µg/L)	445-770	11.5-485	1,070-1,870		2,770
Copper (µg/L)	9,030-18,200	486-5,470	3,850-6,200		
Lead (µg/L)	63-237	3.82-603	128-168	690	690
Zinc (µg/L)	23,100-38,300	72.5-308	4,920-5,680	2,610	NA
pH	12	10.4-11.5	6.5-7.8		

NOTE: NA, not applicable; ND, none detected. The expected source and collection regime for these wastes are presented in Table 2-1. The term "treatment" is used to describe steps involving addition of reagent or water to the EDS and oscillating for some time period prior to opening the chamber. Note that water treatment and rinse water wastes can be combined. To date, the Army has chosen to segregate the three categories of wastes, so as not to foreclose on the options for treating the waste streams that are primarily water.

SOURCE: Lucille Forrest, Office of the Product Manager, Non-Stockpile Chemical Materiel, "Interpretation of Waste Results from EDS GB Bomblet Destruction, Rocky Mountain Arsenal," communication to the committee, February 2001.

^aNeutralent consisting of the initial treatment of agent with active reagent (e.g., MEA) and any subsequent chamber washes with chemical reagent (if used). ^bRinsate consisting of additional agent treatment with water and chamber washes with water after opening the EDS.

^cCleaning solution consisting of washes (water and detergent) made between processing of each munition and final washes (e.g., water and acetic acid), made after completing a munitions campaign.

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sludge limits. Clearly, a site-specific determination must be made to ensure that MEA, arsenic, and other significant constituents do not require pretreatment.

Table C-1 also compares the concentration of the non-stockpile chemical constituents in neutralent and rinsate with federal LDR treatment standards. There are no applicable federal LDRs for constituents of state-listed agent waste. But if the neutralent exhibits a RCRA hazardous waste characteristic, the federal LDRs apply. If the neutralent is not hazardous waste, the Army would have broad discretion to determine what constitutes acceptable treatment.

If the neutralent is a RCRA characteristic hazardous waste, it must be treated in accordance with LDRs before being disposed of in a hazardous waste landfill. Thus, constituent levels must be reduced from those shown in Table C-1 to the treatment technology-based limits before disposal in a landfill. Again, nonstockpile agent is not a listed hazardous waste (except for phosgene), and neither EPA nor the states have specified a treatment technology or treatment limits for the disposal of stockpile or nonstockpile agents.

Assuming the waste is determined to meet a RCRA characteristic, there are treatment standards that apply to several constituents of the EDS neutralent. The LDR treatment standards were developed based on the ability of existing technologies to reduce the concentrations of these constituents, which are typical commercial wastes. They are not based on the alternative treatment technologies being studied by the Army. The LDR treatment standard for a given constituent is generally the same regardless of the other constituents in the waste. One would expect the concentration of constituents in the neutralent to at least periodically exceed these treatment standards. Table C-1 suggests that some treatment might be necessary before disposal in a hazardous waste landfill, assuming that the waste is a RCRA characteristic waste. The average percent reduction in the constituent provides a general sense of the order of magnitude of treatment required if regulatory agencies use a treatment technologybased method to set the treatment goals for the alternative treatment technologies being considered by the Army.

Appendix D

Comparison of MMD and EDS Neutralent Toxicities

The neutralents produced by the EDS have not been tested in animals for toxicity, so it can only be approximated from their chemical composition, which has a much lower degree of certainty than animal testing. Because the neutralizing reagents are present in considerable excess, it can be anticipated that they will make major contributions to the toxicity of the neutralents. Thus, neutralents generated by destruction of HD, GB, and VX will probably have toxicity characteristics of MEA, which include moderate to severe irritation of the skin, eyes, and respiratory tract. This inference is supported by findings that the dermal toxicity of neutralents generated by destruction of HD, GB, and VX in the MMD could not be distinguished from that of the MEA oxidant/solvent system (NRC, 2001a).

As discussed in Chapter 2, the chemical composition of the EDS neutralents may be more complex and variable than that of the neutralents from the MMD owing to the presence of energetics, their decomposition products, metals extracted from the munitions hardware and shaped charge residues, and miscellaneous compounds that may have been present in the munitions. Some of the metals identified in EDS neutralents generated at RMA and Porton Down are quite toxic to humans and/or the environment (e.g., Pb, Hg, Cd, As, and Ag) and, depending on their concentrations, could well contribute to the toxicity of the neutralents. In

general, the energetics tend to be relatively toxic (see Table D-1). The lack of information concerning the identity and concentrations of all of the decomposition products formed by reaction of energetic compounds with MEA may make it difficult to estimate the potential contribution of energetics to the overall toxicity of the neutralent. Even if all chemical components of the neutralents were identified, the toxicity of the neutralents could not be predicted with certainty because (1) toxicity data may not be available for all of the components and (2) chemicals may behave differently in mixtures. Because of this, the toxicity of a neutralent can best be determined by mammalian toxicity studies.

However, since the chemical composition of the neutralents produced by the destruction of different types of munitions could vary substantially, a number of representative neutralents would have to be subjected to toxicity tests in order to accurately predict hazards to humans and the environment. Because the time and cost of such an endeavor would be prohibitive and would strongly reduce the likelihood of meeting the CWC's 2007 deadline, toxicity tests on the neutralents generated by EDS would not be practical, and toxicity estimates should instead be based on the most complete chemical analyses possible using standard EPA risk assessment methodologies.

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TABLE D-1 Toxicity Characteristics of Energetic Compounds

	Effects of Exposure	Effects of Exposure		
Compound	Short-Term Exposure	Long-Term Exposure	Oral RfD (mg/kg) ^a	
HMX^b	Convulsions and other CNS effects; liver injury	Liver and kidney damage; changes in red blood cells; no cancer or reproductive studies available	5E-02	
RDX^b	Irritation of eyes, skin, and lungs; CNS effects (hyperirritability, convulsions)	Damage to liver, kidneys; inflammation of the prostate; testicular degeneration; toxic to fetus. Possible human carcinogen (EPA Group C)	3E-03	
Tetryl ^b	Allergic contact dermatitis	Fatigue, headache, anorexia, nausea, vomiting, upper respiratory tract irritation with sore throat, nose bleeds, coughing; liver damage	Insufficient data	
Trinitrotoluene ^b	Inhalation causes irritation of respiratory passages; skin contact can cause dermatitis; TNT readily absorbed through the skin and all routes of exposure can cause gastrointestinal disorders (e.g., nausea, anorexia, constipation) and cyanosis	Liver damage, anemia, cataracts, neurological disorders. Possible human carcinogen (EPA Group C)	5E-04	

"The oral RfD is an estimate (with uncertainty spanning as much as an order of magnitude) of a daily exposure (by ingestion) to humans (including sensitive subgroups) that is likely to be without an appreciable risk of deleterious effects during a lifetime (EPA, 2001b). For comparative purposes, the Army has proposed RfDs for HD and VX of 7E-06 and 6E-07 mg/kg/day, respectively (NRC, 1999c). The EPA RfDs for some of the chemicals identified in the neutralents produced at Porton Down and RMA are as follows:

	mg/kg/day		mg/kg/day
Benzene ^c ,e	3E-03	$Barium^d$	7E-02
Chlorobenzene ^d	2E-02	Cadmium (in food) d,e	1E-03
1,4-Dichlorobenzene ^{c,d}	3E-02	Cadmium (in water) d,e	5E-04
1,4-Dithiane ^d	1E-02	Trivalent chromium ^d	1.5E+0
		Hexavalent chromium ^{d,e}	3E-03

^bEPA (2000a).

^cEPA (2000b).

 $[^]d\mathrm{EPA}$ (2001a).

^eBenzene and hexavalent chromium are recognized as human carcinogens, and cadmium is considered to be a probable human carcinogen by the EPA (EPA, 2001a).

Appendix E

Criteria for Evaluating Technologies

TOP PRIORITY CRITERIA

Relatively Safe Processes (Low Risk)

Technologies were reviewed to determine if a common process failure (e.g., explosion, corrosion, mechanical failure, operator error, incorrect feeds, service failure, etc.) under normal operating conditions could lead to serious worker, community, or environmental damage. The following factors were considered:

- minimal storage and transportation of hazardous materials.
- · minimal toxicity and flammability of all materials
- temperatures and pressures below the threshold values that challenge reliable containment

Technical Effectiveness

Technologies were evaluated for their consistency in achieving a standard (in this case, destruction) of neutralent. The following factors were considered:

- efficiency of detoxification of the neutralent (i.e., solid wastes could be disposed of in a landfill and liquid wastes released to a POTW)
- integration into a system for the destruction of nonstockpile materiel

Permit Status

Technologies were evaluated for serious regulatory obstacles that would prevent environmental and/or operational permitting. The following factors were considered:

- potential major delays in obtaining permits under federal (and international), state, or local regulations
 - · potential for meeting schedules of international treaties

NOTE: Reprinted from NRC (2001a), pp. 21-22.

Pollution Prevention

The committee evaluated the technologies on the principle of "green chemistry" (Mulholland and Dyer, 1999). In other words, pollution prevention and waste minimization practices are implemented at the beginning of the process (pollution prevention) as opposed to after the fact (pollution abatement). The following factors were considered:

- minimal addition of processing materials¹ that would require treatment, disposal, regeneration, recycling, or other handling
- minimal number of processing steps, which all have an incremental environmental burden in potential leaks and energy, maintenance, shutdown and start-up, and clean-out requirements
- minimal toxicity of emissions, wastes, or other material that require treatment, disposal, regeneration, recycling, or other handling²
- operating temperatures and pressures as close to ambient as possible
- minimal corrosion, plugging, sensitive process-control parameters, and other operating difficulties
- minimal high-temperature vapor streams that require high-quality treatment

¹Processing materials include not only the obvious purchased solvents, acids, bases, etc., and service materials, such as catalysts, filters, and adsorbents, but also common items, such as water, nitrogen for instruments and vapor-space inerting, and nitrogen in air used as a source of oxygen. These materials might be used for the process itself or for support tasks, such as cleaning.

²For example, arsenic, which is present in lewisite neutralent, is a semivolatile metal in a high-temperature process. The arsenic is released as a vapor and condenses in the gases as a very fine, hard-to-capture particulate. The 1999 EPA incinerator regulations added stringent emission limits for semivolatile metals, and incinerator operators are, therefore, very cautious about accepting wastes containing organo-arsenic compounds.

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IMPORTANT CRITERIA

Once the selected technologies had been evaluated according to top priority criteria, they were evaluated by the important criteria.

Robustness

A robust technology can function successfully in stable continuous operation. The term "continuous" means the technology can treat neutralent from beginning to end and does not require another technology as an intermediate step before final disposal. Continuous also means that feedstock can be continuously supplied or supplied in the batch mode. Operation of a robust technology has the following characteristics:

- tolerance of normal variations (differences in concentrations of hazardous materials or chemical agents)
- start-up and shutdown of a facility without major complications or delays
 - operation at small scale or large scale, as required
- capability of treating a wide range of potential feeds (neutralents from the RRS and MMD)

Cost

Although the committee did not conduct a cost analysis for each technology, cost was estimated based on past experience and knowledge. The following cost factors were considered:

- total costs, including capital and operating costs
- · costs per unit of feed

Practical Operability

The following factors related to practicality were considered:

- minimal training for operators (average skill levels for the chemical industry)
- use of standard instrumentation for monitoring and process controls

Continuity

Two factors were considered in this category:

- · likelihood of finding a vendor
- likelihood that supplies of raw materials will be available

Space Efficiency

The main factor in space efficiency was the weight, area, and volume of operating equipment per volume of material processed.

Materials Efficiency

The following factors were considered:

- recycling of materials as part of the internal operation of the facility
 - · shipment of wastes off site for beneficial reuse
 - use of recycled materials from external sources

Appendix F

Explosive Destruction System Phase 1 (EDS-1) Overview and Description

INTRODUCTION

The EDS is a transportable system designed to treat chemical munitions under three scenarios:

- at chemical munition recovery locations when a chemical munition is deemed unsafe to transport by vehicle or store by routine means at the time of recovery
- at chemical munition storage locations when a previously recovered chemical munition is determined not to be safe for continued storage
- at locations that have a limited number of chemical munitions (with or without explosive components) that can be treated in the EDS when the quantities do not justify the use of other destruction systems

The mission of the EDS is to destroy explosively configured chemical warfare munitions, contain the blast and fragments in opening the munition, and treat the chemical fill of the munition, in an environmentally friendly manner. The EDS is intended for use with World War I and World War II vintage chemical warfare materiel (CWM) produced before 1945. Post-World War II munitions have larger bursters that exceed the capacity of the system.

OVERVIEW OF EXPLOSIVE DESTRUCTION SYSTEM

The operational scenario for the EDS consists of Explosive Ordnance Disposal personnel hand-carrying the recovered munition and placing it in the EDS containment vessel. Once the munition is enclosed in the EDS, the conical and linear shaped charges are initiated to explosively open the munition and detonate the burster. Reagents are then added to treat the chemical agent. The treatment process relies on chemistries developed by the U.S. Army for the various

NOTE: This appendix is adapted from DiBerardo and Haroldsen (2000).

chemical agents. The effluent, if defined as hazardous waste, is managed in accordance with state and federal requirements and the system is prepared for the next munition.

The EDS, shown graphically in Figure 1-1, includes the following major components:

- the trailer on which the entire system is mounted
- the explosive containment vessel that contains the blast, fragments, and chemicals
- the explosive accessing system that cuts the munition with a linear shaped charge and attacks the burster with two conical shaped charges
- the fragment suppression system that protects the containment vessel from high-velocity fragments
- the firing system that fires the detonators on the shaped charges
- the chemical storage and feed system that supplies reagents and water to the containment vessel
- the waste handling system that drains the treated effluent and vents vapors from the containment vessel (includes vapor sampling and carbon filtration of effluent vapors)
- the vessel hydraulic oscillation system that mixes the contents of the containment vessel to ensure complete treatment of the chemical agents
 - the electrical instrumentation and control system.

EXPLOSIVE DESTRUCTION SYSTEM TRAILER

The EDS is mounted on an open flatbed trailer, making the system transportable for rapid response in emergency situations. The 2.6 meter by 6.1 meter, tandem-axle trailer weighs about 7,260 kg and has a rating of 8,160 kg. The trailer height for shipping is 2.4 meters.

The working surface of the trailer is about 0.3 meters above the main trailer structure, or about 1 meter above the ground. The working surface has an open grid over a stainless steel secondary containment pan. Stainless steel is used for compatibility with agents and reagents.

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The containment vessel is mounted over the axles of the trailer with the door facing the front of the trailer. The water and reagent tanks are at the front of the trailer. The area between these components serves for preparing and loading the munition. All controls and instrumentation displays are readily accessible from this working area. The electrical supply panels and the hydraulic pump are mounted at the rear of the trailer. Piping and electrical conduit run under the main deck.

EXPLOSIVE CONTAINMENT VESSEL

The purpose of the explosive containment vessel is, first, to contain the explosive shock, fragments, and chemical agent during the munition opening process and then to serve as a process vessel for the subsequent chemical treatment of the agent.

The 189-liter cylindrical vessel and door were fabricated from two 316 stainless steel forgings. The inside diameter is 51 cm with 5.1-cm-thick walls. The vessel is designed to contain at least 500 detonations of up to one pound (0.45 kg) of explosive TNT equivalent. The hinged door is the same diameter as the vessel, allowing easy access for inserting munitions and removing debris. The door is secured with two large clamps that are in turn secured with four threaded rods with hydraulic nuts. The vessel relies on a Grayloc allmetal seal to contain the detonation and the chemical agent. An o-ring provides a backup seal and aids in leak testing.

ACCESSING MUNITIONS WITH SHAPED CHARGES

Details of the system for accessing munitions in the EDS-1 are given in Table F-1. Once the munition has been placed in the EDS vessel, the contents of the munition must be exposed and the burster destroyed before the chemicals can be treated. This is accomplished with a combination of linear and conical shaped charges. Shaped charges were chosen over mechanical, chemical, and thermal mechanisms because they require minimal access through the containment vessel wall, they are exceptionally reliable, and their design is well characterized.

A single preformed length of copper linear shaped charge (LSC) is used to open the main body of the munition and expose the contents for treatment. The LSC is designed to make a complete cut in the munition, separating it into two pieces and fully exposing the chemicals within. Detonators are connected to the LSC at each end for increased reliability.

Two copper conical shaped charges (CSC) are used to break open the burster charge canister in the munition and detonate the burster explosives. The CSCs are fired in the direction of the burster at the same time as the LSC is fired. The CSC is a multi-tapered copper device containing 32 grams of Composition A explosive. It was selected because it meets the initiation requirements of TNT and the need for precision and repeatability.

The CSC design was chosen to exceed the criteria for reliable detonation of the burster explosives by shaped charge impact. However, because the condition of the explosives in aged, recovered munitions is inherently uncertain, detonation of the burster cannot be guaranteed.

For safety, exploding bridge-wire (EBW) detonators are used to initiate the shaped charges. These detonators are very insensitive to unexpected or undesirable energy inputs (static, impact, etc.). Four electrical feed-throughs are in the containment vessel door for the high-voltage EBW detonators. A steel plate is mounted in front of the feed-throughs to protect them from direct impact during the explosion.

FRAGMENT SUPPRESSION SYSTEM

The recovered munition and the shaped charges are placed in a fragment suppression system (FSS) before being loaded into the containment vessel. An FSS is necessary to mitigate high-velocity fragments that could damage the interior of the EDS vessel during operations. Fragments will come from the LSC, the CSCs, the burster charge case, and the munition itself.

The core of the FSS is a steel cylinder separated lengthwise into two sections. The cylinder is connected to a cradle that supports the system inside the EDS vessel. A three-sided steel support is positioned inside the lower half of the cylinder to hold the munition and to provide shock absorption below the munition. A steel block is positioned between the lower half cylinder and the cradle bottom to stop the CSC jet in case of complete penetration.

The LSC and CSCs are attached to the lower and upper halves of the FSS for ease of assembly and to maintain the correct standoff distance.

FIRING SYSTEM AND DETONATORS

The firing system initiates the LSC and CSC burster charges. The firing system is a high-voltage capacitor discharge unit (CDU) capable of reliably firing four detonators (1.5 x 40 mil EBW) over cable lengths of up to 15.2 meters. The firing system is modular so that parts can be tested and replaced easily. The firing system consists of a CDU, a high-voltage trigger module, a high-voltage power supply, a control module, monitoring and diagnostics equipment, and safety controls. The entire system can be operated from an easily accessible panel. A redundant system is mounted in the same panel. A high-potential breakdown tester is mounted on the panel to enable testing of the cables and feed-through connectors associated with the firing system.

CHEMICAL TREATMENT

The EDS uses a low-pressure, low-temperature chemical treatment method to reduce the hazardous properties of the chemical agents so that the resulting waste can be disposed 58 APPENDIX F

TABLE F-1 System for Accessing Chemical Munitions

Element	Purpose	Description/Configuration
Linear shaped charge (LSC)	Open main body of munition and expose the contents for chemical treatment.	Preformed lengths of RDX-based, copper-sheathed LSC. The shape and length of the LSC is specific to the type of munition being destroyed.
Conical shaped charge (CSC)	Puncture the burster in the munition and attempt to detonate the burster explosive.	The CSC consists of 32 grams of Composition A-3, multitapered and copper-lined. Depending on the munition, one or two CSCs are used.
Fragment suppression system (FSS)	Absorb shock from high-velocity fragments, thus preventing damage to the interior of the EDS vessel. Fragments are generated from the LSC, the burster casing, and the munition itself.	The core of the FSS is a mild steel cylinder separated lengthwise into two sections. A three-sided steel support is connected to the bottom cylinder section to center the munition and provides shock absorption in the downward direction. Cylinder endplates absorb shock and protect the ends of the EDS vessel.
Firing system and detonators	Simultaneously initiate the LSC and CSC charges.	Reynolds type RP-85 EBW detonators for LSC. For CSCs, Reynolds type RP-1 and RP-2 EBW detonators are used. These contain RDX explosive.

SOURCE: U.S. Army (2000).

of at commercial hazardous waste facilities. The process, which is referred to as neutralization, relies on chemistries developed by the Army. Treatment is done inside the containment vessel after the munition is opened to prevent transfer or release of untreated chemical agent.

Three 95-liter, stainless steel tanks provide short-term storage for water and reagents used for chemical treatment. The liquids are pumped from the tanks to the containment vessel. The pump is mounted directly below the tanks. The tanks are heated to make viscous liquids easier to pump and to speed the treatment process.

A valve panel on the vessel door allows the operator to control the transfer of reagent or water, collect samples for chemical analysis, and drain the liquid effluent. Each port has redundant valves. The high-pressure valves have metal-to-metal seals and Teflon packing. Near the top are two spray nozzles for injecting the reagents and collecting gas samples. Liquid samples are collected through the dip tube that extends to the bottom of the vessel. After treatment, the effluent is drained to standard 55-U.S. gallon (208-liter) drums through two sieved ports near the bottom of the door.

Liquid effluent is collected in the drums, while gaseous overpressure is vented through a silica gel/ASZM-TEDA carbon filter. The waste handling system includes secondary spill containment for the drums, scales to measure liquid content, and pressure relief rupture disks.

HEATING AND OSCILLATION SYSTEM

The speed of treatment is limited by the solubility of the chemical agent in the reagent. If the agent has polymerized

or degraded, treatment may be prolonged. Inorganic chlorides may yield copious precipitates of oxides/hydroxides under these conditions, so agitation and excess reagent are required. In the EDS, the vessel can be heated to near the boiling point of the reagents and agitated to accelerate the reactions.

Since any hardware inside the vessel must withstand the explosive detonation, the vessel is externally heated and agitated. The vessel uses 12 1-kW band heaters with a feedback control system. The reagents are heated to about 60° C before they are injected into the vessel. It takes about 2 hours to heat the contained fluids to 100° C. Fluid temperature can be controlled within $\pm 4^{\circ}$ C.

The vessel is mounted on pillowblock bearings, allowing it to tilt forward and backward. A hydraulic system oscillates the vessel between ± 40 degrees from the horizontal position. The entire stroke through 80 degrees takes about 15 seconds. The vessel can be stopped in any position to aid in draining or sample collection.

ELECTRICAL INSTRUMENTATION AND CONTROL SYSTEM

Two control and instrument panels are mounted at the front of the trailer near the water and reagent tanks. One panel contains pressure and level displays and pump controls. The second panel contains temperature readout and controls. Controls for the hydraulic oscillation system and hydraulic nuts are in a panel on the side of the trailer. Two electrical distribution panels at the back of the trailer contain circuit breakers and other electrical equipment.

Appendix G

Use of Tracking Compounds to Assess the Performance of a Treatment Technology

The effectiveness of a waste destruction process can be tracked by following the disappearance of a chemical compound that is especially resistant to the process conditions. The working assumption is that, if the tracking compound is completely destroyed, other less stable chemicals will also be absent in the process effluents. The fate of certain chemical species of particular regulatory or public concern, such as persistent organic pollutants (POPs) or toxic heavy metals, may also be used to track the performance of treatment technologies.

NERVE AGENTS

Sarin, Soman, and VX

The common nerve agents sarin (GB), soman (GD), and VX are derivatives of methylphosphonic acid (MPA)—chemical formula: CH₃PO(OH)₂. In fact, the presence of a methyl–phosphorus chemical bond is a key feature setting these agents apart from the organophosphorus compounds widely used as agricultural insecticides. Hydrolysis of the nerve agents yields esters of MPA or MPA itself. MPA is very resistant to further hydrolysis and to oxidative processes. This characteristic makes it useful as a tracking compound, allowing us to assure the absence of more toxic organophosphorus compounds in a waste stream.

MPA can be metabolized by selected species of bacteria but requires carefully controlled conditions, such as restriction of phosphate nutrient (DeFrank and Fry, 1996). It can also be oxidized by SCWO under harsh conditions to give phosphoric acid salts and oxidation products of the CH₃ group (CO, CO₂, and H₂O). At 550°C and 4,000 psi, MPA is >99.9 percent oxidized at 14.4 seconds of contact time. In the presence of excess NaOH, the conversion is reduced to 95.2 percent under the same conditions.¹

MPA is a white solid that is very soluble in water (>20 g/L). MPA itself does not exhibit the extremely high order of toxicity of the nerve agents derived from it, but is sufficiently acidic to cause irritation or burns to the eyes, skin, respiratory tract, and mucous membranes (MDL, 1997). It is a CWC Schedule 2 intermediate subject to control under the treaty protocol.

Sulfur Mustard

To track the destruction of mustard agent, one may need to monitor for the presence of by-products rather than compounds derived from HD itself. Hydrolysis of HD produces thiodiglycol (TDG), a common industrial chemical, which—like MPA—is a CWC Schedule 2 intermediate. However, TDG is too easily oxidized by chemical or biochemical processes to be a good tracking compound. Some chemical oxidizing reagents convert TDG sequentially to a sulfoxide and a sulfone, which might track the disappearance of HD and TDG, but there are other oxidation pathways that bypass the TDG sulfoxide.

A better tracking compound may be the heterocycle 1,4-dithiane. Most HD is contaminated with 1,4-dithiane, which is present as a by-product of the HD manufacturing process. For example, the ton containers of HD stored at the Aberdeen Proving Grounds contain, on average, 1.5 percent dithiane (U.S. Army, 1996). This compound is sufficiently resistant to hydrolysis that its disappearance may signal the absence of HD. It is likely to be oxidized by chemical means, but no data on its oxidation by SCWO are known to the committee.

Other potential tracking compounds for the destruction of the carbon–chlorine chemical bonds associated with the toxicity of HD are the chlorinated hydrocarbons that usually are present as impurities in sulfur mustard (U.S. Army, 1996). The C–Cl bonds in 1,2-dichloroethane, 1,1,2,2-tetrachloroethane, tetrachloroethylene, and hexachloroethane are more resistant to hydrolysis than those bonds in the agent itself.

¹E.F. Gloyna and L. Li, "Supercritical Water Oxidation of Methylphosphoric Acid," presentation to the Committee on Alternative Chemical Demilitarization Technologies, August 28, 1997.

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COMPOUNDS OF CONCERN

High-temperature processes for posttreatment of EDS neutralents can yield chemical species that were not present in the neutralent. Some of these compounds—dioxins, for example—are persistent organic pollutants (POPs), which may pose significant risks to human health and the environment. Such compounds are the subject of much public concern, because they tend to accumulate in the environment and in fatty tissues in the human body. An international treaty calling for phasing out the production of 12 of the most prevalent POPs has been signed but not submitted to the U.S. Senate for ratification. Thus, tracking the potential formation of these compounds is an important metric of the technology's performance.

Chloride-containing wastes in particular are apt to generate POPs under temperature regimes such as those involved in quenching the gases resulting from incineration or plasma treatment of liquids. Certain agents (HD, CG, and L) contain high percentages of chloride, and their neutralents are chloride-rich.

Dioxins and Furans

Some high-temperature, vapor-phase alternatives to incineration, such as plasma arcs and secondary oxidizers, generate low levels of polychlorinated dibenzodioxins and dibenzofurans when used for processing chlorinated organic compounds such as sulfur mustard and lewisite. As explained below, these low-level by-products have aroused concern about the potential negative health effects of using alternative technologies of this type. For example, the stack gas from a PLASMOX plasma arc system contained detectable levels (0.25 ng TEQ/cu. m) of dioxins/furans in HD neutralent processing demonstrations early this year (Stone & Webster, 2001). As noted in the reference, the dioxins/furans may have been an artifact of the specific test conditions, but this issue must be resolved by further tests.

The organic chemicals commonly termed "dioxins" generally refer to about 30 polychlorinated and polybrominated dibenzodioxins and dibenzofurans out of the hundreds of possible chloro- and bromo-substituted isomers of these compounds. Polychlorinated dioxins are produced by many thermal processes, including incineration, wood-burning stoves, and natural phenomena. As a consequence, they are widely distributed in the environment. A major concern is that, when absorbed in the body, they persist in fatty tissues for long periods of time. They are associated with human health effects such as chloracne, even at extremely low concentrations. The mixture of dioxins to which humans may be exposed has been characterized as a "likely human carcinogen" by the EPA (EPA, 2000c). Of the dioxins, 2,3,7,8tetrachlorodibenzo-p-dioxin (TCDD) is the most toxic and is recognized as one of the most potent of all carcinogens, with EPA long having classified it as B2, or probable human carcinogen (EPA, 2000d). The National Toxicology Program has proposed removing TCDD from the list of carcinogens for which there is "sufficient evidence in experimental animals" and adding it to the list of chemicals "known to be human carcinogens" (U.S. Department of Health and Human Services, 2001). The recent EPA draft dioxin reassessment (EPA, 2000d) summarizes the weight of evidence on dioxin's reproductive effects, immunological impacts, and developmental toxicity.

These compounds are extremely stable in the environment and are found throughout the world at very low levels. According to the EPA (EPA, 2001e), municipal incinerators are the largest single source of dioxin emissions (38.4 percent) and backyard refuse burning contributes 18.6 percent. The best of the hazardous waste incinerators, such as the U.S. Army's stockpile chemical disposal facilities, have extremely low emissions of dioxins.

Polychlorinated Biphenyls

Polychlorinated biphenyls were used for decades as cooling fluids in electrical transformers because of their chemical inertness and thermal stability. They were also used widely as components of lubricants, paints, and copy paper. Their stability, which was an asset for industrial uses, has proved to be a liability in other contexts, because PCBs that have leaked into soil or streams can linger for decades. Their presence is of particular concern because several mixtures of PCBs have been shown to be carcinogenic in laboratory animals. "Based on sufficient evidence of carcinogenicity in experimental animals," the National Toxicology Program considers that PCBs are "reasonably anticipated to be human carcinogens" (U.S. Department of Health and Human Services, 2001), and EPA has classified PCBs as Group B2, or probable human carcinogens (EPA, 2000c). However, recent studies found no link between risk of breast cancer and the presence of PCBs (Laden, 2001). In some situations, low levels of PCBs have been detected in emissions from incinerators, but the major source appears to be industrial spills and discharges. The discharges have been dramatically reduced since production of PCBs was restricted.

Metals

Several heavy metals that may occur in EDS neutralents are toxic. Special consideration should be given to their analysis and disposal. Generally speaking, their toxicity is inherent and is not destroyed by posttreatment processing. The general approach to dealing with them is to reduce their mobility and, hence, their bioavailability. Several posttreatments convert these metals to salts that have low solubility in water and are therefore resistant to leaching into groundwater. Leachability may be further reduced by stabilization with Portland cement or other reagent.

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The committee has given particular consideration to the problems associated with arsenic, because it may occur in relatively high concentrations in neutralents derived from agents such as lewisite. Other heavy metals listed below can be expected to occur in lower concentrations because they derive from munition components such as fuzes, solders, and alloys. However, their toxicity is such that even low concentrations may pose significant risks.

Arsenic

Arsenic is not generally present in chemical munitions, but some chemical agents such as lewisite, adamsite, and clark-2 are organoarsenic compounds. These agents yield neutralents containing substantial amounts of arsenic in the form of soluble compounds such as sodium arsenite. The general approach to rendering the arsenic less dangerous to human health and the environment is to convert the soluble compounds to less soluble species such as an arsenate salt. Ferric arsenate has very low solubility in water.

The toxicity of arsenic compounds is well known, but the lethality varies widely with the form of arsenic ingested or inhaled (Kaise et al., 1989). Two common organoarsenic compounds, methylarsonic acid and dimethylarsinic acid, have LD₅₀ values of 1.8 and 1.2 g/kg, respectively. On the other hand, sodium arsenite (Na₃AsO₃), the usual hydrolysis product of lewisite agent, has an LD₅₀ of 0.0045. Because of this general toxicity as well as the carcinogenicity of arsenic compounds, the allowable concentrations in drinking water and in the workplace are low. In 1976, the EPA acted under the Safe Drinking Water Act to propose an interim maximum concentration limit of 50 µg/L. This standard is in the process of being lowered, based in part on an NRC review of the scientific evidence concerning the carcinogenicity of arsenic compounds (NRC, In press). The report shows increased risk of cancer in humans from arsenic concentrations as low as 3 ppb, based on studies in both Taiwanese and U.S. populations. It is also considered to be a human carcinogen through exposure by inhalation.

Lead

Lead is often found at low concentrations in neutralents. It may derive from munition components such as solder or from detonating compounds such as lead azide. Lead compounds are strong neurotoxins and have been associated with developmental mental retardation in children. Like other divalent metal cations (e.g., zinc and cadmium), lead(II) salts can be removed from aqueous streams by precipitation with sulfide or by ion exchange.

Mercury

Mercury is sometimes present in low concentrations in neutralents. A potential source is the mercury fulminate present in some detonator compositions. Metallic mercury is sufficiently volatile that it can pose an inhalation danger in closed workspaces. A similar danger exists with organomercury compounds such as dimethylmercury. Mercury salts in an aqueous environment can be methylated by microorganisms to produce highly toxic monomethylmercury compounds.

Elemental mercury vapor can be removed from gas streams (e.g., flue gas from coal-burning power plants) by adsorption, although with limited efficiency.

Cadmium

Cadmium is sometimes encountered in neutralents derived from EDS treatment of metal parts containing cadmium in an alloy or as a corrosion-resistant plating. The metal is toxic and is volatile when heated, but the major risk appears to lie in aqueous streams that may enter the environment.

