



**Alternative Technologies for the Destruction of Chemical Agents and Munitions**

Committee on Alternative Chemical Demilitarization Technologies, National Research Council

ISBN: 0-309-59635-1, 342 pages, 8.5 x 11, (1993)

**This PDF is available from the National Academies Press at:  
<http://www.nap.edu/catalog/2218.html>**

Visit the [National Academies Press](http://www.nap.edu) online, the authoritative source for all books from the [National Academy of Sciences](http://www.nap.edu), the [National Academy of Engineering](http://www.nap.edu), the [Institute of Medicine](http://www.nap.edu), and the [National Research Council](http://www.nap.edu):

- Download hundreds of free books in PDF
- Read thousands of books online for free
- Explore our innovative research tools – try the “[Research Dashboard](#)” now!
- [Sign up](#) to be notified when new books are published
- Purchase printed books and selected PDF files

**Thank you for downloading this PDF. If you have comments, questions or just want more information about the books published by the National Academies Press, you may contact our customer service department toll-free at 888-624-8373, [visit us online](#), or send an email to [feedback@nap.edu](mailto:feedback@nap.edu).**

**This book plus thousands more are available at <http://www.nap.edu>.**

Copyright © National Academy of Sciences. All rights reserved.  
Unless otherwise indicated, all materials in this PDF File are copyrighted by the National Academy of Sciences. Distribution, posting, or copying is strictly prohibited without written permission of the National Academies Press. [Request reprint permission for this book](#).

# **Alternative Technologies for the Destruction of Chemical Agents and Munitions**

**COMMITTEE ON ALTERNATIVE CHEMICAL  
DEMILITARIZATION TECHNOLOGIES  
BOARD ON ARMY SCIENCE AND TECHNOLOGY  
COMMISSION ON ENGINEERING AND TECHNICAL SYSTEMS  
NATIONAL RESEARCH COUNCIL**

National Academy Press  
Washington, D.C. 1993

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

This report has been reviewed by a group other than the authors according to procedures approved by a Report Review Committee consisting of members of the National Academy of Sciences, the National Academy of Engineering, and the Institute of Medicine.

The National Academy of Sciences, is a private, nonprofit, self-perpetuating society of distinguished scholars engaged in scientific and engineering research, dedicated to the furtherance of science and technology and to their use for the general welfare. Upon the authority of the charter granted to it by the Congress in 1863, the Academy has a mandate that requires it to advise the federal government on scientific and technical matters. Dr. Frank Press is president of the National Academy of Sciences.

The National Academy of Engineering was established in 1964, under the charter of the National Academy of Sciences, as a parallel organization of outstanding engineers. It is autonomous in its administration and in the selection of its members, sharing with the National Academy of Sciences the responsibility for advising the federal government. The National Academy of Engineering also sponsors engineering programs aimed at meeting national needs, encourages education and research, and recognizes the superior achievements of engineers. Dr. Robert M. White is president of the National Academy of Engineering.

The Institute of Medicine was established in 1970 by the National Academy of Sciences to secure the services of eminent members of appropriate professions in the examination of policy matters pertaining to the health of the public. The Institute acts under the responsibility given to the National Academy of Sciences by its congressional charter to be an adviser to the federal government and, upon its own initiative, to identify issues of medical care, research, and education. Dr. Kenneth I. Shine is president of the Institute of Medicine.

The National Research Council was organized by the National Academy of Sciences in 1916 to associate the broad community of science and technology with the Academy's purposes of furthering knowledge and advising the federal government. Functioning in accordance with general policies determined by the Academy, the Council has become the principal operating agency of both the National Academy of Sciences and the National Academy of Engineering in providing services to the government, the public, and the scientific and engineering communities. The council is administered jointly by both Academies and the Institute of Medicine. Dr. Frank Press and Dr. Robert White are chairman and vice chairman, respectively, of the National Research Council.

This is a report of work supported by Contract DAAL03-90-C-0035 (CLIN 001) between the U.S. Department of the Army and the National Academy of Sciences.

Library of Congress Catalog Card Number 93-84706

International Standard Book Number 0-309-04946-6

Copies available from:

National Academy Press

2101 Constitution Avenue, N.W.

Box 284

Washington, D.C. 20418

1-800-624-6242

(202) 334-3313 (in the Washington Metropolitan area)

B-170

Copyright 1993 by the National Academy of Sciences. All rights reserved.

Printed in the United States of America

---

## COMMITTEE ON ALTERNATIVE CHEMICAL DEMILITARIZATION TECHNOLOGIES

JOHN P. LONGWELL (*Chairman*), Massachusetts Institute of Technology, Cambridge  
GEORGE APOSTOLAKIS, University of California, Los Angeles  
JOSEPH F. BUNNETT, University of California, Santa Cruz  
PETER S. DALEY, Waste Management International, London, England  
GENE H. DYER, Consultant, San Raphael, California  
DAVID S. KOSSON, Rutgers, The State University of New Jersey, Piscataway  
WALTER G. MAY, University of Illinois, Urbana  
MATTHEW MESELSON, Harvard University, Cambridge, Massachusetts  
HENRY SHAW, New Jersey Institute of Technology, Newark  
THOMAS O. TIERNAN, Wright State University, Dayton, Ohio  
BARRY M. TROST, Stanford University, Stanford, California  
JAMES R. WILD, Texas A&M University, College Station

### Staff

DONALD L. SIEBENALER, Study Director  
JAMES J. ZUCCHETTO, Co-Study Director  
MARGO L. FRANESCO, Senior Program Assistant  
ALLISON P. KNIGHT, Administrative Secretary  
ANN COVALT, Consulting Editor

---

## BOARD ON ARMY SCIENCE AND TECHNOLOGY

PHILIP A. ODEEN (*Chairman*), BDM International, Inc., McLean, Virginia  
LAWRENCE J. DELANEY (*Vice Chairman*), Montgomery and Associates, Washington, D.C.  
ROBERT A. BEAUDET, University of Southern California, Los Angeles  
WILLIAM K. BREHM, Systems Research Applications Corporation, Arlington, Virginia  
WILLIAM H. EVERS, JR., W. J. Schafer Associates, Inc., Arlington, Virginia  
JAMES L. FLANAGAN, Center for Computer Aids in Industrial Productivity, Piscataway, New Jersey  
CHRISTOPHER C. GREEN, General Motors Research Laboratories, Warren, Michigan  
THOMAS MCNAUGHER, The Brookings Institution, Washington, D.C.  
GENERAL GLENN K. OTIS (*Retired*, U.S. Army), Coleman Research Corporation, Fairfax, Virginia  
NORMAN F. PARKER, Varian Associates (*Retired*), Cardiff by the Sea, California  
HARVEY W. SCHADLER, General Electric Company, Schenectady, New York  
F. STAN SETTLES, Office of Science and Technology, Washington, D.C.  
JOYCE L. SHIELDS, Hay Systems, Inc., Arlington, Virginia  
DANIEL C. TSUI, Princeton University, Princeton

### Staff

BRUCE A. BRAUN, Director, Board on Army Science and Technology  
DONALD L. SIEBENALER, Senior Program Officer  
JAMES J. ZUCCHETTO, Senior Program Officer  
HELEN D. JOHNSON, Staff Associate  
ANN M. STARK, Program Officer  
MARGO L. FRANCESCO, Senior Program Assistant  
ALLISON P. KNIGHT, Administrative Secretary  
KELLY NORSINGLE, Administrative Secretary (until 4/16/93)

## Preface

The unitary chemical warfare agents and munitions that are the focus of this study have not been manufactured in the United States since 1968. Some agent and munitions have been destroyed, but approximately 25,000 tons of agent remain in thousands of tons of munitions and bulk containers in the U.S. stockpile. In 1978 the U.S. Army began to test various large-scale disposal methods at the Tooele Army Depot, Utah, where over 42 percent of the stockpile is located. These methods included several techniques to handle and disassemble munitions to gain access to the agent therein. Techniques tested for agent destruction included chemical treatment and incineration.

At the request of the Army, the National Research Council (NRC) studied the overall disposal program and endorsed the Army's choice of incineration of agents and thermal treatment of energetics, metal parts, and containers in a 1984 report. A pioneer plant constructed at Johnston Island in the Pacific Ocean in the late 1980s recently completed Operational Verification Testing of a baseline technology involving incineration. At Tooele, construction of a larger, continental facility is nearing completion. Construction of similar but smaller facilities is proposed by the Army for seven additional storage sites in the continental United States.

As a result of growing interest in alternatives to the baseline technology, in 1992 Congress instructed the Army to recommend disposal technologies for all sites by December 31, 1993. These recommendations are to be based on two NRC studies. The first by the Committee on Alternative Chemical Demilitarization Technologies is reported here. The second, by the Committee on Review and Evaluation of the Army Chemical Stockpile Disposal Program, will use the information and analyses provided here to formulate recommendations for the Army to use in developing its own recommendations to Congress. Thus, this report is the first step in a three-part national advisory process.

On January 13-15, 1993, an important step was taken when 132 countries signed the International Convention on Prohibition of the Development, Production, Stockpiling, and Use of Chemical Weapons and on their Destruction, known as the Chemical Weapons Convention. This convention specifies that stockpiled chemical warfare agents be destroyed in an "essentially irreversible manner" and that the weapons to apply them be rendered unusable. These demilitarization goals are to be met by December 31, 2004, with some possibility of schedule extension. The disposal technology to be used is not specified; however, within the United States the waste streams created by the chemical demilitarization system must be environmentally acceptable. Any gas stream from combustion-based processes is of particular concern to the public. Consequently, technologies to ensure environmental and public acceptability of this waste stream are also considered in this report.

This study was initiated with the first meeting of the committee in March 1992, followed by a workshop in June 1992. The workshop included presentations on proposed alternative technologies, with time for commentary by interested observers. Subsequent discussions and written submissions were additional important sources of information. The committee ended its data collection efforts in February 1993. More recent data may be available, especially for those technologies that have substantial development programs. The workshop was followed by three additional meetings, in September, October, and November 1992. Specific recommendations are not made in this report, but it is hoped that the information and discussion presented will provide a basis for more specific recommendations to be developed by the NRC and the Army.

The rapid pace of this study, the large number of contributions made to it, and the complexity of the subject offered substantial organizational and editorial challenges. The NRC staff, especially Margo Francesco, Allison Knight, Donald Siebenaler, and James Zucchetto, deserve special thanks and recognition for their essential roles in this study.

John P. Longwell, *Chairman*

Committee on Alternative Chemical Demilitarization Technologies

Contents

EXECUTIVE SUMMARY	1
1 INTRODUCTION	22
The U.S. Chemical Stockpile Disposal Program	22
Risk and Community Concerns	27
Alternative Demilitarization Systems	29
Transportation of Untreated Weapons and Agents	31
Primary Goals and Strategies for Demilitarization	31
Scope and Organization of the Study	34
2 THE U.S. CHEMICAL WEAPONS STOCKPILE	37
Description of the Agents	37
Description of the Munitions	42
Geographical Distribution of the Stockpile	49
Summary	53
3 U.S. AND FOREIGN EXPERIENCE WITH CHEMICAL WEAPONS DESTRUCTION	54
U.S. Chemical Demilitarization Experience	54
Chemical Warfare Agent Destruction in Other Countries	62
Summary	74
4 REQUIREMENTS AND CONSIDERATIONS FOR CHEMICAL DEMILITARIZATION TECHNOLOGIES	75
Chemical Composition of Agents and Their Breakdown Products	76
Waste Streams in Chemical Weapons Destruction	77
Processing Rates	78



Performance Standards	81
Worker Standards	81
Air Quality Standards	81
Liquid Wastes	81
Solid Wastes	82
General Considerations in Assessing Untested Alternative Technologies	83
Decontamination Standards	84
Chlorinated Dioxins	85
Monitoring	86
Effluent Retention Time Requirements	88
Time Required for Technology Development and Demonstration	89
Technology Development and Demonstration Costs	91
Assessment Criteria for Alternative Technologies	92
 5 THERMAL TREATMENT AND PREPROCESSING THE POSTPROCESSING OPERATIONS	 94
Preprocessing Operations	95
Cryoprocessing	95
Mechanical Disassembly of Explosives, Propellants, and Solidified Agent	96
Thermal Treatment	97
Postprocessing Operations	98
Solid Wastes	98
Control of Nitrogen Oxides	101
Water Recycle	101
Reduction of Waste Gas Volume	102
Waste Gas Storage Requirement	103
Storage and Retention Technologies	105
Activated-Carbon (Charcoal) Adsorption Systems	106
 6 LOW-TEMPERATURE, LIQUID-PHASE PROCESSES	 109
Chemical Detoxification Processes	110
GB (Sarin)	112
VX	116
H (Mustard)	118
Reduction Methods Conceivably Applicable to GB, VX, and H	121
Detoxication with Ionizing Radiation	122
Low-Temperature and Low-Pressure Oxidation Processes	123
Chemical Oxidation	123

Electrochemical Oxidation	124
Oxidizing Agents Plus UV Light	125
Biological Processes	126
Introduction and Overview	126
Direct Destruction of GB and VX	128
Biodegradation of the Reaction Products from the Chemical Processing of GB and VX	131
Chemical Hydrolysis and Bioremediation of Mustard	132
Bioremediation of Explosives and Energetics	132
Engineering Prospects	132
Summary of the Potential Application of Biological Processes	136
 7 PROCESSES AT MEDIUM AND HIGH TEMPERATURES	 137
Moderate-Temperature, High-Pressure Processes	138
Wet Air Oxidation	138
Supercritical Water Oxidation	146
High-Temperature, Low-Pressure Pyrolysis	152
Molten Metal Pyrolysis	152
Plasma Arc Processes	156
Gasification Processes	160
Synthetica Detoxifier	163
High-Temperature, Low-Pressure Oxidation	169
Catalytic Fluidized-Bed Oxidation	169
Molten Salt Oxidation	171
Catalytic Oxidation	174
Other Processes	176
Hydrogenation Processes	176
The Adams Process—Reaction with Sulfur	180
 8 APPLICATION OF ALTERNATIVE TECHNOLOGIES TO THE DESTRUCTION OF THE U.S. CHEMICAL WEAPONS STOCKPILE	 185
Destruction Technologies	185
Low-Temperature, Low-Pressure, Liquid-Phase, Detoxification	186
Low-Temperature, Low-Pressure, Liquid-Phase Oxidation	190
Moderate-Temperature, High-Pressure Oxidation	190
High-Temperature, Low-Pressure Pyrolysis	191
High-Temperature, Low-Pressure Oxidation	192
Waste Stream Handling Processes	193

CONTENTS		x
	Solid Waste	193
	Gas Waste Streams	194
	Liquid Wastes	196
	Goals, Strategies, and Systems for Chemical Demilitarization	196
	Program Goals	196
	Strategies for Disposal	197
	System Considerations	200
	General Observations	205
	APPENDICES	209
Appendix A,	Statement of Task	209
Appendix B,	Letter from James R. Ambrose, Dated October 21, 1987	210
Appendix C,	Letter from Charles Baronian, Dated August 7, 1992	213
Appendix D,	Biographical Sketches	237
Appendix E,	Technology Developers That Supplied Information	244
Appendix F,	Committee Meetings and Activities	250
Appendix G,	Technology Status Worksheet	259
Appendix H,	Excerpt From the U.S. Army's 5X Decontamination Review	262
Appendix I,	Ionizing Radiation	271
Appendix J,	Electrochemical Oxidation	274
Appendix K,	Additional Data and Material Balances for Wet Air Oxidation, Supercritical Water Oxidation, and the Synthetica Detoxifier	279
	REFERENCES	292
	INDEX	311

## Figures

1-1	Schematic of the baseline technology.	25
2-1	Principal Chemical warfare agents in the U.S. stockpile.	38
2-2	M55 rocket and M23 land mine.	43
2-3	105-mm, 155-mm, 8-inch, and 4.2-inch projectiles.	44
2-4	Bomb, spray tank, and ton container.	45
2-5	Physical envelopes of chemical munitions.	50
2-6	Types of agent and munitions and percentage of total agent stockpile (by weight of agent) at each storage site.	50
4-1	JACADS Demilitarization process.	79
7-1	WAO flow diagram.	140
7-2	SCWO flow sheet (MODAR type).	147
7-3	The Molten Metal Technology.	154
7-4	Process flow sheet of the Elkem Multipurpose Furnace and associated equipment.	155
7-5	The Westinghouse plasma system.	158
7-6	The Electro-Pyrolysis, Inc. (EPI) furnace design.	159
7-7	Lurgi gasifier.	162
7-8	Schematic flow sheet for the Synthetica Steam Detoxifier.	164
7-9	Molten salt oxidation system.	172
7-10	Block flow diagram of the UOP HyChlor conversion process.	177
7-11	A process flow sheet for the Adams process as presented by CHEMLOOP, L.P.	181
8-1	Unit processes in demilitarization Strategy 1: disassembly and agent detoxification, with storage or transportation of residue.	198
8-2	Unit processes for demilitarization Strategy 2: mineralization.	199
K-1	Apparent first-order arrhenius plot for oxidation of model compounds in supercritical water at 24.6 MPa.	286
K-2	Heat and Material Balances for the Synthetica System.	289

## Tables

1-1	Schedule for the Construction and Operation of Chemical Stockpile Disposal Facilities	27
2-1	Physical Properties of Chemical Warfare Agents	39
2-2	Composition of Munitions in the U.S. Chemical Stockpile	47
2-3	Composition of Selected Chemical Munition Types, by Weight	48
2-4	Chemical Munitions Stored in the Continental United States	51
2-5	Approximate Amounts of Metals, Energetics and Agent Contained in the Chemical Weapons Stockpile (tons), by Site	52
3-1	U.S. Army Experience with Destruction of H (Mustard) by Incineration	55
3-2	U.S. Army Experience with Destruction of GB (Sarin) by Neutralization	56
3-3	U.S. Army Experience with Destruction of GB (Sarin) by Incineration, at CAMDS	57
3-4	U.S. Army Experience with Destruction of GB (Satin) by Incineration, at JACADS	58
3-5	U.S. Army Experience with Destruction of VX by Incineration, at CAMDS	59
3-6	U.S. Army Experience with Destruction of VX by Incineration, at JACADS	60
3-7	U.S. Army Experience with Destruction of HD by Incineration, at JACADS	61
3-8	Canadian Experience with Mustard Agent Destruction (1974 to 1976)	63
3-9	Canadian Experience with Mustard Destruction in 1990 to 1991	64
3-10	Canadian Experience with Nerve Agent Destruction	65
3-11	German Experience with Mustard Agent Destruction	66
3-12	Former Soviet Union Experience with Agent Destruction	67
3-13	Former Soviet Union Experience with VX Destruction	68
3-14	U.K Experience with Destruction of Mustard and World War I Gases	69

TABLES		xiii
3-15	U.K. Experience with GB Destruction	70
3-16	U.K. Experience with Mustard Destruction	71
3-17	U.N. Experience with Destruction of Mustard in Iraq	72
3-18	U.N. Experience with Destruction of Nerve Agents in Iraq	73
4-1	Permissible Agent Hazard Concentrations in Air and Lethal Doses	82
4-2	Time Estimates for Development and Demonstration of Alternative Technologies	91
5-1	Salt Formation from GB Oxidation Products	100
6-1	Oxidation Potential of Different Chemical Species	126
6-2	Enzymes Capable of Degrading Organophosphorus Neurotoxins	129
7-1	Recommended WAO Operating Temperatures and Saturation Pressures for Destruction of Chemical Warfare Agents and Propellants	142
7-2	Estimated Effluent Gas Composition for Two-Step Destruction of GB, Hydrolysis Followed by WAO (Using Air)	145
7-3	Some Characteristics of Gasifiers	161
8-1	Summary of Process Capabilities and Status	187
8-2	Low-and Moderate-Temperature Agent Detoxification Processes	201
8-3	Agent Mineralization Processes	202
8-4	Processes for Treatment of Energetics and Metal Parts and Containers	204
K-1	Chemicals Successfully Treated by Supercritical Water Oxidation and Typical Destruction Efficiencies	282

# Acronyms and Abbreviations

<b>ACAMS</b>	Automatic Chemical Agent Monitoring System
<b>AChE</b>	Acetylcholine
<b>AChE</b>	Acetylcholinesterase
<b>ANAD</b>	Anniston Army Depot
<b>APG</b>	Aberdeen Proving Ground
<b>ARPA</b>	Advanced Research Projects Agency
<b>ASC</b>	Allowable Stack Concentration
<b>BOD</b>	Biological oxygen demand
<b>BRA</b>	Brine Reduction Area
<b>CAMDS</b>	Chemical Agent Munitions Disposal System
<b>CIS</b>	Commonwealth of Independent States, formerly the Soviet Union
<b>COD</b>	Chemical oxygen demand
<b>CRDEC</b>	Chemical Research, Development and Engineering Center
<b>CS</b>	Riot control agent
<b>CSDP</b>	Chemical Stockpile Disposal Program
<b>DAAMS</b>	Depot Area Air Monitoring System
<b>DMSO</b>	Dimethyl sulfoxide
<b>DOD</b>	U.S. Department of Defense
<b>DOE</b>	U.S. Department of Energy
<b>DPE</b>	Demilitarization Protective Ensemble
<b>DRE</b>	Destruction and Removal Efficiency
<b>DRMO</b>	Defense Reutilization and Marketing Office
<b>EIS</b>	Environmental Impact Statement
<b>EPA</b>	Environmental Protection Agency
<b>FRP</b>	Fiberglass Reinforced Plastic

---

<b>GA</b>	Tabun
<b>GB</b>	Sarin
<b>GPL</b>	General Population Levels
<b>H, HD, and HT</b>	Blister or mustard agents
<b>HLE</b>	High Level Exposure
<b>IARC</b>	International Agency for Research on Cancer
<b>IDLH</b>	Immediately Dangerous to Life and Health
<b>IUPAC</b>	International Union of Pure and Applied Chemistry
<b>JACADS</b>	Johnston Atoll Chemical Agent Disposal System
<b>L</b>	Lewisite
<b>LBAD</b>	Lexington Blue Grass Army Depot
<b>MBE</b>	Moving bed evaporator
<b>MDL</b>	Minimum Detection Limits
<b>MEO</b>	Mediated electrochemical oxidation
<b>MMT</b>	Molten Metal Technology
<b>MPF</b>	Metal Parts Furnace
<b>NAAP</b>	Newport Army Ammunition Plant
<b>NAS</b>	National Academy of Sciences
<b>NEPA</b>	National Environmental Policy Act
<b>NESHAP</b>	National Emission Standards for Hazardous Waste Pollutants
<b>NRC</b>	National Research Council
<b>OTA</b>	Office of Technology Assessment
<b>OVT</b>	Operational verification testing
<b>PBA</b>	Pine Bluff Arsenal
<b>PCB</b>	Polychlorinated biphenyl
<b>PCP</b>	Pentachlorophenol
<b>PEIS</b>	Programmatic Environmental Impact Statement
<b>PL</b>	Public Law
<b>PUDA</b>	Pueblo Army Depot
<b>R&amp;D</b>	Research and development
<b>RCRA</b>	Resource Conservation and Recovery Act
<b>RDEC</b>	Research, Development and Engineering Center



<b>SANA</b>	Scientists Against Nuclear Arms
<b>SCWO</b>	Supercritical water oxidation
<b>SNG</b>	Synthetic natural gas
<b>SRI</b>	Southwest Research Institute
<b>TCDD</b>	Tetrachlorodibenzodioxin
<b>TCDF</b>	Tetrachlorodibenzofuran
<b>TEAD</b>	Tooele Army Depot
<b>TNT</b>	Trinitrotoluene
<b>TSCA</b>	Toxic Substances Control Act
<b>TSDF</b>	Treatment, Storage, and Disposal Facilities
<b>TWA</b>	Time Weighted Average
<b>UMDA</b>	Umatilla Army Depot
<b>USATHAMA</b>	U.S. Army Toxic and Hazardous Materials Agency
<b>UV</b>	Ultraviolet
<b>VX</b>	Organophosphate nerve agent
<b>WAO</b>	Wet air oxidation

# **ALTERNATIVE TECHNOLOGIES FOR THE DESTRUCTION OF CHEMICAL AGENTS AND MUNITIONS**



## Executive Summary

The U.S. Department of Defense, through its executive agent the U.S. Army, is embarked on a Chemical Stockpile Disposal Program (CSDP) to destroy the nation's unitary chemical weapons.<sup>1</sup> There are about 25,000 tons of chemical warfare agents in the U.S. stockpile, primarily the nerve agents GB and VX and the blister, or mustard, agents H, HD, and HT. These agents are contained in a variety of munitions and in bulk containers that are distributed among eight continental U.S. sites and Johnston Island in the Pacific Ocean. The baseline incineration technology, developed by the Army, has undergone Operational Verification Testing at Johnston Island, to demonstrate that it can be used to destroy agent and weapons safely and meet all environmental standards.

The baseline technology entails the transport of weapons from storage to destruction areas, manual unpacking, and automated disassembly. This approach results in four primary process streams requiring treatment: agent, energetics, metals parts, and dunnage (packing materials and other miscellaneous solid wastes).<sup>2</sup> Agent is destroyed in one incinerator, energetics (explosives and propellants) are destroyed in a second, and metal parts are

---

<sup>1</sup> The U.S. chemical weapons stockpile contains unitary and binary chemical weapons. Unitary chemical weapons contain agents that, by virtue of their molecular composition and structure, are highly toxic or lethal. By comparison, binary chemical agents consist of two nonlethal chemicals that, upon mixing, form a lethal chemical agent. Although slated for destruction in the same time frame as unitary weapons, binary weapons are not included in the CSDP and are not addressed in this report. These weapons will be destroyed as part of a separate Army program.

<sup>2</sup> The critical materials to be destroyed are the agent (including that on metal parts and dunnage) and energetics. Agents are large molecules containing carbon, chlorine, hydrogen, phosphorus, fluorine, sulfur, nitrogen, and oxygen. To detoxify these agents, the molecular bonds need to be broken and the components reacted to produce less hazardous materials. Complete oxidation (mineralization) of molecules produces carbon dioxide, water, and nitrogen (N<sub>2</sub>), and fluorides, phosphates, and sulfates that can be removed as salts. Combustion is the most common oxidation process.

detoxified in a third. A fourth incinerator, designed for dunnage, has not yet been used for hazardous waste disposal at Johnston Island.<sup>3</sup> Afterburners that use fuel combustion are then used to destroy any further contaminants emitted by the incinerator and to achieve a high degree of oxidation. Exhaust from the afterburners is treated in a pollution abatement system.

The Army has proposed a program plan to build similar plants at the eight continental storage sites. This plan must be approved by Congress.

Concerns have been raised about the baseline incineration approach. Some groups and individuals have claimed that the Army's baseline technology poses risks to surrounding populations and the environment, risks that could be reduced by using alternative disposal technologies. Congress has also shown interest in the use of alternative technologies for disposal of the chemical stockpile. It has directed the Army to submit a report on the subject by December 31, 1993, based in part on the present study by the National Research Council (NRC) Committee on Alternative Chemical Demilitarization Technologies.

The present report addresses the possible use of alternative destruction technologies to replace partly or wholly or to be used in addition to the current baseline technology. The report considers the principal technologies that might be applied to the CSDP, strategies that might be used to manage the stockpile, and combinations of technologies that might be used. However, no specific recommendations are made here about the use of these technologies in the Army's disposal program. Another NRC Committee, the Committee on Review and Evaluation of the Army Chemical Stockpile Disposal Program, which provides continuing technical advice to the Army, will issue a report later this year that, based partly on the present report, may offer specific findings and recommendations for the use of alternative technologies in the CSDP.

The present report is summarized here in sections on the requirements and other considerations for alternative technologies, the characteristics of proposed alternative technologies, options for gas and other waste stream handling to manage risks of special concern, strategies and system issues regarding the use of alternative technologies in the disposal program, and concluding observations.

In its study, the committee examined a variety of technologies and processes, in part through a workshop at which developers made presentations on their technologies. Companies also provided information in writing. Although the committee has used such information provided by individual developers, it has not compared one company's technology with another's

---

<sup>3</sup> Dunnage (packing materials, used protective suits, etc.) must be either destroyed or sent to a disposal site. Although incineration is one option, shipment to a hazardous waste landfill is an alternative.

but instead has assessed generic approaches to chemical weapons destruction. The committee did not have access to proprietary information in this study.

### REQUIREMENTS AND CONSIDERATIONS

Destruction of the chemical stockpile is a complex undertaking. Determining the appropriate technologies to perform this task must include cognizance of a number of requirements and considerations.

- A number of process streams must be treated. Destruction technologies must be able to treat liquid nerve and mustard agents and the products of their aging, such as gels and reaction products. Because agent is stored both in bulk in metal containers and in weapons containing explosives and propellants, destruction technologies must also be able to manage solids contaminated with agent, both with and without explosives and propellants. The committee focused on these process streams, recognizing that dunnage, ventilation air, and spent decontamination fluids must also be treated and disposed of.
- An integrated system of unit processes will be required. As the name of this committee suggests, the word "technology" is usually applied to processes that are or might be used to destroy the chemical stockpile, such as baseline technology or plasma arc technology. However, many unit processes are entailed in any technology. The baseline technology, for example, encompasses transport and dismantling of weapons, separation of agent from explosives, agent combustion, combustion of by-products in an afterburner, and cleanup of waste gas streams.

Alternative approaches to these processes may be useful, but alone they are often unable to demilitarize the chemical stockpile. For example, chemical hydrolysis might be used to detoxify the chemical agent drained from munitions. The products of this process might then be oxidized by a biological process, a wet air oxidation, or a supercritical water oxidation to further destroy organic materials. The effluents of this step might require yet further treatment, for example, in a catalytic oxidizer, before release to the environment. Such a sequence of processes might be viewed as one technology for the destruction of a given agent. Other processes would still be required to destroy or detoxify agent on metal parts, dunnage, and energetics. These system considerations must be taken into account when assessing the likely potential value of alternative technologies and unit processes.

- International treaty deadlines should be met. The international treaty on chemical weapons, the Chemical Weapons Convention (signed by the United States and a number of other nations January 13-15, 1993), specifies that chemical agents should be converted essentially irreversibly (to

a form unsuitable for the production of chemical weapons) and that munitions and other devices should be rendered unusable as such. The convention, when ratified, will require destruction of all chemical weapons within a 10-year period, with provision for a one-time extension. For the deadline to be met, technologies must be developed and demonstrated in a timely fashion, and they must be able to process weapons at an acceptable rate. Hence, the development stage of a technology and the time likely required to demonstrate its effectiveness become important considerations. Although treaty deadlines may change, there also remains the risk of agent release from any continued storage of weapons, which should be balanced against the risks of demilitarization.

- Waste streams must meet environmental standards. All technologies used to destroy chemical weapons will produce liquid, solid, and gas waste streams in proportions depending on the technology. All systems, including the baseline technology, must meet regulatory standards for effluents.

This requirement implies that liquid wastes, such as salt solutions, spent decontamination fluid, and contaminated water, must be converted to dry solids and water and that the water be treated to allow recycling. Solid wastes consist mainly of salts and decontaminated metal parts. For solid wastes, the Army has developed a classification of degrees of decontamination achieved. Level 3X, established primarily for worker safety, applies to once-contaminated or potentially contaminated material that has since been decontaminated to show zero residual contamination as indicated by air monitoring above the material. Worker contact is allowed with such materials, but they cannot be released to the public. A level 5X rating is applied to a fully decontaminated solid that can be released to the public for uncontrolled use; this level is achieved by a thermal treatment of at least 1000°F for at least 15 minutes. To achieve 5X solids decontamination with technologies that do not operate at such temperatures would require treatment equivalent to this thermal treatment.

- Agent release must be avoided. For gas waste streams, the highly toxic nature of chemical warfare agents requires that any demilitarization system encompass safety systems to prevent agent release to the environment. In addition, discharge of other toxic materials in air generated by the destruction process must be below regulatory requirements for both design operation and operation in the case of equipment or operational failure. Alternative demilitarization technologies must be able to meet these criteria.
- Time for development must be weighed. All alternative technologies will require some time for development dependent on their stage of development. Although there is a treaty deadline, the committee did not eliminate from consideration any technology because of the development time it would require; development time is one factor that must be weighed by the

political process when determining a technology's acceptability. Precise estimates of development times are also hard to make, because these times will depend on the quality and level of development effort. The committee estimated that about 12 years are typically required for a technology to progress from concept through demonstration. Once a technology is demonstrated, time for construction and startup of a production facility would probably be similar to that for the existing program, in which design, construction, and systematization of a facility require about 5 years.

- Costs must ultimately be considered. The committee decided that cost estimates were premature until the number of options is narrowed and more detail about them is known. Thus, no cost projections are made here. However, the committee believes that the selection of any alternative technology would likely incur additional program costs, largely because of technical development requirements and program delays.

### CHARACTERISTICS OF ALTERNATIVE DESTRUCTION TECHNOLOGIES

In characterizing alternative processes and technologies for chemical weapons destruction, the committee focused on the following:

- Functional performance. The capability of the technology to treat or process the different agents, solid parts, explosives, propellants, dunnage, and air streams; the liquid, solid, and gas waste streams generated; and any requirements for further treatment of solid parts or waste streams.
- Engineering factors. The degree and manner in which engineering factors (e.g., explosion potential or extreme conditions such as very high pressures or corrosivity) may affect a technology's effectiveness, its potential for successful development, and its safety and hazard potential during operation.
- Development status. The development and demonstration stage of the technology (whether laboratory, conceptual design, pilot plant, in commercial use for similar operations, or used previously to destroy one or more chemical warfare agents). Development status is an indicator of the time required for full development. As discussed above, this time is difficult to estimate because it is determined by many factors, such as the level of development effort. Typically, to progress through the end of demonstration from the laboratory stage takes 9 to 12 years; from the conceptual design stage, 10 to 11 years; from the pilot plant stage, 7.5 to 9 years; and from the beginning of demonstration itself, 3 years (see [Table 4-2](#)).



The committee investigated a variety of alternative destruction processes (see Chapters 6 and 7). Table E-1 summarizes their status and applicability. For convenience, the technologies and processes are grouped in the following categories: (1) low-temperature, low-pressure, liquid-phase detoxification processes that convert agent to less toxic compounds; (2) low-temperature, low-pressure, liquid-phase oxidation processes, including biological oxidation, which react agent with oxygen to form carbon dioxide, water, and salts (for complete oxidation, or mineralization); (3) moderate-temperature, high-pressure oxidation; (4) high-temperature, low-pressure pyrolysis, which uses heat to destroy molecular bonds; (5) high-temperature, low-pressure oxidation; and (6) other technologies.

Destruction technologies investigated by the committee include those under development for disposal of other types of toxic wastes (especially chlorinated hydrocarbons) and those being developed specifically for chemical warfare munitions destruction. Other technologies reviewed, such as high-temperature ovens, are commercially available components that have been more widely used.

### **Low-Temperature, Low-Pressure, Liquid-Phase Detoxification**

Chemical treatment of agents can reduce their toxicity. Such treatment, with relatively low temperatures and pressures, has been used for the agent GB, and a large number of other chemical processes have been proposed. Various results suggest that chemical reaction in basic (high pH) solutions offers the potential to convert all three agents to products of much lower toxicity by what is called detoxification:

- GB has been detoxified by sodium hydroxide in water solution in the United States and worldwide.
- Limited laboratory studies suggest that VX can be detoxified by sodium hydroxide and hydrogen peroxide in water solution.
- HD has been successfully detoxified by calcium hydroxide in water solution at higher temperatures (90° to 100°C).
- Using an alcohol or ethanolamine in place of water increases agents' solubility and is also believed capable of converting all three agents.

Chemical reactions in acidic (low pH) solutions can use oxidizing agents ( $\text{Cl}_2$ , peracids, hypochlorites, or hydrogen peroxide), a method by which all three agents should be treatable; however, except for VX, little information on this approach was found.

At ambient temperatures, HD solubility in water is very low, and its high viscosity, when it contains thickeners, makes adequate contact with

TABLE E-1 Summary of Process Capabilities and Status

Process	Stream Treated			Metal and Energetics			Next Step	Comments
	Agent	Initial Agent	Complete Organic Oxidization	Metal	Need Gas	Energetics		
		Detox			Afterburner			
Low-temperature, Low-pressure detoxification								
Base hydrolysis (NaOH)	GB		No	No	?	No	pp	Has been used in field; for HD, limited by contacting problems
NaOH + H <sub>2</sub> O <sub>2</sub> Ca(OH) <sub>2</sub> (at 100°C)	VX		No	No	Yes	No	Lab	New finding
	HD		No	No	?	No	Lab/pp	Limited use in England
KOH + ethanol Hypochlorite ion	HD, GB, VX		No	No	?	No	Lab	Difficult
	HD		No	No	Yes	No	Lab	contacting problem with HD
Organic base (ethanolamine)	GB, HD, possibly VX		No	No	?	No	Lab/pp	Limited use in Russia; increase in organic waste
Acidic systems HCl hydrolysis Peracid salts (OXONE, others) Chlorine	GB		No	No	?	No	Lab/pp	Increased waste
	VX, perhaps GB and HD		No	No	Yes	No	Lab/pp	Increased inorganic waste
	VX, perhaps GB and HD		No	No	Yes	No	Lab/pp	High conversion
Ionizing radiation	GB and HD		No	Yes?	?	Yes?	Lab	not yet established
	All		No	Yes?	?	Yes?	Lab	not yet established

Stream Treated							
Agent							
Metal and Energetics							
Process	Initial Agent Detox	Complete Organic Oxidation	Need Gas Afterburner	Energetics	Metal	Afterburner Needed	Next Step
Low-temperature, low- pressure oxidation Peroxydisulfate, ClO <sub>2</sub> , H <sub>2</sub> O <sub>2</sub> , O <sub>3</sub>	All	Yes	Yes	No	No	N.A.	Lab
							Catalysts generally needed for complete conversion; spent peroxydisulfate can be electrochemically regenerated Very large power requirement; applications have been for very dilute solutions
UV light with O <sub>3</sub> and H <sub>2</sub> O <sub>2</sub>	N.A.	Yes	Yes	No	No	N.A.	pp
Electrochemical oxidation	All	Yes	Yes	No	No	N.A.	Lab
Biological oxidation Moderate-temperature, high-pressure oxidation	N.A.	Yes	Yes	No	No	N.A.	Lab
Wet air and super- critical water oxidation	All	Partially	Yes	Yes?	No	Yes	pp
							Residual organic components can be low for supercritical; residual materials are believed suitable for biodegradation

Stream Treated		Metal and Energetics					
Agent		Metal		Energetics		Afterburner Needed	
Process	Initial Agent Detox	Complete Organic Oxidation	Need Gas Afterburner	Energetics	Metal	Next Step	Comments
High-temperature, low - pressure pyrolysis Kiln (external heat)	All	Partially	Yes	Yes	Yes	Demo	May need more than one unit to deal with all streams
Molten metal	All	No	Yes	Yes?	Yes	pp	
Plasma arc	All	No	Yes	Yes?	Yes	Lab/pp	
Steam reforming	All	Yes	Yes	No?	No	Lab/pp	
High-temperature, low - pressure oxidation							
Catalytic, fixed bed	N.A.	N.A.	N.A.	No	No	Lab/pp	Useful for afterburner
Catalytic, fluidized bed	All	Yes	Yes	Yes	No	pp	Possible use for afterburner and acid gas removal
Molten salt	All	Yes	Yes	Yes?	No	pp	Baseline technology
Combustion	All	Yes	Yes	Yes	Yes	—	
Other technologies							
Hydrogenation	All	No	Yes	No	No	Lab	
Reactions with sulfur	All	Yes	Yes	No	No	Lab	

NOTE: Question mark (?) indicates uncertainty about the noted application. N.A., not applicable; pp, pilot plant; demo, demonstration; lab, laboratory.

aqueous solutions difficult. HD is quite reactive; with an adequate area of HD-liquid interface, many of the reactions useful for GB are likely to be effective for HD. Greater surface area of the interface can be obtained by high-energy physical dispersion or use of emulsifying agents. The latter approach, for microemulsions, requires about equal quantities of agent and emulsifier, which increases the amount of organic waste. Operations at 70° to 100°C may alleviate the interface problem, as illustrated by the successful treatment of GB with calcium hydroxide at such temperatures. Physical dispersion may still be required for the gelled HD found in the stockpile.

Although the above reactions convert agent to less toxic compounds, some reaction products could be converted back to the original agent and would not meet the treaty demilitarization requirement of irreversibility of agent products under storage. However, these reaction products would be more suitable feed for subsequent processing steps that accomplish further conversion by oxidation.

The development and demonstration of such detoxification processes will require substantial laboratory and pilot plant work for all three agents.

### **Low-Temperature, Low-Pressure, Liquid-Phase Oxidation**

Demilitarization treaty requirements can be met by detoxification, but further conversion, possibly by oxidation, may be needed for general environmental, storage, safety, and other reasons. There has been little investigation of the use of low-temperature oxidation processes for waste streams resulting from low- and medium-temperature detoxification processes. However, treatment of industrial waste and contaminated groundwater by low-temperature oxidation is being actively investigated and provides some leads on the use of chemical and biological processes for treating agent waste streams.

At temperatures below the boiling point of water, very active oxidizing agents (with catalysis) are required for oxidation. Peroxydisulfate salts can oxidize most organic compounds to carbon dioxide but would produce a very large waste stream. It has been proposed that to optimize the process the spent reagent be recycled by electrolytic regeneration; use of catalyzed hydrogen peroxide might reduce the regeneration requirements.

Ultraviolet light can activate aqueous solutions of ozone and hydrogen peroxide and is an option for treating contaminated groundwater. However, the large electricity requirements of this process when treating large reaction product streams place it at a disadvantage with alternatives.

Biological oxidation is commonly applied to industrial and municipal waste streams. Although its application to the liquid waste streams from

demilitarization processes has not been developed, with research this approach might well be successful.

All the above low-temperature, low-pressure, liquid-phase processes might be used to treat liquid waste streams but not be directly applicable to contaminated metal parts or energetics.

### **Moderate-Temperature, High-Pressure Oxidation**

In wet air oxidation, organic materials in a dilute aqueous mixture are oxidized at elevated temperatures and pressures. Supercritical water oxidation operates at still higher temperatures and pressures (above the critical point of water at which hydrocarbons, for example, are highly soluble). Both wet air and supercritical water oxidation processes can detoxify and convert residual organics to carbon dioxide. Wet air oxidation requires residence times of greater than 1 hour. Even then, more refractory organic compounds remain; however, these compounds are judged to be suitable for subsequent biological degradation.

Supercritical water oxidation can achieve a greater conversion of all organics in less than 10 minutes. Because pure oxygen is used in this process, waste gas is primarily carbon dioxide, which can, if necessary, be removed as solid calcium carbonate (limestone). Adaptation of wet air oxidation to use pure oxygen would require a pilot plant program.

Both processes can treat all three principal agents in the U.S. stockpile (GB, VX, and the mustard compounds). Both are expected to be capable of treating a slurry of finely divided energetics if care is exercised in the control of feed rates. Some mechanical addition to the disassembly process would be required to remove and make a slurry of the energetics. Their removal from containers is not expected to be complete, so some energetics residues would still need to be destroyed in a metal deactivation process involving high-temperature treatment, as in the baseline system.

Supercritical water oxidation could also be used as an afterburner to oxidize gas products of pyrolysis or other processes. This approach is an alternative to the combustion variations discussed later. It has the disadvantage of requiring gas compression to 3,000 psi or higher. However, it also offers high conversion efficiency.

Application of these processes to chemical agents would still require a problem-solving stage and would require pilot plant studies. The high operating pressure would require appropriate confinement, as in industrial practice. Currently, baseline facilities are remotely operated and designed for energetics explosions and capture of agent release. The high-pressure oxidation process would call for some extension of these safeguards.

### High-Temperature, Low-Pressure Pyrolysis

Some of the high-temperature pyrolysis and oxidation processes are capable of treating all major stockpile components (agent, energetics, and metal; see [Table E-1](#)). High temperatures are required to decontaminate metal parts and to ignite and destroy energetics (see [Chapter 5](#)). These temperatures must be sufficient to achieve the equivalent of the 5X criterion (treatment at 1000°F for 15 minutes) for metal decontamination.

Kilns with electrical heating can meet these requirements and avoid dependence on the internal firing now used, an alternative approach that has the advantage of reducing total flue gas volume. However, air (or oxygen) must be supplied to oxidize unburned pyrolysis products. This step can be achieved within the kiln or in a secondary burner. An afterburner would be needed to ensure complete oxidation. Variations of this system can accept bulk containers as well as energetics and small metal parts.

Plasma arc torches, which generate ionized plasmas at temperatures of up to 12,000 K, are being developed to destroy toxic wastes. Molten metal processes are electrically heated melting furnaces adapted for hazardous waste disposal. Both approaches use electrical heat and operate at higher temperatures than ovens or kilns under oxygen-deficient conditions. They generally introduce air to burn the products resulting from the initial pyrolysis but still require an afterburner. In principle both can handle chemical warfare agents and fragmented energetics and metal parts; the molten metal system would likely be able to handle a larger range of material sizes than would the plasma arc systems.

In steam gasification processes, steam is reacted with carbon-containing feed at high temperatures to produce a gas containing the combustible components hydrogen, carbon monoxide, soot, and low-molecular-weight hydrocarbons. Other elements (S, P, F, and Cl) require oxidation and removal. Steam gasification is more limited than pyrolysis, since it does not appear directly useful for metal decontamination. However, an approach combining pyrolysis and steam gasification is under private development for use in hazardous waste destruction.

### High-Temperature, Low-Pressure Oxidation

High-temperature, low-pressure oxidation is the current workhorse for destroying toxic waste materials. There are several variations of interest. Molten salt and fluidized-bed oxidation, because of the large heat capacity of the molten salt and the pulverized-solids bed, are less likely to suffer flame-out (flame extinction) than is the fast-response gaseous system of conventional combustion. These alternative methods also provide good contact

between air and fuel. There would be some tendency for bubble formation to result in agent bypassing the combustion zone and afterburners are still needed. These systems can also retain much of the oxidized halogens, sulfur, and phosphorus if appropriate basic acceptors are part of the salt or solids system; and they can also deal with energetics of small particle size, although their ability to handle metal parts seems limited. Both molten salt and fluidized-bed systems are used for toxic waste disposal. To apply either to demilitarization would probably be possible by proceeding directly to design and construction of a demonstration unit.

The catalytic fixed bed is of special interest for use as an afterburner for the final oxidation of any unoxidized material in gas effluents from another destruction process. The familiar automobile catalytic converter is an example of this application. The presence of halogens, phosphorus, and sulfur in the destruction products from agents and energetics will probably preclude the use of very active catalysts. However, operation at higher temperatures could allow use of rugged catalysts or even common ceramics. For many situations, external electrical heating will minimize dependence on heat generation in the catalytic oxidation unit and minimize production of waste gas.

An important variation on all these high-temperature oxidation systems is their operation with pure oxygen instead of air. As discussed below, the volume of waste gas can be greatly reduced by substituting oxygen for air. Although technology is available to shift from air to oxygen, demonstration of operation with oxygen would be required.

Various combinations of all these systems as they might be used in the stockpile disposal program are considered later.

## **WASTE STREAM HANDLING**

Chemical demilitarization waste streams that require special treatment are gas effluents, metal parts and containers, salts from the neutralization of acid gases, and liquids.

### **Gas Effluents**

The risks to surrounding communities from gas effluents of destruction operations can be controlled and reduced by several approaches: use of activated-carbon beds (charcoal filters); temporary storage of gas waste streams, with chemical analysis before release; or approaches that minimize or eliminate the discharge of gas wastes. The techniques involved are generally well-known, but would have to be tailored to address very low



contaminant concentrations and would require testing and demonstration for use in chemical demilitarization.

For stockpiles located in populated areas, activated-carbon filters could be installed on waste gas outlets to remove any remaining agent and other trace organic compounds. These filters would also capture any transient emissions (puffs) of agent that might escape from the destruction system. This approach could greatly reduce the probability of dangerous releases of agent or other toxic materials in air to the atmosphere during both design and off-design operations.

Alternatively, a dosed-loop system could store waste streams until chemical analysis established their suitability for disposal. For large combustion facilities (e.g., as for general-purpose hazardous waste incineration), gas storage volume requirements are too large to represent an economically viable option. However, for the stockpile disposal program, the relatively small scale of operations and extremely toxic nature of chemical warfare agents lend interest to this approach. Preliminary calculations by the committee suggest that commercial gas holders may be large enough for this application. The use of gas holders would allow exhaust gases to be retained and analyzed before their release. If unacceptable contaminants were detected, the gas could be recycled through the destruction system. The use of oxygen instead of air would also significantly reduce the size of the gas holders needed.

Finally, gas waste streams could be minimized or eliminated. Oxygen could be used instead of air to reduce gas waste streams, but revised designs would be required for those systems now designed to operate with air. Another strategy for eliminating gas waste streams would be to convert them to solid products. The carbon dioxide gas resulting from oxidation, for example, could be converted to solid calcium carbonate.

### **Treated Metal Parts and Containers**

Metal parts and bulk (ton) containers are heated to the 5X criterion in the baseline approach; they would also be heated to this extent in several high-temperature alternative technologies. Such treatment allows these materials to be recycled as scrap metal. The materials could instead be chemically decontaminated to a level that allows their transportation and disposal as toxic waste, eliminating the need for equipment to heat the larger metal parts, such as drained artillery shells and ton containers.

### **Salts**

Waste salts are formed by neutralization of the acid products of agent and energetics oxidation. The amount of waste salts varies, from around 2 pounds per pound of agent, when no carbon dioxide is captured, to about 10 pounds per pound of agent, when carbon dioxide is captured and excess base is used. These waste salts must be dried, heated, and tested to establish the absence of agent before their disposal as hazardous waste, or they must be given 5X decontamination treatment (1000°F for 15 minutes), which eliminates any residual agent and other organic compounds.

### **Liquid Wastes**

Water is formed by oxidation of agent, energetics, and fuel. In addition, it is used for cooling, waste gas scrubbing, and decontamination. It can be discarded as vapor in flue gas or as liquid waste. After treatment to remove contaminants, it could also be recycled in the facility to minimize discharge to the environment. Liquid water discharge from the facility must meet applicable standards for purity. Technology is available for water purification and must be integrated into the total operation.

## **STRATEGIES AND SYSTEM IMPLICATIONS FOR DEMILITARIZATION**

As mentioned above, alternative technologies and processes could be applied in many combinations to achieve demilitarization of chemical weapons. Although this report does not offer recommendations for specific processes that the Army should pursue, it does suggest some general strategies.

The committee identified two broad strategies that could be used to achieve demilitarization of agent and weapons, eliminate risks to surrounding communities from continued storage of agent, and dispose of waste streams appropriately and safely.

*Strategy 1. On-site disassembly and agent detoxification to meet treaty demilitarization requirements and permit transportation to another site or continued local storage of residues.*

In Strategy 1, liquid-phase processes could be used to decompose agent to meet demilitarization requirements. Final oxidation of all organic residues, energetics destruction, and decontamination of metals could be deferred by

continued local storage or conducted at another site to which the materials could be transported for final treatment. Criteria to establish the acceptability of materials for transport to other sites would still need to be determined on the basis of both technical and political considerations.

*Agent.* In Strategy 1, several processes or technologies might be used for agent detoxification:

- low-pressure, liquid-phase chemical detoxification;
- low-pressure, liquid-phase oxidation with the use of oxidizing compounds; and
- high-pressure, wet air or supercritical water oxidation.

Again, all the low-temperature, liquid-phase processes are still at the stage of laboratory research. Each type of chemical warfare agent may require a separate chemical destruction process, in which case three new processes would have to be developed. However, it may be possible to use common equipment if the same materials can be used for all three processes. Waste gas production is generally small for such processes.

High-pressure, wet air oxidation and high-pressure supercritical water oxidation can detoxify and demilitarize agent; however, some organic compounds remain. The waste gas stream contains organic chemical compounds and may require further treatment. The gas handling problem is reduced if pure oxygen is used, which is normal practice for supercritical water oxidation but would require additional development of wet air oxidation. The waste gas stream from all these processes could be further reduced by capture of carbon dioxide with lime.

*Energetics and contaminated metal pans and containers.* In Strategy 1, energetics and contaminated parts and containers would be treated with decontamination fluid to allow continued storage or transportation to another site. In some cases, drainage of agent from containers is quite incomplete (especially for some batches of mustard agent). Facilities to remove most of the remaining undrained agent would be needed to detoxify the containers with decontamination fluid.

Strategy 1 could essentially eliminate local discharge of flue gas, meet the treaty requirements for demilitarization, and eliminate the risk of agent release from continued storage. However, it would require additional time (5 to 12 years) for research, development, and demonstration of new technologies. The medium-temperature, high-pressure, wet air and supercritical water oxidation systems are in the pilot plant stage and would require development and special attention to ensure safety. The process to remove the residual agent from drained weapons and containers would also

need to be developed. However, this strategy would allow delaying final disposal of energetics, metal parts contaminated with agent, and residual salts.

*Strategy 2 Conversion of agent and disassembled weapons to salts, carbon dioxide, water, and decontaminated metal (complete oxidation or mineralization).*

In Strategy 2, mineralization is completed and there is therefore no requirement for transportation or long-term storage of organic residues from detoxification and treatment of agent, energetics, metal parts, or containers. Demilitarization is achieved by oxidation and heat treatment.

*Agent.* Agent mineralization can be accomplished in two steps: preliminary detoxification followed by additional processing to complete oxidation, as in the treatment of GB by hydrolysis and then incineration (see [Chapter 3](#)). Mineralization can also be accomplished in one step as in the baseline process.

One-step approaches for complete oxidation of agent include the following:

- the current baseline system plus charcoal-filter adsorption of flue gas;
- the current baseline system plus storage and certification of flue gas;
- low-temperature, liquid-phase oxidation;
- medium-temperature, high-pressure, wet air or supercritical water oxidation plus follow-up oxidation (chemical, biological, or with an afterburner);
- fluidized-bed or molten salt oxidation with the use of an afterburner;
- plasma arc or molten metal pyrolysis with an afterburner; and
- steam gasification with an afterburner.

For the two-step approach, one of the processes above would be preceded by one of the processes identified under Strategy 1.

The alternative system that would entail the least increase in delay and complexity for the Army disposal program would be the baseline technology augmented by the use of activated-carbon beds (charcoal filters) or by storage and certification of gas waste streams.

Low-temperature, liquid-phase oxidation with the use of strong oxidizing compounds is attractive because of low emissions of waste gas, but it is only in the research stage. Supercritical water and wet air oxidation with the use of oxygen might also be used for complete oxidation, but a final oxidizing

process for residual organic compounds might also be necessary; pilot plant studies of these processes with hazardous compounds are underway. However, several more years of development are probably needed before demonstration.

Fluidized-bed combustion and molten salt oxidation operate at lower temperatures than those for conventional combustion. Both have been used for toxic waste disposal, but both would require further development and demonstration for agent destruction. The oxidation efficiency of these operations can be high, but afterburners for the waste gas streams would still be required.

The waste gas products from plasma arc and molten metal pyrolysis must be burned, probably in a primary burner combined with an afterburner system. Because electrical energy instead of fuel combustion supplies the heat in these processes, the volume of waste gas would be reduced. Use of oxygen in the follow-up burners can further reduce flue gas, as in other high-temperature systems. Demonstration pilot plants for these processes could probably be designed and built to solve operational problems and demonstrate the performance of the developed systems.

High-temperature reaction with steam has most of the features of the high-temperature pyrolysis systems.

*Energetics and contaminated metal parts and ton containers.* In Strategy 2, high-temperature processes are needed to handle the very heterogeneous waste stream of energetics and metal parts and containers. The baseline technology uses two internally fired kilns. There are several alternatives to this approach:

- the baseline kilns plus charcoal adsorption or gas storage and certification;
- externally heated kilns plus a new afterburner (types of afterburners that would not require internal firing include electrically heated catalytic combustion and supercritical water oxidation); and
- molten metal or plasma arc melting furnaces plus a new afterburner.

Addition of storage and certification capability or activated-carbon adsorption to the baseline kilns would convert them to closed-loop systems without requiring additional demonstration. The amount of flue gas resulting from internal firing with fuel is large, however, and could be reduced by the use of electrically heated kilns and afterburners. Demonstration and testing would be needed for both these kilns and their afterburners. Modification and testing of the pollution abatement system, which removes acid gases, would also be necessary.

The molten metal furnace is capable of handling metal parts and energetics, but pilot plant work is required. Plasma arc furnaces might also handle these materials but may not be as useful for large metal parts. Further development of this approach is also required.

All of these processes could also be used to destroy bulk agent. Treatment of all streams in one device offers equipment simplification but with some loss of control of the composition of the feed streams and the products resulting from destruction of the several streams.

### Afterburners

For all systems that produce waste gas, afterburners are needed to ensure complete oxidation. The baseline practice is to use internal firing with fuel if additional heat is needed. Substituting oxygen for air and external heating for internal firing would minimize waste gas, but the first option would require demonstration. Catalytic oxidation could reduce the temperatures required, but the use of highly active catalysts is made difficult by the deactivation potential of the P, F, Cl, and S content of the agents. Molten salt systems might also serve as afterburners as well as for acid gas removal. Another variation would be to complete gas oxidation by supercritical water oxidation. In this approach, it would be necessary to compress the gas to 3,000 psi.

With the use of afterburners, gas streams from any of the processes can be brought to specified levels of agent and destruction of organic material, which can be confirmed by storage and certification. Thus, waste gas purity can be ensured independently of the process used.

### GENERAL OBSERVATIONS

- 1. The risk of toxic air emissions can be virtually eliminated for all technologies through waste gas storage and certification or treatment by activated-carbon adsorption. Either of these options can be combined with methods to reduce the volume of gas emissions.**

Agent releases from accidents in the destruction facility and releases to the atmosphere of residual unreacted agent or toxic products from equipment malfunction can all be avoided for any alternative technology by applying a dosed system concept to all gas streams leaving the facilities. That is, gas streams can be stored until chemical analysis has demonstrated their compliance with regulatory standards. The storage volume needed to handle

gaseous oxidation products can be made adequate to store any accidental release of vaporized agent from the destruction facility. Large activated-carbon (charcoal) adsorbers can perform much the same function. In this case, agent and products of incomplete combustion are captured and retained on the charcoal.

The amount of gas released can be greatly reduced by the use of pure oxygen in destruction processes instead of ordinary nitrogen diluted air. Waste gas can be further reduced by capturing the carbon dioxide it contains with lime, as well as capturing HCl, HF, SO<sub>2</sub>, and P<sub>2</sub>O<sub>5</sub>, at the cost of increasing the amount of solid waste produced. These techniques can be applied to all technologies.

**2. There are many possible destruction processes.**

A wide variety of processes have been proposed to replace or augment components of the current baseline destruction system. The scope of possible modifications ranges from simply replacing one component, such as the agent combustion process, to replacing all current combustion-based processes. New components would likely require 5 to 12 years for research and demonstration, the lower figure representing the time required for construction and testing of demonstration facilities, the higher figure including research and pilot plant work as well.

**3. Initial weapons disassembly and agent detoxification and partial oxidation could meet international treaty demilitarization requirements and eliminate the risk of catastrophic agent releases during continued storage.**

The strategy of disassembling weapons and applying liquid-phase processes to destroy agent can meet treaty demilitarization requirements. By destroying the stored agent, the risk of catastrophic agent release during storage is avoided. Final disposal of the wastes generated would be delayed until complete oxidation processes are developed.

**4. There are a number of promising chemical processes for agent detoxification or oxidation.**

Chemical techniques could allow agent detoxification in low-temperature, aqueous systems. The reaction products could be confined and tested to determine whether further processing is needed to meet demilitarization requirements and also for suitability for release to a disposal facility or to local storage. The best results with such processes have been

seen in GB destruction. Although there are laboratory leads for similar VX and mustard treatments, this work is at the early laboratory stage.

The combined use of peroxysulfates and hydrogen peroxide shows promise for detoxification of agent and also for complete oxidation of its organic components. Biological and electrochemical processes might be used to further oxidize liquid wastes from detoxification processes, but they are in an early stage of research.

**5. Processes used in combination with an afterburner can be used to oxidize agent.**

Processes proposed for oxidation of agent or of products from its chemical detoxification include wet air and supercritical water oxidation, molten salt oxidation, fluidized-bed combustion, steam gasification, plasma arc (electric arc) furnaces, and molten metal baths. All require an afterburner to complete oxidation, and all are promising but would require development and demonstration.

**6. There are technologies to replace the baseline metal parts furnace.**

Alternative technologies to destroy energetics and reliably detoxify metal parts and containers involve heating to high temperatures. Using electrically heated ovens in place of the baseline internally fired kilns would reduce the amount of flue gas produced. Molten metal or salt baths could also treat these stockpile materials. Like the combustion-fired kilns, all these approaches require the use of afterburners to ensure complete oxidation.

**7. Afterburner technologies might be used to control waste gas purity.**

Alternative afterburner options include external heating, catalytic combustion, molten salt or supercritical water oxidation. Afterburners can be designed to meet requirements for contaminant oxidation for both baseline and alternative processes and are essential in control of waste gas purity.



# 1

## Introduction

The focus of this study is the alternative technologies that might be used to partly or wholly replace or to supplement the U.S. Army's currently planned system to destroy the U.S. unitary chemical weapons stockpile (see [Appendix A](#) for the study's full statement of task).<sup>1</sup> This chapter briefly reviews the current U.S. program to destroy its unitary chemical weapons stockpile by incineration, current interest in the alternatives to incineration that might be used, general strategies for disposal of the stockpile, and the scope of the present study and report.

### THE U.S. CHEMICAL STOCKPILE DISPOSAL PROGRAM

The U.S. Department of Defense (DOD) is now engaged in a program to destroy the nation's stockpile of unitary chemical weapons through its executive agent for the program, the U.S. Department of Army. The Chemical Stockpile Disposal Program was initiated in 1985, when Public Law (P.L.) 99-145 directed that DOD destroy at least 90 percent of this stockpile by September 30, 1994. As the program moved forward, its pace was slower than anticipated, and its date for completion has been revised several times. In 1988, Congress extended the completion date to 1997, and in 1990, P.L. 101-510 extended this date to July, 1999.

The United States and the former Soviet Union (now the Commonwealth of Independent States, CIS) signed a memorandum of agreement on June 1, 1990, to cease chemical weapons production, dispose of inventories, share disposal technology, and develop inspection procedures. In addition, on September 3, 1992, the Conference on Disarmament approved

---

<sup>1</sup> Unitary chemical weapons contain agents that, by virtue of their molecular composition and structure, are highly toxic and lethal in themselves. Processes to destroy these agents, such as incineration, break down the compounds and convert them into simpler chemical structures that are nonlethal. Binary chemical agents consist of two nonlethal chemicals that, upon mixing, form a lethal chemical agent.

the Chemical Weapons Convention, signed on January 13-15, 1993, by the United States and several other nations, forbidding the development, production, stockpiling, or use of chemical weapons (Gordon, 1992). Language in the convention does not restrict the destruction technology used so long as it converts chemical agents irreversibly to a form unsuitable for production of chemical weapons and so long as it renders munitions and other devices unusable.

The convention also stipulates that "such destruction shall begin not later than two years after this convention enters into force for it and should finish not later than 10 years after entry into force of this convention" (it does include provisions for individual countries to request a 5 year extension if technical problems are encountered). Upon ratification, the deadline (which supersedes previous deadlines) for stockpile destruction will be December 31, 2004 or later.<sup>2</sup>

The U.S. chemical weapons stockpile contains two classes of agents, namely, organophosphate nerve agents (sometimes called nerve gas) and blister (or mustard) agents. The nerve agents are usually referred to by their Army code designations: VX, GB (Sarin), and GA (Tabun). The blister agents are H, HD, and HT.

These agents are contained in a variety of munitions as well as in bulk containers stored at eight continental U.S. sites and at Johnston Island in the Pacific Ocean. As discussed in more detail in [Chapter 2](#), there are about 25,000 total tons of agent in the stockpile (Ember, 1992; Picardi et al., 1991). To put the scale of operations into perspective, about 30,000 tons/year of hazardous waste are incinerated in a typical U.S. hazardous waste incinerator (Vogel, 1989). After testing different disposal technologies in the 1970s, in 1982 the Army chose the approach of component disassembly of the munitions (so-called reverse assembly), followed by incineration and treatment of the off-gases by a pollution abatement system. The bulk storage containers are drained of agent, the agent is destroyed by incineration, and the containers are thermally decontaminated. The NRC's Committee on Demilitarizing Chemical Munitions and Agents reviewed a number of alternative disposal technologies in 1984 and endorsed the Army's choice

---

<sup>2</sup> The 1993 National Defense Authorization Act stipulated a change in the stockpile disposal deadline: "Section 1412(b)(5) of the Department of Defense Authorization Act, 1986 (50 U.S.C. 1521(b)(5)), is amended by striking out 'July 31, 1999' and inserting in lieu thereof 'December 31, 204'."

(NRC, 1984).<sup>3</sup> Recent environmental concerns have prompted the Army and Congress to revisit the topic of alternative technologies (OTA, 1992).

The Army's process (hereafter, the baseline technology) is designed as a four-stream incineration process (Figure 1-1). At any given storage site, munitions or bulk containers are transported from storage (in igloos or open storage) to the destruction facility, where they are received in an unpack area. Unpacking munitions, draining agent, and disassembling weapons produces four primary waste streams, namely, dunnage (packing materials), energetics (explosives and propellants), metal parts, and liquid agent. These streams are processed, respectively, in separate incinerators: a dunnage incinerator, a deactivation furnace system (rotary kiln), a metal parts furnace, and a liquid incinerator (see Chapter 4 for details). Because dunnage can be sent to hazardous waste landfills, alternatives to dunnage incineration are not a major focus here.

Each of the four furnaces is equipped with an afterburner and a pollution abatement system to dean exhaust gases, which then exit through a common stack. Ventilation air moves from areas of lower to higher potential contamination and, after passing through the disassembly and furnace rooms, is exhausted to the environment after passing through charcoal adsorption beds.

The Army's program includes the pilot demonstration of disposal technologies. The Chemical Agent Munitions Disposal System at Tooele Army Depot (TEAD) in western Utah is a pilot plant for production facilities and a prototype of the baseline technology. Research facilities are also located at Edgewood Research, Development and Engineering Center, Aberdeen Proving Ground, Maryland.

In the mid-1980s, the Army began constructing its pioneering full-scale facility, the Johnston Atoll Chemical Agent Disposal System (JACADS). JACADS recently completed operational verification testing (OVT), conducted to demonstrate that the baseline technology can safely and effectively destroy the different agents and munitions in the U.S. stockpile while meeting all environmental requirements. OVT is also intended to help identify design improvements to the prototype baseline technology so that appropriate modifications can be introduced before construction and operations begin at the eight mainland sites. P.L. 100456 requires the Army to complete OVT at JACADS before proceeding with equipment tests at

---

<sup>3</sup> A second method, known as the cryofracture process, has also been under development by the Army. In this approach non-bulk munitions are submerged in a liquid nitrogen bath, and fractured in a hydraulic press, and frozen agent and fractured parts are then thermally treated in a single rotary kiln. Both the baseline technology and the cryofracture process end with incineration followed by cleanup of final waste streams. Cryofracture is not reviewed in this report but was the subject of a previous NRC study (NRC, 1991).



Source: PEIS (1988).

other U.S. sites. Construction of full-scale facilities at TEAD is now underway and scheduled to begin operations in 1995 (OTA, 1992; U.S. Department of the Army, 1991).

OVT had four campaigns (tests). The first, from July 1990 to February 1991, resulted in the successful destruction of approximately 7,500 M55 rockets containing GB, 77,200 pounds of agent, and 81,600 gallons of spent decontamination solution (Menke et al., 1991; U.S. Army, 1991). Engineering modifications were made during a subsequent shutdown to improve the throughput processing rate. In the second campaign, from October 1991 to February 1992, 13,900 M55 rockets filled with VX were successfully destroyed. In the third, from September to October 1992, 68 ton containers were processed and 113,031 pounds of HD were destroyed. The fourth and final campaign, from September 1992 to March 1993, resulted in the destruction of 105-mm mustard-filled artillery projectiles. Environmental test burns to support the Resource Conservation and Recovery Act (RCRA), the Toxic Substances Control Act (TSCA), and Environmental Protection Agency (EPA) permits were also required for all four furnace systems (U.S. Department of the Army, 1991).<sup>4</sup> After the completion of OVT and the receipt of all required permits, JACADS will also dispose of remaining munitions on the island.

After each of the four OVT campaigns, the MITRE Corporation prepared separate evaluation reports. A summary report is also available (MITRE Corporation, 1993). The NRC's Committee on Review and Evaluation of the Army Chemical Stockpile Disposal Program will review MITRE's final evaluation of OVT for the Army as part of its ongoing role to provide scientific and technical advice to the Army in carrying out the disposal program.

Construction and operation of the disposal facilities at the eight continental sites are scheduled to begin at different times (Table 1-1 shows the schedule as of October 1992). Construction is more than 90 percent complete for most planned facilities at TEAD in Utah. There are uncertainties at some sites. For example, construction at the Newport Army Ammunition Plant in Indiana, scheduled for early 1995, may be delayed pending decisions by the Army and Congress about disposal technologies.

Similarly, duration of operations will depend on the amount of agent and types of munitions that have to be destroyed and these vary greatly among sites (see Chapter 2). The greatest duration of operations expected is about 5 years, a relatively short time compared with commercial industrial facilities, which may operate for many decades.

---

<sup>4</sup> RCRA trial burns in the liquid incinerator showed a destruction removal efficiency (DRE) of greater than 99.999999 and 99.99999 percent for VX and GB, respectively, as compared with RCRA requirements of 99.99 percent (SRI, 1992a, b).

TABLE 1-1 Schedule for the Construction and Operation of Chemical Stockpile Disposal Facilities

Installation	Construction	Systemization <sup>a</sup>	Operations
Johnston Atoll (JACADS)	Nov. 1985	Aug. 1988	July 1990-Oct. 1995
Tooele Army Depot (TEAD)	Sept. 1989	Aug. 1993	Feb. 1995-Apr. 2000
Anniston Army Depot	June 1993	Apr. 1996	Oct. 1997-Nov. 2000
Pine Bluff Arsenal	Jan. 1994	Sept. 1996	Mar. 1998-Nov. 2000
Umatilla Depot Activity	Jan. 1994	Nov. 1996	May 1998-Dec. 2000
Lexington-Blue Grass Army Depot	May 1994	Mar. 1997	Sept. 1998-Feb. 2000
Pueblo Depot Activity	May 1994	Mar. 1997	Sept. 1998-May 2000
Newport Army Ammunition Plant	Jan. 1995	June 1997	June 1998-Apr. 1999
Aberdeen Proving Ground	Jan. 1995	June 1997	June 1998-June 1999

<sup>a</sup> Testing the facility before operations begin.  
Source: Program Manager for Chemical Demilitarization, U.S. Army, Aberdeen, Maryland.

RISK AND COMMUNITY CONCERNS

Risks associated with the storage and disposal of the U.S. chemical weapons stockpile can be classified as follows:

- health risks to individuals in surrounding communities;
- risks to workers at military sites in storing or destroying weapons; and
- risks of the failure of the chosen destruction technology to perform satisfactorily, resulting in shutdowns and delays.

The first type of risk is critical in the choice of technology. Such risk can itself be broken into several components:

- risks of agent release from continued storage (from deterioration, sabotage, or accidents);
- risks of agent release from accidents while transporting agent from storage to destruction site;
- risks of agent release from unpacking and disassembly operations;
- risks of agent release during the destruction operation; and
- health risks related to the discharge of waste streams.

This study focuses on the last two specific kinds of risk and the choice of technologies to best address related concerns.

Air quality and the health effects of air contaminants are closely related to the choice of destruction technology. The ability of the baseline incineration technology to provide adequate safeguards against air contamination is frequently questioned, which is a principal impetus for this study (OTA, 1992; PEIS, 1988).<sup>5</sup>

These same concerns might be expressed for any continuous destruction system that produces a large stream of flue gas and in which outlet monitoring cannot ensure against short periods of unacceptable operations. The closed-loop concept, in which all waste streams are stored until chemical analyses have established satisfactory purity, is commonly mentioned as a way of addressing such concerns (OTA, 1992; Picardi et al., 1991). This particular approach, referred to as storage and certification, can be applied to all waste streams, and will be discussed in some detail later in this report. Technologies that greatly reduce or eliminate waste gas discharge from the destruction system offer another way to minimize concern about this potential source of air quality degradation.

Risk analyses presented in the Programmatic Environmental Impact Statement (PEIS) focused on catastrophic releases of agent from continued storage or transportation and on the effects of earthquakes and fires on agent storage in the unpack, disassembly, and destruction facilities. In general, this last kind of risk was judged to be less than the risks of transport or long-term storage.

These analyses are not directly applicable to assessment of the smaller releases that might occur during disassembly and destruction (PEIS, 1988). Such releases would usually enter the ventilation air streams and could be captured by a properly sized charcoal scrubbing system. Use of charcoal bed adsorption to purify ventilation air is part of the baseline design and, as an

---

<sup>5</sup> A compilation of several hundred statements regarding citizens concerns can be found in the Programmatic Environmental Impact Statement (PEIS, 1988).

alternative to storage and certification, could be extended to include gas streams leaving the destruction equipment.

### ALTERNATIVE DEMILITARIZATION SYSTEMS

Recent studies of different approaches to the destruction of the Army's unitary chemical weapons stockpile have used the term "alternative technologies," a term reflected in the name of the committee preparing this report. However, most technologies reviewed here or by other investigators are actually unit processes: they represent only part of a system of processes required to demilitarize the U.S. stockpile. For example, separation of agent from munitions and explosives, chemical neutralization of agent, oxidation of the neutralization products, and oxidation of remaining agent on the metal parts are all unit processes, which together might represent an alternative demilitarization system. Alternative demilitarization processes might partly or wholly replace or be used in addition to the current baseline system to handle agent, explosives, propellants, metal parts, dunnage, or any other waste streams potentially contaminated with agent.

Chemical weapons demilitarization has been studied and practiced for decades. A National Academy of Sciences (NAS) study in 1969 assessed the hazards of different disposal methods for several types of obsolete and defective chemical warfare stocks: Air Force M34 bomblet clusters containing GB, bulk containers of mustard, M55 rockets containing GB, contaminated and water-filled bulk containers, and drums containing cans of a riot control agent called CS (NAS, 1969). This study advised against then-current plans for ocean dumping, recommending instead that the M34 clusters be disassembled, the withdrawn GB be chemically destroyed by acid or alkaline hydrolysis, and the mustard be burned in government establishments where storage was safe and local air pollution from SO<sub>2</sub> and HCl would not be a problem. The report also suggested that a systematic study be undertaken regarding disposal of the chemical weapons and munitions on military installations without hazard to the general population or pollution of the environment.

In the early 1980s, alternative approaches to destroy the U.S. stockpile were considered and evaluated by the NRC Committee on Demilitarizing Chemical Munitions and Agents (NRC, 1984). The major alternatives evaluated in this study were placement in the deep ocean, thermal destruction processes such as pyrolysis and combustion, chemical processes, nuclear explosions, and a number of novel methods including in-shell combustion, steam pyrolysis, drain-in-furnace, underground combustion or caustic hydrolysis, and high-temperature pyrolysis. After considering the advantages and disadvantages of each method, the committee concluded that thermal destruction would be preferred for disposal of the U.S. stockpile. Again, this



conclusion supported the Army's selection of combustion as the most appropriate method. (For a brief review of actual U.S. and foreign experience with chemical demilitarization, see [Chapter 3](#).)

As the time to transfer the baseline technology from JACADS to mainland sites has come closer, several national and local organizations and many individuals have voiced opposition to the use of incineration as part of the Army's chemical weapons destruction program (Ember, 1992; OTA, 1992). Discussions with representatives of Kentucky citizens groups concerned about proposed activities at the Lexington-Blue Grass Army Depot led the Office of Technology Assessment to identify the following issues as those generating opposition: concern over possible health risks associated with incinerator effluents, the possibility that the facilities will be used for other types of waste disposal once the stockpile is destroyed, the proximity of destruction facilities to major population centers, and the risk to citizens in communities near chemical weapons storage sites during munitions transport from storage igloos to the on-site incinerator facility (OTA, 1992). The Office of Technology Assessment also briefly addressed some possible alternative technologies, namely, chemical neutralization, supercritical water oxidation, steam gasification (or steam reforming), and plasma arc technology, all of which are also reviewed here.

In addressing these and other unit processes that might be applied to stockpile destruction, the committee considered the concerns raised by local communities. As mentioned above, special attention is given here to storage and certification of gas waste streams. In this regard, note that all possible alternative technologies will produce some set of wastes (gas, liquid, and solid) that must be appropriately managed within governing regulatory requirements. In particular, the heteroatoms contained in chemical agents (fluorine [F], chlorine [Cl], sulfur [S], and phosphorus [P]) contribute to the formation of salt wastes that may need disposal in hazardous waste landfills.

Opponents of the baseline incineration technology have also claimed that it poses significant risks of exposure to surrounding populations and to the environment, risks that could be reduced by alternative technologies. Greenpeace has sponsored a report reviewing alternatives to incineration for destruction of the chemical weapons stockpile, including biological, chemical, photochemical, electrochemical, and thermal processes (Picardi et al., 1991). These processes would have to be combined to manage the various components of the stockpile. Many of these processes are also addressed here.

Finally, Congress has taken a serious interest in the technologies to be used to destroy the U.S. stockpile and is looking to the mandated evaluation of potential alternatives that the Army will submit to Congress by December 31, 1993 (National Defense Authorization Act of 1993). This Army report is required to include an analysis of the present report. Until the Army's report is submitted, the Army may not prepare sites or construct a disposal facility

based on the baseline technology (with some exceptions noted in the act). The present report provides one basis for the national evaluation of possible alternatives to the baseline chemical weapons destruction technology.

### **TRANSPORTATION OF UNTREATED WEAPONS AND AGENTS**

The Army previously decided against the transport of the existing untreated stockpiles to one or more central facilities, as documented in the Final Programmatic Environmental Impact Statement (PEIS, 1988). There are also legal and political considerations behind this decision, with states and communities prohibiting transport through their territories.

The studies reported in the Army's environmental assessment recognize that safety hazards and potential environmental impacts would differ for transporting bulk liquid chemical agent and weapons containing chemical agent. The assessment included a feasibility study of shipping ton containers of bulk mustard by sea from Aberdeen, Maryland, to the JACADS facility for destruction in lieu of constructing an incineration facility at Aberdeen.

However, this study was never completed, as indicated by a 1987 letter from James R. Ambrose, Under Secretary of the Army, which was included as an appendix to the PEIS (see PEIS, 1988, Volume 3, Appendix S; see also Appendix B of this report). Reasons for not completing this study included the desire to avoid 'further delay in the program, envisioning that the ocean transport alternative would entail lengthy and extensive studies, and the belief that studies of rail transportation would provide a reasonable comparison of the alternatives. However, the letter concluded, "a national programmatic decision does not foreclose subsequent consideration of site-specific alternatives at a later date."

Although not convinced that transportation of agents and munitions to one or two major disposal facilities should be excluded from consideration, the committee has not considered such options because they are not within the scope of its study. The alternative of substantially decontaminating chemical weapons and transporting the detoxified material to another site for further destruction is addressed in the next section on strategies for demilitarization.

### **PRIMARY GOALS AND STRATEGIES FOR DEMILITARIZATION**

The committee believes that in destroying the stockpile safely and expeditiously, the following should be the primary goals of the U.S. Army Chemical Stockpile Disposal Program:

- meet congressionally mandated and international treaty demilitarization and schedule requirements;
- reduce the risk to nearby communities of agent release from either continued storage or demilitarization operations;
- ensure acceptable concentration of toxic chemicals in gas waste streams resulting from demilitarization operations;
- minimize liquid waste disposal problems by minimizing water discharges; and
- minimize solid waste disposal problems by oxidation or conversion of organic compounds to innocuous forms.

At all demilitarization sites, after agents and munitions are removed from storage igloos, transported to the treatment site, unpacked, and disassembled into components, final disposal is necessary. To meet the goals outlined above, the committee delineates two strategies for final disposal, briefly reviewed below. [Chapter 8](#) considers the use of different alternative technologies in these strategies.

*Strategy 1. On-site disassembly and agent detoxification to a level that meets treaty demilitarization requirements and permits transportation to another site or continued local storage of residues.*

The Army's current demilitarization program is based on thermal decontamination by incineration to a specified 5X level, that is, treatment at 1000°F for 15 minutes (see [Chapter 4](#) for further discussion), and the release of the dry, solid incineration wastes to commerce for potential metal recovery. An alternative is to disassemble weapons and treat the drained agent to meet demilitarization treaty requirements and to reduce the toxicity for ease of handling, without further oxidation or full mineralization of organic residues.<sup>6</sup> Agent could also be fully oxidized with an alternative process. For the first strategy, low-temperature and low-pressure liquid-phase detoxification processes, such as chemical hydrolysis, or liquid-phase processes that completely oxidize the agent could be used. International treaty obligations for demilitarization would be met and the risk from continued agent storage eliminated. Metal parts would be initially decontaminated, to the same end,

---

<sup>6</sup> Mineralization refers to complete oxidation, that is, the breakdown of chemical compounds into basic minerals or inorganic compounds, such as carbon dioxide, water, nitrogen, oxygen, and other gases. For example, the complete combustion of an organic compound, such as agent, results in these primary compounds. If it was desirable to minimize gas emissions, the gaseous carbon dioxide could be captured and converted to solid carbonates.

with decontamination fluid,<sup>7</sup> fluid which is also used to manage spills and dean up work areas, such as the disassembly rooms. Such decontamination fluid contains organic residues, and waste streams generated would be managed according to appropriate regulations. Depending on the process used, this option could entail the storage or shipment of large quantifies of water or the installation of facilities for water removal and purification.

Shipment of detoxified material within the existing transportation rules and regulations seems quite feasible, although no specific analysis has been conducted. Sealed shipping containers would be required to prevent the release of any toxic agent that might remain and to conform with the rules for the shipping of toxic chemicals. The risk of transporting detoxified material would be substantially less than the risk of transporting agent.

Such liquid-phase detoxification and storage or transport would increase both the volume and mass of the resultant material that requires handling. Transportation costs would probably be high, but they might be offset by decreased facility construction costs (see [Appendix C](#) for some discussion of landfill disposal costs). The implications of transport and the disposal rules for the transport of larger quantities of materials should be studied before such an approach is recommended.

For some alternatives to agent incineration, such as hydrolysis, very little fixed gas or carbon dioxide would be generated. Gas exhausted to the atmosphere would be reduced or eliminated for this phase of the operation by using these alternatives.

Explosives and propellants (energetics), which are present at seven of the nine sites, present special problems. Particularly with the M55 rockets, it is difficult to separate the energetics from agents. Although their temporary storage is feasible and their transportation to another site is possible, local destruction will probably be required. In this process, some evolution of carbon dioxide and fixed nitrogen compounds can be expected.

Under Strategy 1, the ventilation air volume for work areas will not substantially differ from that in Strategy 2.

*Strategy 2. Conversion of agent and disassembled weapons to salts, carbon dioxide, water, and decontarninated metal (mineralization).*

---

<sup>7</sup> Initial decontamination is the rapid removal of most of the agent from contaminated surfaces. A decontamination solution used, DS2, is a general-purpose reactive decontaminant composed of 70 percent diethylenetriamine, 28 percent ethylene glycol monomethyl ether, and 2 percent sodium hydroxide, by weight. Final decontamination, to a level allowing release of decontaminated parts to the public, requires a thermal process to the 5X level, as discussed above.

In Strategy 2, complete oxidation (mineralization) is accomplished without the need for long-term storage of agent, energetics, metal parts, and containers. This strategy meets all goals by oxidation and heat treatment. Agent destruction can be accomplished by a detoxification step, as in Strategy 1, followed by oxidation of the by-products or by direct oxidation as in the baseline technology. Energetics and metal parts are thermally decontaminated. An afterburner would generally be required to ensure complete destruction of all products of incomplete oxidation.

### SCOPE AND ORGANIZATION OF THE STUDY

In response to a request from the Assistant Secretary of the Army for Installations, Logistics and Environment, the NRC formed the Committee on Alternative Chemical Demilitarization Technologies to study alternatives to the baseline technology for the destruction of unitary chemical agents and munitions. The main required steps in the destruction of this stockpile include (1) transport of weapons from storage to the destruction area, (2) unpacking of weapons, (3) disassembly of weapons, (4) destruction of agent and weapons, and (5) waste stream treatment and management. The focus here is on Steps 4 and 5.

In particular, the primary task of the committee is to objectively characterize alternative destruction technologies, assess their state of development, identify their advantages and disadvantages for chemical demilitarization, and identify the research and development (R&D) they would require if they were to be used in demilitarization. The committee's charter does not include selecting or recommending any specific technology to the Army (see [Appendix A](#) for the statement of task). Results of this study will be used by the NRC's Committee on Review and Evaluation of the Army Chemical Stockpile Disposal Program to generate specific recommendations on disposal technologies.

As mentioned above and discussed in more detail later, many of the technologies reviewed here cannot handle all components of the chemical weapons stockpile that must be destroyed. Hence, in its assessment, the committee considered the possible use of individual alternative technologies to demilitarize parts of the stockpile and combinations of technologies to form alternative demilitarization systems.

The committee took a number of steps to identify technologies for review. Initially, an attempt was made to list all possible alternative technologies without concern for development status, cost, time required for implementation, suitability, or any other constraint. During this early study phase, the committee used many sources, including prior Army experience, proposals submitted to the Army since 1984, the NRC report *Disposal of*

*Chemical Munitions and Agents* (NRC, 1984), a 1991 report on alternative technologies prepared for Greenpeace International (Picardi et al., 1991), a report by the Scientists Against Nuclear Arms (SANA, 1991), the EPA's Superfund Innovative Technology Evaluation Program (EPA, 1991), suggestions from outside the committee in response to an announcement of the study, and the committee's own suggestions and experience (see [Appendix D](#) for committee members' backgrounds).

Using all these sources, the committee identified and collected information on technologies that appear to be developed to a point where an assessment can be made. For many of the processes considered, such limited data were available on their use in chemical weapons destruction that assessments of these processes are necessarily highly judgmental. Where the data were dearly insufficient or there appeared to be great constraints on the use of alternatives, these alternatives were not further evaluated. In particular, the committee did not consider the following as viable alternatives:

- open atmospheric dispersion and/or burning;
- ocean dumping, including placement in the subducting subsea regions of adjacent plates;
- placing chemical agent in extraterrestrial orbit;
- destruction by underground nuclear weapons explosions;
- burial in volcanoes;
- destruction of weapons in existing industrial facilities; and
- minor modifications to incineration systems that have already been reviewed, such as different mechanical configurations of the combustion chamber.

All but the last of these concepts was automatically eliminated from further consideration because all require extensive transportation of weapons to disposal sites, a method not within the scope of this study. Some of these methods would also violate environmental regulations. In addition, the Chemical Weapons Convention excludes dumping in any body of water, land burial, and open-pit burning of chemical weapons. The last item in the list above was eliminated because such systems were reviewed in an earlier report on the choice of an incineration system (NRC, 1984).

The committee did not develop a numerical rating system for screening criteria but instead established general considerations and requirements to assess alternative technologies (see [Chapter 4](#)). Specific information on many of the technologies was provided to the committee by technology developers (see [Appendix E](#)). However, in its assessment the committee focused on general approaches rather than specific technologies of specific companies, although it received information from companies on their technologies. (Proprietary information was not used in this study. Some of the processes are

under intensive development and data concerning their operation are changing rapidly.) The committee held a June 1992 workshop for presentations and discussions on the technologies selected for assessment (see [Appendix F](#) on committee activities for a list of workshop presentations). Additionally, a worksheet was developed by the committee for obtaining and organizing important information on each technology (see [Appendix G](#)).

Invited observers were asked to comment on the formal presentations at the workshop. Observers included technology developers; independent scientists and engineers; members of public interest groups, such as Greenpeace International, Concerned Citizens for Maryland's Environment, and the Kentucky Environmental Foundation; and representatives of federal and state organizations. The committee solicited information in writing from developers working on potentially applicable technologies who were unable to attend the workshop.

The information collected, the technical literature, and the committee's own expertise and judgment served as resources in formulating this report. The committee has grouped the processes addressed into preprocessing and postprocessing options, such as charcoal beds (see [Chapter 5](#)); low-temperature, liquid-phase processes, such as chemical detoxification reactions (see [Chapter 6](#)); and processes at higher temperature and pressure, such as wet air and supercritical water oxidation (see [Chapter 7](#)). [Chapter 8](#) integrates and summarizes the information: it summarizes the assessment of the various processes, considers strategies for destroying the chemical weapons stockpile, and delineates how the various unit processes might be applied to the Army's Chemical Stockpile Disposal Program.

## 2

# The U.S. Chemical Weapons Stockpile

This chapter presents a brief description of the U.S. chemical weapons stockpile, covering the physical properties of chemical agents, their toxicities, associated weapons, and the nature and distribution of stockpile storage sites.

### DESCRIPTION OF THE AGENTS

The U.S. chemical weapons stockpile contains nerve agents, or nerve gas, and blister, or mustard, agents. (Mustard was used extensively in World War I, whereas nerve agents were first used in war by Iraq in its war with Iran.) These two fundamental types of chemical warfare agents are contained in the U.S. stockpile in a variety of munitions and bulk containers.

Nerve agents in the U.S. stockpile include persistent VX, nonpersistent Sarin (GB), and a small quantity of Tabun (GA). All the nerve agents are organophosphonate compounds, which contain phosphorus double-bonded to an oxygen atom and single-bonded to a carbon atom. VX also contains sulfur in its chemical structure, GB contains fluorine, and GA contains the cyanide group (see [Figure 2-1](#) for the chemical structures of major U.S. chemical agents and [Table 2-1](#) for some of their physical properties).<sup>1</sup>

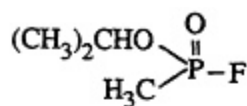
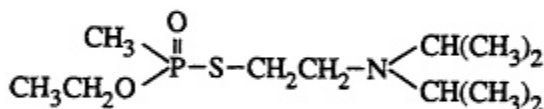
Nerve agents are highly toxic or lethal in both liquid and vapor forms.<sup>2</sup> Although they are often referred to as gases, they are liquids at normal

---

<sup>1</sup> VX is O-ethyl-S-[2-diisopropyl aminoethyl]methylphosphonothiolate; GB is isopropyl methyl phosphonofluoridate, and GA is ethyl-N, N-dimethyl phosphoramidocyanidate.

<sup>2</sup> Terms used in the literature include: *lethal*, danger of quick death on exposure; *toxic*, serious impairment of health, or even death, on substantial exposure; *poisonous*, dangerous if not handled carefully (e.g., gasoline or household bleach); and hazardous, known or suspected to pose a risk to human health or the environment. In this report, the term toxic is sometimes used in a general sense, encompassing all levels of toxicity.



GB (*Sarin*)

VX

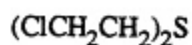
HD (*Mustard*)

FIGURE 2-1 Principal chemical warfare agents in the U.S. stockpile.

temperatures and pressures. GB has a boiling point about 5°C lower than that for kerosene or diesel fuel. It evaporates at about the same rate as water and is relatively nonpersistent in the environment. VX evaporates much more slowly, and spills of liquid VX can persist for a long time under average weather conditions. Thus, GB presents mainly a vapor hazard, although contact with its liquid form can also be fatal. In contrast, VX presents mainly a contact hazard, although its vapor buildup in enclosed spaces can also reach lethal levels. In their pure form, all these nerve agents are nearly odorless and colorless.

The blister agents include H, HD, and HT. The active ingredient in H and HD and a major component (60 percent) of HT is the same chemical substance, bis(2-chloroethyl)sulfide, or mustard.<sup>3</sup> The agent H, sometimes called Leinstein mustard, contains 70 percent mustard and 30 percent

<sup>3</sup> Mustard gas, sulfur mustard, yperite, and other names have also been applied to this agent. Although 'mustard gas' is often used, the chemical is a liquid at ordinary ambient temperatures; its initial boiling point is comparable with that of the more volatile parts of kerosene.

TABLE 2-1 Physical Properties of Chemical Warfare Agents

Agent Characteristic	Nerve Agents				Blister (Mustard) Agents		HT
	GB (Sarin)	VX	H/HD	HT	(CH <sub>3</sub> ) <sub>2</sub> CHO(CH <sub>3</sub> )FPO	(CICH <sub>2</sub> CH <sub>2</sub> ) <sub>2</sub> S	
Chemical formula	(CH <sub>3</sub> ) <sub>2</sub> CHO(CH <sub>3</sub> )FPO	C <sub>11</sub> H <sub>26</sub> NO <sub>2</sub> PS	(CICH <sub>2</sub> CH <sub>2</sub> ) <sub>2</sub> S	60% (CICH <sub>2</sub> CH <sub>2</sub> ) <sub>2</sub> S, 40% sulfur and chlorine compounds			
Molecular weight	140.10	267.38	159.08	Not available			
Boiling point, °C	158	298	217	228			
Freezing point, °C	-56	< -51	14.45	0 to 1.3			
Vapor pressure, mm Hg	2.9 @ 25°C	0.0007 @ 25°C	0.072 @ 20°C	Not available			
Volatility, mg/m <sup>3</sup>	4,100 @ 0°C	10.5 @ 25°C	75 @ 0°C (solid)	831 @ 25°C			
	22,000 @ 25°C		610 @ 20°C (liquid)				
Diffusion coefficient for vapor in air, cm <sup>2</sup> /sec	0.061 @ 20°C	4 @ 20°C	0.060 @ 20°C	0.05 @ 25°C			
Surface tension, dynes/cm	26.5 @ 20°C	32.0 @ 20°C	43.2 @ 20°C	44 @ 25°C			
Viscosity, cS	1.28 @ 25°C	12.256 @ 20°C	3.95 @ 20°C	6.05 @ 20°C			

Agent Characteristic	Nerve Agents		Blister (Mustard) Agents		H/HD	HT
	GB (Sarin)	VX	VX	H/HD		
Liquid density, g/cm <sup>3</sup> at 20°C	1.0887	1.0083	1.0083	1.2685	Not available	Not available
Latent heat of vaporization, cal/g	80	78.2	78.2	94	Not available	Not available
Solubility, g/100 g of distilled water	100; soluble in organic solvents	5 @ 25°C; best solvents are dilute mineral acids	5 @ 25°C; best solvents are dilute mineral acids	0.92 @ 22°C; soluble in acetone, CCl <sub>4</sub> , CH <sub>2</sub> Cl <sub>2</sub> , tetrachloroethane, ethyl benzoate, ether	Not available	Not available
Heat of combustion, Btu/lb (cal/g)	10,000 (5.55)	15,000 (8.33)	15,000 (8.33)	8,100 (4.5)	Not available	Not available

Source: Chemical Systems Laboratory (1983); Programmatic Environmental Impact Statement (PEIS) (1988). U.S. Departments of the Army and Air Force (1975).

sulfur-containing impurities. HD, which is a distilled form of H, consists of nearly pure mustard. HT is a mixture of 60 percent HD with 40 percent other sulfur and chlorine compounds. I-IT is similar in appearance and biological activity to H and HD but is somewhat more active biologically. There is also the blister agent Lewisite (L), an arsenic compound, which is stored in only small amounts in the U.S. stockpile.

Mustard has a garlic-like odor, with significant volatility at ordinary temperatures. It thus presents both vapor and contact hazards. Because mustard is nearly insoluble in water, it is very persistent in the environment and can contaminate soils and surfaces for long periods of time.

All the chemical agents above are soluble in organic solvents; GB is also very soluble in water and VX is somewhat soluble. None of these chemical agents exists in pure form in either munitions or bulk containers. In munitions, GB and VX are stabilized with various compounds to prevent acid formation and decomposition of the agent.<sup>4</sup> Various impurities present at the time of manufacture and products of polymerization and decomposition (aging) are also present in the stockpiled agents. During Operational Verification Testing (OVT) at the Johnston Island storage site, for example, mustard agent was frequently been found in gel as well as liquid form.

### Toxicity of the Agents

Nerve agents are the most lethal of the chemical warfare agents. VX is more toxic than GB, which is more toxic than GA. The peripheral nervous system of the human body uses either norepinephrine or acetylcholine (ACh) for neurotransmission. The neurons of the sympathetic nervous system release norepinephrine to carry the final impulse to the end organs. Those of the parasympathetic system release acetylcholine. Acetylcholine also plays a vital role in the control of skeletal muscles autonomic ganglia and many structures within the central nervous system.

The lethal effects of nerve agents result principally from inhibiting and inactivating of acetylcholinesterase (ACHE), an enzyme responsible for the normal breakdown of ACh.<sup>5</sup> This inhibition results in the failure of the

---

<sup>4</sup> For example, diisopropyl carbodiimide is used as a stabilizer for GB and VX and tributylamine is used as a stabilizer for GB. Trace metals such as nickel, copper, aluminum, and iron can also be found in stored agents. HD is often thickened by the addition of 5 to 10 percent polymer (Yang et al., 1992).

<sup>5</sup> Once inside the body, VX not only inhibits AChE but also reacts directly with ACh receptors and other neurotransmitter receptors. The high toxicity of VX is also attributable to its high specificity for, and thus inhibition of, AChE.

nervous system to operate properly. The resulting accumulation of ACh profoundly interferes with the transmission of nerve impulses at cholinergic synapses. In cases of lethal intoxication, the immediate cause of death is asphyxiation, resulting from interference with the nervous control of the muscles of the diaphragm (U.S. Departments of the Army and Air Force, 1975).

Mustard agents affect the eyes and lungs and blister the skin. They cause severe chemical burns and painful blisters, and are lethal at high dosages, especially if inhaled. Symptoms are generally delayed for several hours after exposure. Prolonged worker exposure in wartime mustard manufacturing facilities caused cancer in a significant percentage of those exposed (IARC, 1975; U.S. Department of the Army and Air Force, 1975). (See [Chapter 4](#) for more detail on the toxicities and airborne exposure limits for both mustard and nerve agents.) More details on the medical, health, and physiological effects of exposure to agents and on treatment and therapy can be found in selected references (Compton, 1987; Goodman and Gilman, 1985; Namba, 1971; U.S. Departments of the Army and Air Force, 1975).

### DESCRIPTION OF THE MUNITIONS

There are a number of munition types in the U.S. chemical weapons stockpile. Some contain, in addition to chemical agent, propellant or explosive components, or both (see Figures 2-2 to 2-5 and Tables 2-2 and 2-3). These munitions include 105-mm, 155-mm, and 8-inch artillery projectiles, mortar cartridges, land mines, and M55 115-mm rockets. The 155-mm artillery projectiles, for example, are filled with mustard, GB, or VX, and the 8-inch artillery projectiles are filled with GB or VX. Some munitions, such as aircraft-delivered nerve agent bombs, are stockpiled without explosives.<sup>6</sup>

In addition, about two-thirds of the chemical stockpile is stored in bulk liquid form in steel ton containers, including GA, GB, VX, mustard, and Lewisite (PEIS, 1988). GA and Lewisite are stored only at Tooele Army Depot (TEAD) in relatively small quantities. Lewisite will have to be handled separately from other agents and is not a major consideration here.

---

<sup>6</sup> These include the MC-1 750-lb Air Force bomb, the MK-94 500-lb Navy bomb, the MK-116 ("weteye") 525-lb Navy bomb (all GB-filled), and the TMU-28/B aerial spray tanks filled with VX.

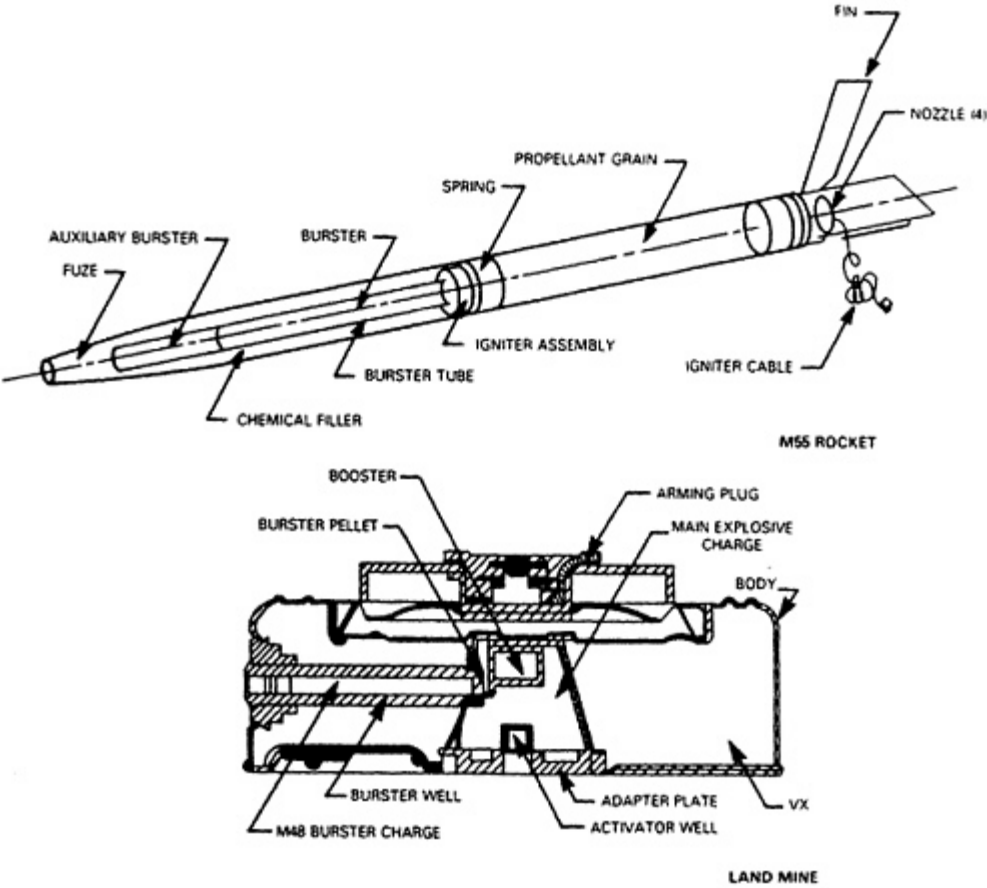


FIGURE 2-2 M55 rocket and M23 land mine.  
Source: USATHAMA (1982, 1983).

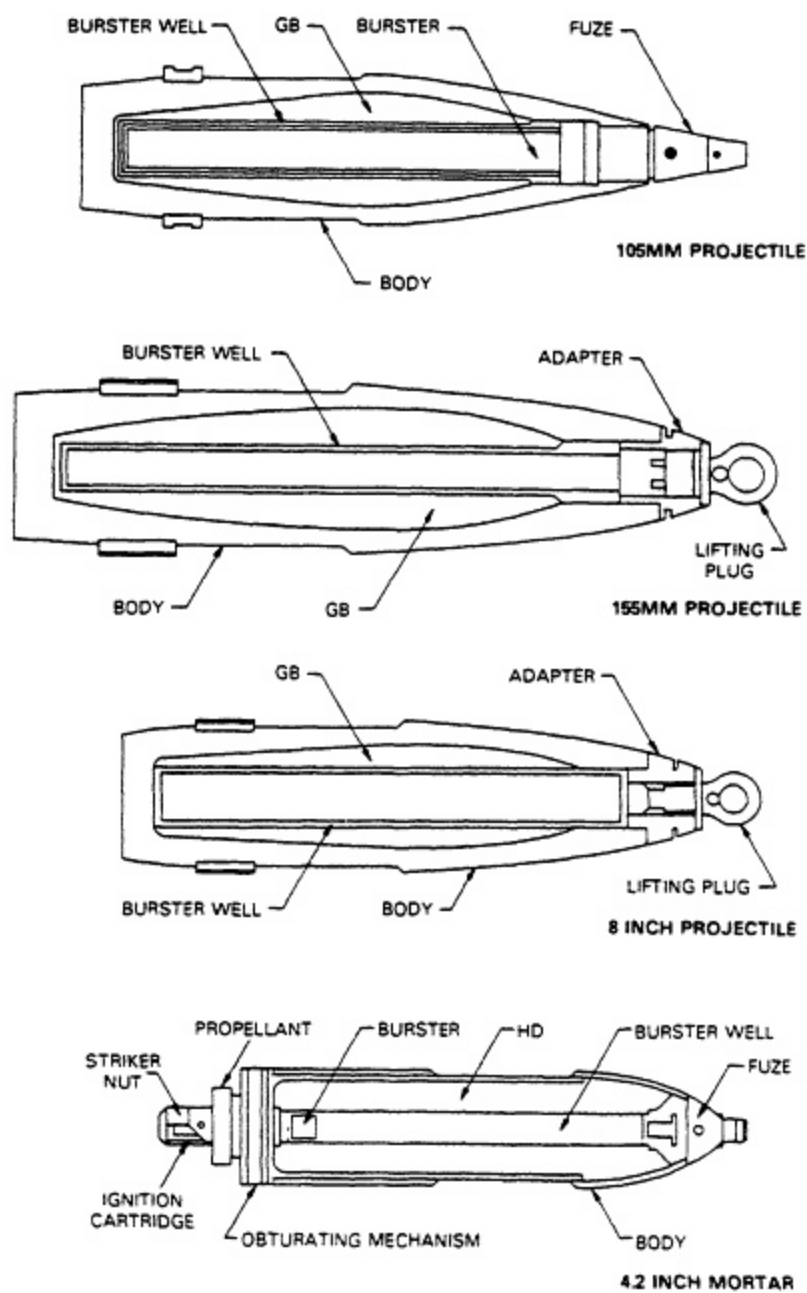


FIGURE 2-3 105-mm, 155-mm, 8-inch, and 4.2-inch projectiles.  
Source: USATHAMA (1982, 1983).

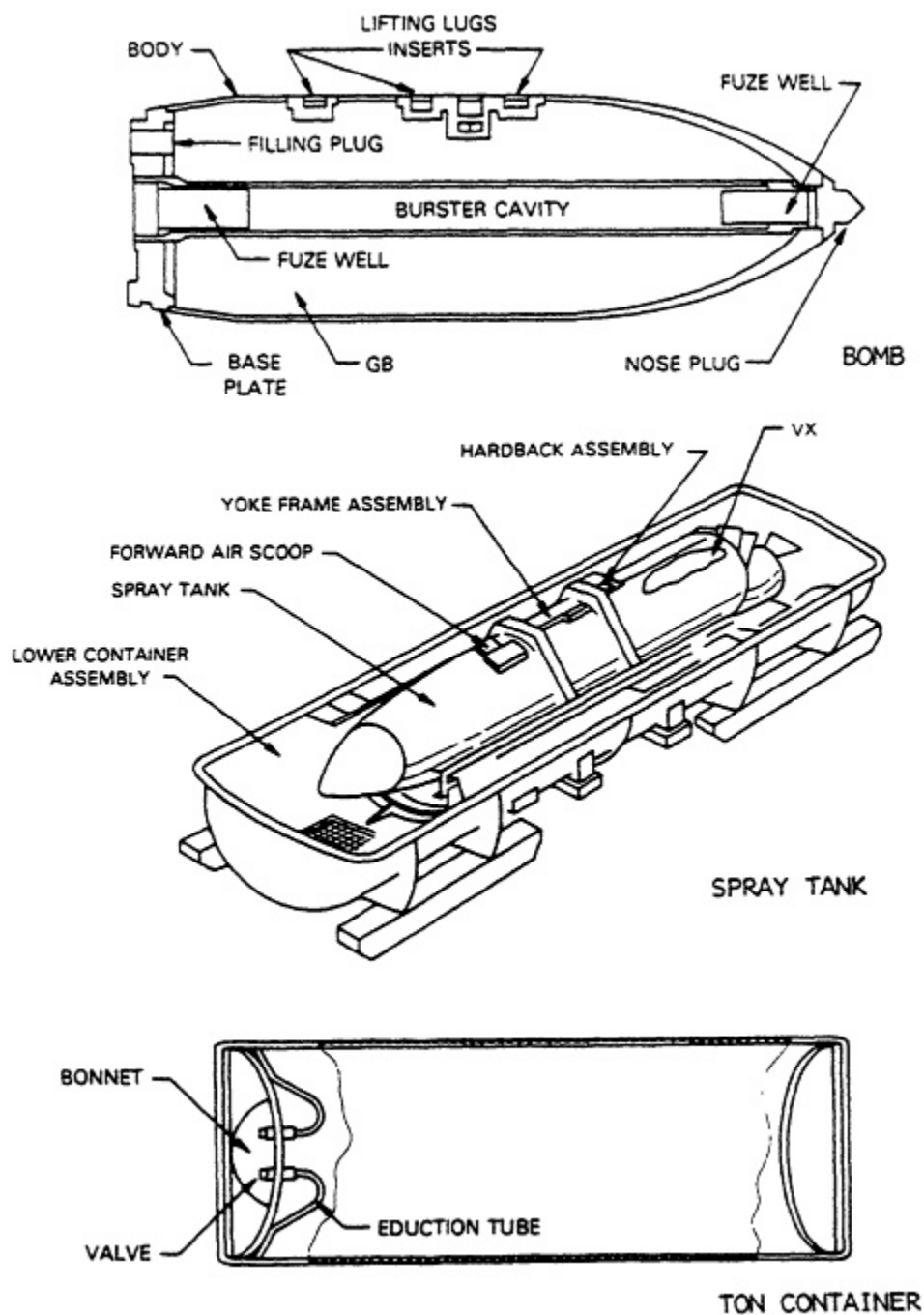


FIGURE 2-4 Bomb, spray tank, and ton container.  
Source: USATHAMA (1982, 1983).



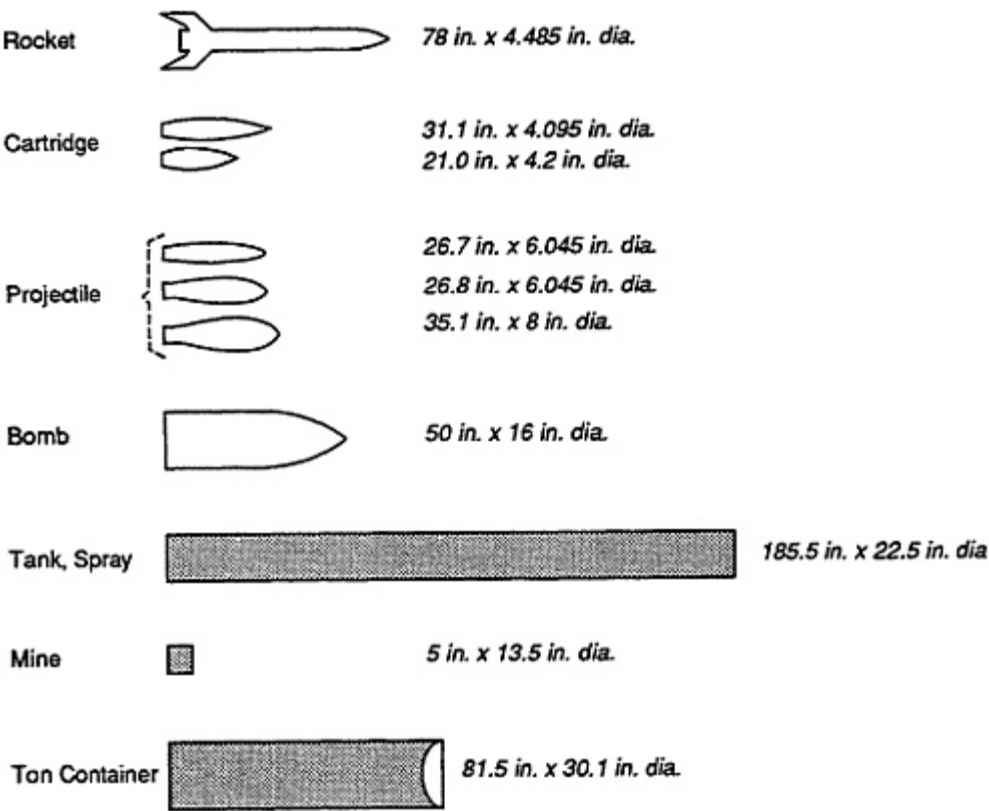


FIGURE 2-5 Physical envelopes of chemical munitions.  
Source: General Atomics (1982).

TABLE 2-2 Composition of Munitions in the U.S. Chemical Stockpile

Munition Type	Agent	Fuze	Burster	Propellant	Dunnage
M55 115-mm rockets <sup>a</sup>	GB, VX	Yes	Yes	Yes	Yes
M23 land mines	VX	Yes <sup>b</sup>	Yes	No	Yes
4.2-in. mortars	Mustard	Yes	Yes	Yes	Yes
105-ram cartridges	GB, mustard	Yes	Yes	Yes	Yes
105-ram projectiles	GB, mustard	Yes <sup>c</sup>	Yes <sup>c</sup>	No	Yes
155-mm projectiles	GB, VX, mustard	No	Yes <sup>c</sup>	No	Yes
8-in. projectiles	GB, VX	No	Yes <sup>c</sup>	No	Yes
Bombs (500-750 lb)	GB	No	No	No	Yes
Weteye bombs	GB	No	No	No	No
Spray tanks	VX	No	No	No	No
Ton containers	GB, VX, GA, mustard, Lewisite	No	No	No	No

<sup>a</sup> M55 rockets are processed in individual fiberglass shipping containers.  
<sup>b</sup> Fuze and land mines are stored together but not assembled.  
<sup>c</sup> Some projectiles have not been put into explosive configuration.  
Source: PEIS (1988).

TABLE 2-3 Composition of Selected Chemical Munition Types, by Weight

Munition Type	Chemical	Weight (lb)			
	Agent	Agent	Explosive	Propellant	Metal
M55 rocket	VX, GB	10.5	3.2	19.3	23.8
155-mm projectile	VX, GB, HD	6.3	2.4	--- <sup>a</sup>	92.6
Ton container	VX, GB, HD	1,600	--- <sup>a</sup>	--- <sup>a</sup>	1,400

<sup>a</sup> Not applicable.  
Source: PEIS (1988).

Many of the chemical munitions contain explosives in the form of fuzes and bursters, as well as propellants. Fuzes are mechanically activated detonation devices that set off the bursting charge of a projectile, rocket, or land mine. The bursters axe explosive charges that, on detonation, disperse agent and metal fragments into the surrounding area. Propellants axe energetic materials necessary for the propulsion of the rockets and 105-ram artillery cartridges. In the following discussion, explosives and propellants will be referred to collectively as energetics. These munition components incorporate a variety of chemical compounds that must also be destroyed as part of chemical weapons destruction.<sup>7</sup>

Disposal requires consideration of other chemical compounds and materials as well. For example, the fiberglass shipping and firing tubes for

<sup>7</sup> Fuzes include cyclonite, lead styphnate, lead oxide, barium nitrate, antimony sulfide, tetracine, and potassium chlorate. Bursters include tetryl, tetrytol (tetryl plus trinitrotoluene [TNT]), or Composition B (cyclonite plus TNT). Propellants include nitrocellulose, dinitrotoluene, lead stearate, triacetin, dibutylphthalate, and diphenylamine.

M55 rockets were found to contain small quantities of polychlorinated biphenyls (PCBs). Munitions are often stored in configurations suitable for transport during wartime, such as in boxes or protective robes. Such packing and handling materials are referred to as dunnage. For chemical munitions, dunnage includes wood pallets (some treated with pentachlorophenol [PCP]), metal fasteners, steel drums, and polystyrene packing. Used protective suits and spent decontamination solution also require disposal. All these materials must be covered in any program for chemical weapons destruction. However, dunnage may be handled by disposal in a hazardous waste site.

### GEOGRAPHICAL DISTRIBUTION OF THE STOCKPILE

The U.S. chemical weapons stockpile is distributed among Army bases at eight continental U.S. sites and at Johnston Island in the Pacific Ocean ([Figure 2-6](#) and [Table 2-4](#)). Some of these storage locations are quite remote; others, such as Aberdeen Proving Ground, Newport Army Ammunition Plant, and Lexington Blue Grass Army Depot, are close to populated areas.

Chemical agents at all these sites total about 25,000 metric tons, with 40 percent stored in Utah at TEAD (Ember, 1992; Picardi et al., 1991). Quantities at other locations range from 1.6 percent of the stockpile, at Bluegrass Army Depot, to 12 percent, at Pine Bluff Arsenal.

The character of the stockpile also differs among storage sites. Aberdeen Proving Ground and Newport Army Ammunition Plant store only ton containers of HD and VX, respectively. Pueblo Army Depot maintains only mustard agents (HD) and HT) in cartridges and projectiles. The other locations store both nerve and mustard agents as well as a variety of munition types. Johnston Island has approximately 100,000 artillery projectiles filled with nerve agent that were removed ("retrograded") from West Germany in 1990. (Some weapons stored at Johnston Island will be destroyed during OVT of the baseline technology.) [Table 2-5](#) indicates the differences among sites in the amounts of metals, explosives, propellants, and agents stored.

At all sites, containers of agents and weapons containing agents must be prepared for destruction. These operations produce contaminated or hazardous waste streams that must also be dealt with in the disposal process (see [Chapter 4](#) for further details on the requirements of disposal).

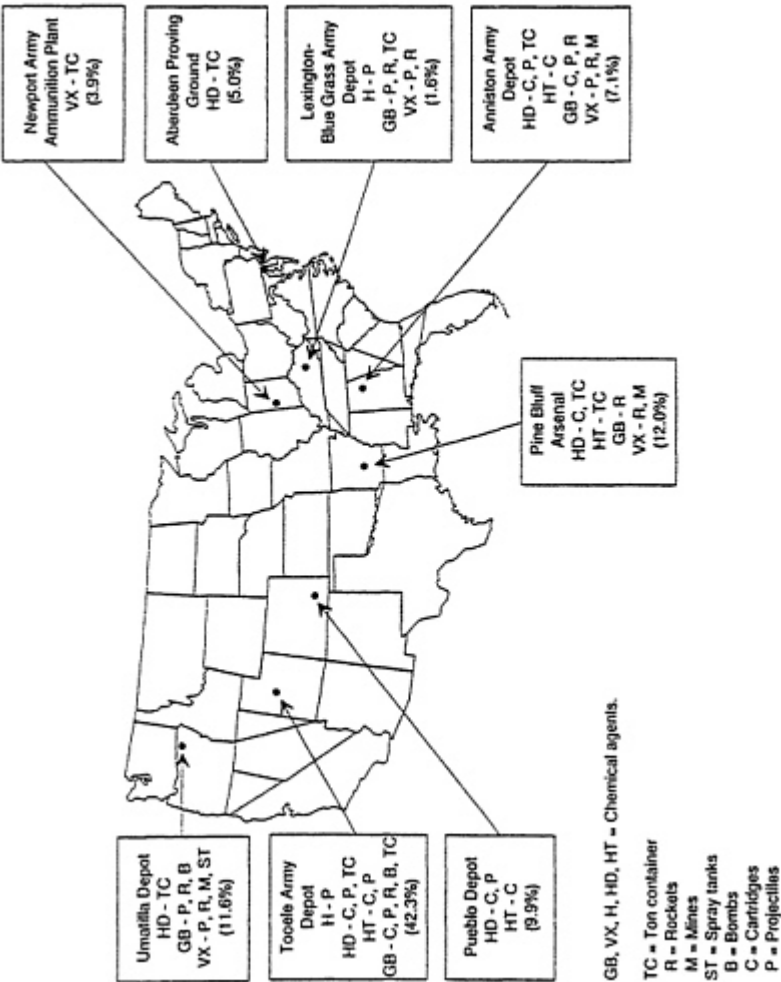


FIGURE 2-6 Types of agent and munitions anti percentage of total agent stockpile (by weight of agent) at each storage site. Source: OTA (1992).

TABLE 2-4 Chemical Munitions Stored in the Continental United States

Chemical munitions (Agent)	APG	ANAD	LBAD	NAAP	PBA	PUDA	TEAD <sup>a</sup>	UMDA
Mustard agent (H, HD, or HT)								
105-mm projectile (HD)		X				X		
155-mm projectile (H, HD)		X	X			X		
4.2-in. mortar (HD, HT)		X				X		
Ton container (HD)	X	X			X	X <sup>b</sup>		X
Ton container (HT)					X			
Agent GB								
105-mm projectile		X					X	
155-mm projectile		X					X	X
8-in. projectile		X	X				X	X
M55 rocket		X	X		X		X	X
500-lb bomb								
750-lb bomb							X	X
Weteye bomb							X	
Ton container							X	X
Agent VX		X <sup>b</sup>	X <sup>b</sup>		X <sup>b</sup>			
155-mm projectile		X	X				X	X
8-in. projectile							X	X
M55 rocket		X	X		X		X	X
M23 land mine		X			X		X	X
Spray tank							X	X
Ton container				X				X

<sup>a</sup> Small quantities of Lewisite and Tabun (GA) are stored in ton containers at TEAD.

<sup>b</sup> Small quantities of agent drained as part of the Drill and Transfer system assessment for the M55 rockets.

APG, Aberdeen Proving Ground, Md.; AMAD, Anniston Army Depot, Ala.; LBAD, Lexington/Blue Grass Army Depot, Ky.; NAAP, Newport Annex Army Depot, Ind.; PBA, Pine Bluff Arsenal, Ark.; PUDA, Pueblo Depot Activity, Colo.; TEAD, Tooele Depot Activity, Utah; and UMDA, Umatilla Depot Activity, Ore.

TABLE 2-5 Approximate Amounts of Metals, Energetics, and Agent Contained in the Chemical Weapons Stockpile (tons), by Site

Site	Ferrous Metal	Aluminum	Explosive	Propellant	Agent <sup>a</sup>
Tooele	22,000	570	350	175	10,500(?)
Anneton	13,700	1,020	451	757	1,800 (?)
Umatilla	7,930	1,380	338	1,030	2,900 (?)
Pine Bluff	2,644	1,431	180	1,060	3000 (?)
Lexington	1,631	904	115	670	400 (?)
Pueblo	10,910	0	124	0	2,500(?)
Newport	2,455	0	0	?	1000 (?)
Aberdeen	?	0	0	0	1,300 (?)
JACADS	?	?	?	?	1,700(?)
TOTAL	71,270(?)	5,305(?)	1,558(?)	3,692(?)	24,800 (?)

<sup>a</sup> Estimated values, based on percentages of the total stockpile at each site, multiplied by 25,000 tons.  
Source: Information supplied by the Program Manager for Chemical Demilitarization at a meeting of the Committee on Review and Evaluation of the Army Chemical Stockpile Disposal Program, March 9-10, 1992, National Academy of Sciences.

**SUMMARY**

In summary, the U.S. chemical weapons stockpile consists of a diverse assemblage of lethal chemical agents and associated munitions, representing a complex disposal task, regardless of the technology used. Amounts and types of agents and munitions vary greatly among storage sites. In particular, Aberdeen Proving Ground and Newport Army Ammunition Plant have only ton containers of HI) and VX, respectively, while other storage sites maintain a variety of other agent-containing weapons.



### 3

## U.S. and Foreign Experience with Chemical Weapons Destruction

This chapter briefly reviews U.S. and foreign experience with the destruction of chemical weapons in Canada, Germany, Iraq, the former Soviet Union, United Kingdom, and United States. Such information provides one basis for the committee's analysis of alternative demilitarization technologies.

### U.S. CHEMICAL DEMILITARIZATION EXPERIENCE

In 1969, a National Academy of Sciences report concluded that dumping at sea of chemical warfare agents or munitions should be avoided (NAS, 1969). Three years later, the Marine Protection, Research and Sanctuaries Act of 1992 (P.L. 92-532) prohibited ocean dumping of chemical agents. Since 1969, the United States has disposed of over 7,000 tons of chemical warfare agents by incineration and chemical neutralization (Tables 3-1 to 3-7). Early work was carried out at Rocky Mountain Arsenal in Denver, Colorado, with the incineration of nearly 3,100 tons of H (mustard) in a furnace that had been used to burn the rocket fuel hydrazine. Flue gases were scrubbed with alkali (NaOH) to trap acidic combustion products and then passed through an electrostatic precipitator to remove particulates, such as rust.

Between 1973 and 1976, nearly 4,200 tons of GB (Sarin) were destroyed by reaction with alkali (neutralization) mainly at Rocky Mountain Arsenal but partly in developmental work at Tooele Army Depot (TEAD) in Utah, at the Chemical Agent Munitions Disposal System (CAMDS) facility. Problems were encountered at both sites, leading the Army to decide against neutralization as a major chemical demilitarization process: "the rationale for abandoning neutralization was based on a number of factors: (1) the sheer complexity of the process (as compared to incineration...)..., (2) the quantity and nature of the waste that was produced, and (3) the high capital...and operating costs" (Flamm et al., 1987). A perplexing but frequently observed and disconcerting feature of the tests was that even when presumed large excesses of alkali were

TABLE 3-1 U.S. Army Experience with Destruction of H (Mustard) by Incineration

Destruction Method Characteristic	Site Data
Site	Rocky Mountain Arsenal, Denver, Colo.
Duration	October 1969—July 1974
Amount	3,071 tons
Form	Bulk agent and minor components of filled munitions
Process	Agent burned in modified hydrazine furnace
Metal parts	Ton containers detoxified in ton container furnace
Waste streams	Furnace flue gases passed through scrubber and then electrostatic precipitator before stack discharge wastewater and scrubber brines were dried in spray dryer to salt, which was placed in a hazardous waste landfill meeting Resource Conservation and Recovery Act (RCRA) regulations
Efficiency	Data not available
Monitoring	Data not available
Rate	2 gallons/minute (0.64 ton/hour), maximum
Comments	Early operations

Source: Flamm et al. (1987).

TABLE 3-2 U.S. Army Experience with Destruction of GB (Sarin) by Neutralization

Destruction Method Characteristic	Site Data
Site	Rocky Mountain Arsenal, Denver, Colo.; CAMDS (TEAD, Utah)
Duration	October 1973—November 1976
Separation	Munitions disassembled and liquid GB drained and stored in tank
Amount	4,188 tons
Form	Bulk storage in tanks and filled munitions
Process	GB mixed with caustic (NaOH) solution in water; spontaneous reaction caused heat evolution
Metal parts	Drained munitions were rinsed with caustic, mechanically cut, and passed through incinerator furnace (those containing explosive put through a special deactivation furnace that could withstand explosions)
Waste streams	Neutralization and scrubber brines and wastewater from equipment washdown evaporated in spray or drum dryer to salt, which was placed in RCRA hazardous waste landfill; ventilation air and incinerator flue gases passed through scrubber
Efficiency	Apparently inadequate (analyses showed minute amounts of GB in the brines after supposed end of reaction. In addition, spray dryer emissions contained trace quantities of agent in the early operating time; see comment below)
Rate	Data not available
Comments	Brine analysis indicated that GB destruction was not quite complete and that some reaction batches took weeks to arrive at zero GB assay; subsequent research suggests residual GB could have been an artifact of the method of assay

Source: Flamm et al. (1987).

TABLE 3-3 U.S. Army Experience with Destruction of GB (Sarin) by Incineration, at CAMDS

Destruction Method Characteristic	Site Data
Site	CAMDS (TEAD, UT)
Duration	April 1981—August 1986
Amount	38 tons
Form	Ton containers, drained projectiles and M55 rockets, and undrained 155-mm projectiles
Process	Agent pumped from tanks into a furnace (some into metal parts furnace, most into liquid incinerator) and burned
Metal parts	Drained projectiles and M55 rockets conveyed into metal parts furnace or deactivation furnace system and heated to about 890°C
Waste streams	Furnace flue gases passed through scrubber and then demister; stack discharge wastewater and scrubber brines dried in a drum dryer to salt, which was placed in landfill
Efficiency	>99.9999995%
Monitoring	<0.00006 mg/m <sup>3</sup>
Rate	500 lbs (0.25 ton) per hour, maximum
Comments	Testing of CAMDS system

Source: Flamm et al. (1987).

TABLE 3-4 U.S. Army Experience with Destruction of GB (Sarin) by Incineration, at JACADS

Destruction Method Characteristic	Site Data
Site	JACADS (Johnston Island)
Duration	October 31-November 14, 1991
Amount	40 tons
Form	M55 rockets
Process	Rockets are disassembled, agent drained and incinerated
Metal parts	Deactivated in metal parts furnace
Waste streams	Furnace flue gases passed through quench, venturi, scrubber, and then demister, stack discharge wastewater and pollution abatement system brines disposed of through two mechanisms: deep-well injection and drying in a drum dryer to salt, which was placed in landfill
Efficiency	>99.99999%
Monitoring	<0.00006 mg/m <sup>3</sup> . Continuous monitoring for GB, CO, O <sub>2</sub> , NO <sub>x</sub> , and SO <sub>2</sub> ; intermittent monitoring for HCl, particulates, trace metals, volatile and semivolatile products of incomplete combustion, tetrachlorodibenzodioxins (TCDDs), tetrachlorodibenzofurans (TCDFs), and total hydrocarbons
Rate	750 lbs (0.38 ton) per hour
Comments	Destruction during Operation Verification Test (OVT) One

Source: Baronian and Wojciechowski (1992).

TABLE 3-5 U.S. Army Experience with Destruction of VX by Incineration, at CAMDS

Destruction Method Characteristic	Site Data
Site	CAMDS (TEAD, UT)
Duration	June—August, 1984
Amount	8 tons
Form	Ton containers
Process	VX drained from tanks, pumped into metal parts furnace system, and burned mainly with either fuel oil or liquified petroleum gas
Metal parts	Data not available
Waste streams	Furnace flue gases passed through scrubber and then demister; stack discharge wastewater and scrubber brines dried in a drum dryer to salt, which was placed in landfill
Efficiency	>99.9999998%
Monitoring	<0.003 mg/m <sup>3</sup> . Continuous monitoring for VX, CO, O <sub>2</sub> , NO <sub>x</sub> , SO <sub>2</sub> , and CO <sub>2</sub> ; intermittent monitoring for HCl, particulates, trace metals, volatile and semivolatile products of incomplete combustion
Rate	400 lbs (0.2 ton) per hour
Comments	Same methods used as for incineration of GB

Source: Flamm et al. (1987).

TABLE 3-6 U.S. Army Experience with Destruction of VX by Incineration, at JACADS

Destruction Method Characteristic	Site Data
Site	JACADS (Johnston Island)
Duration	October 31-March 5, 1992
Amount	54 tons
Form	M55 rockets
Process	Rockets disassembled, agent drained and incinerated
Metal parts	Deactivated in metal parts furnace
Waste streams	Furnace flue gases passed through pollution abatement system quench, venturi, scrubber, and then demister; stack discharge wastewater and brines disposed of through two mechanisms: deep-well injection and drying in a drum dryer to salt, which was placed in a landfill
Efficiency	99.999999%
Monitoring	<0.00006 mg/m <sup>3</sup> . Continuous monitoring for VX, CO, O <sub>2</sub> , NO <sub>x</sub> , and SO <sub>2</sub> ; intermittent monitoring for HCl, particulates, trace metals, volatile and semivolatile products of incomplete combustion, TCDDs, TCDFs, and total hydrocarbon
Rate	30.2 rockets (containing a total of 0.15 ton of agent) per hour, during up time; feed rate to the liquid incinerator was 699 lbs per hour
Comments	Destruction during OVT Two

Source: Wojciechowski (1992).

TABLE 3-7 U.S. Army Experience with Destruction of HD by Incineration, at JACADS

Destruction Method Characteristic	Site Data
Site	JACADS (Johnston Island)
Duration	August 3-September 5, 1992
Amount	56.5 tons
Form	Ton containers
Process	Ton containers are drained and agent incinerated
Metal parts	Deactivated in metal parts furnace
Waste streams	Furnace flue gases passed through quench, venturi, scrubber, and then demister, stack discharge wastewater and pollution abatement brines dried in drum dryers to salt, which was placed in a landfill
Efficiency	>99.99995%
Monitoring	<0.008 mg/m <sup>3</sup>
Rate	1,076 lbs an hour
Comments	Destruction during OVT Three

Source: Evans (1993).



used, and reaction times were as long as weeks, traces of GB remained. However, subsequent research has suggested that this result was probably an artifact of the analytical method used (Beaudry et al., 1992). The large amount of waste that resulted from the tests (predominantly salts from evaporation of the neutralization product solutions that were buried in landfill) was due in part to the use of large quantities of alkali in attempting to attain complete GB destruction.

In the early 1980s, small amounts of GB (38 tons) and VX (8 tons) were destroyed by incineration at the CAMDS facility. Recently, similar amounts of GB (40 tons) and VX (54 tons) were destroyed by incineration at the Johnston Atoll Chemical Agent Disposal System (JACADS) facility during Operational Verification Testing (OVT) campaigns (tests) One and Two (for further discussion see [Chapter 1](#)). The main purpose of these campaigns was to observe and debug the moderately complex JACADS operations. Numerous problems were encountered during these tests, as often occurs in initial operation of a new chemical plant. Some problems related to the Army's demanding standards for low agent concentration in the air within the buildings and the high sensitivity of the agent detection meters. Destruction of H, GB, and VX by incineration has, however, been demonstrated to be technically feasible.

### CHEMICAL WARFARE AGENT DESTRUCTION IN OTHER COUNTRIES

Other countries have experience with destruction of chemical warfare agents of the types held by the United States by technologies of current interest. The basic technologies used, chemical neutralization and controlled incineration, have also been used in the United States. Nevertheless, the experience of others with variations on the basic technologies may prove valuable regarding alternative methods to destroy the U.S. chemical weapons stockpile. Such foreign experience is summarized in [Tables 3-8 to 3-18](#).

Among destruction methods used in other countries, the two of greatest interest are variations on the method of chemical neutralization:

- reaction with alkali in an alcohol, as used in Canada for neutralization of small quantities of GB and VX ([Table 3-10](#)); and
- reaction with ethanolamine, as used in the former Soviet Union for neutralization of GB and perhaps mustard ([Table 3-12](#)).

TABLE 3-8 Canadian Experience with Mustard Agent Destruction (1974 to 1976)

Destruction Method Characteristic	Site Data
Site	Defence Research Establishment Suffield (DRES)
Amount	About 700 tons
Form	Bulk agent
Separation	Pumped from lead-lined vats into steel hydrolysis tank
Neutralization	Hydrolyze g-ton batches by adding lime. Reaction conducted with agitation at 95° C, keeping pH above 10 (principal products are thiodiglycol and calcium salts)
Incineration	Batch-incinerated at 1085°C with caustic scrubbing using a liquid incinerator
Effluents	CO <sub>2</sub> , H <sub>2</sub> O, SO <sub>2</sub> , and calcium salts in flue discharge
Efficiency	Data not available
Monitoring	SO <sub>2</sub> stack monitoring;,, site monitoring for mustard carried out using liquid impinger (bubblers)
Disposal	Much of the hydrolysis products incinerated (some spread on prairie land for further degradation; sludge left in the reaction vats to be buried)
Duration	3 years, completed October 1976; Incineration program, 10 months
Rate	1400 gallons/day (incineration of hydrolyzate)
Cost/ton	\$60/ton (incineration of hydrolyzate)

Source: Conference on Disarmament, CD/173, Geneva, April 3, 1981.

TABLE 3-9 Canadian Experience with Mustard Destruction in 1990 to 1991

Destruction Method Characteristic	Site Data
Site	Defence Research Establishment Suffield Experimental Proving Grounds
Amount	12 tons, some thickened or aged
Form	About 3 tons bulk and 9 tons in munitions
Separation	Preheated and drained bulk containers; batch-introduced agent into incinerator frozen, in polyethylene-lined cardboard boxes; froze and explosively punctured nonexplosive munitions with shaped charges and incinerated directly; froze and used shaped charges to cut off fuzes of explosive munitions and destroyed fuzes by ass detonation at remote site (freezing achieved by exposure to winter ambient air)
Incineration	Batch-incinerated at 900°C for about 30 minutes, then at 1200°C for 2 seconds; scrubbed flue gas with aqueous NaOH; passed scrubbed flue gas through 1-µm filter to remove particulate matter
Effluents	CO <sub>2</sub> and H <sub>2</sub> O in discharged vapor, NaCl and Na <sub>2</sub> SO <sub>4</sub> in scrubber brine, and spent filters
Efficiency	>99.99999%
Monitoring	Continuous stack monitoring for mustard, CO, HCl, SO <sub>2</sub> , NO <sub>x</sub> , hydrocarbons, and particulate matter, discontinuous for trace metals, TCDDs, and TCDFs; mobile laboratory used to monitor air quality for mustard, CO, HCl, NO <sub>x</sub> , SO <sub>2</sub> , and particulates on a continuous basis
Disposal	Scrubber brine discharged to impermeable lined pit and allowed to evaporate; resulting salts and spent filters placed in landfill; metal residues sold to commercial foundry and melted down
Duration	Winter of 1990-1991
Rate	Incinerator capacity 1.5 tons/hour (actual rate kept down to 180 kg/hour to reduce particulate emissions)
Cost/ton	About \$5,000 (Canadian) per ton of mustard, scrap metal, dunnage, and neutralized nerve agent solution (not including costs of field ,separation and packaging and public communications programs) and environmental monitoring programs
Comments	Also incinerated were 375 tons of contaminated shredded metal, 4 tons of dunnage packed in cardboard boxes, 4 tons of neutralized nerve agent solution (cardboard boxes caused excess particulate matter that necessitated use of filters and reduced processing rate; incinerated scrap metal melted in a foundry and recycled); high community participation, including membership on committee to write impact statement; project completed and incinerator removed

Source: McAndless (1992a,b).

TABLE 3-10 Canadian Experience with Nerve Agent Destruction

Destruction Method Characteristic	Site Data
Site	Defence Research Establishment Suffield, Willis Centre Complex
Agent	VX, GA, GB, and other G-type nerve agents
Amount	0.3 tons
Form	Munitions without explosives
Separation	Munitions drilled and agents drained
Neutralization	Batch-neutralized in methanolic 20% KOH (1,500 L of neutralized solution) diluted with water to 3X total volume increase (4,500 L total)
Incineration	Incinerated together with mustard-contaminated scrap metal in transportable unit (see Table 3-9); scrubbed flue gas with aqueous NaOH
Effluents	CO <sub>2</sub> and H <sub>2</sub> O in discharged vapor and potassium and sodium chloride, fluoride, nitrate and phosphate in scrubber brine
Efficiency	Neutralization >99.9999%; incineration >99.9999%
Monitoring	Batch analysis of neutralizing solution to verify destruction of nerve agent; continuous monitoring of incinerator emissions as in Table 3-9; particulate emissions (samples) analyzed for phosphorus content
Disposal	Scrubber brine discharged to impermeable lined pit and allowed to evaporate; resulting salts and spent filters placed in landfill
Duration	4 months intermittent to complete neutralization; 5 days for incineration of neutralized solution (hydrolyzate)
Rate	0.8 tons/day as hydrolysate incinerated together with mustard-contaminated scrap metal (Table 3-9)
Cost/ton	\$30,000/ton (includes operating costs, equipment, and supplies)
Comments	See Table 3-9

Source: McAndless (1992a,b).

TABLE 3-11 erman Experience with Mustard Agent Destruction

Destruction Method Characteristic	Site Data
Site	Munster/Oertze
Agent	Mustard and thickened mustard containing arsenicals
Amount	About 70 metric tons/year total agent, ongoing program
Form	Old munitions and bulk containers
Separation	Cleaned with water jet, explosive ordinance demolition evaluation, transport, x-rayed, and cut, or drilled and drained; drained with steam injection if agent solidified; explosives and fuzes separated; intermediate storage of agent
Incineration	Batch-incinerated agent (hold at 300°C for 10-12 hours in inert gas atmosphere, then at 1000-1200°C for 2 seconds; empty munitions and containers kept about 12 hours at 1000°C); scrub flue gases with NaOH solution; precipitate arsenic in scrubber brine as ferric arsenate; pass flue gas through aerosol separator
Effluents	CO <sub>2</sub> and H <sub>2</sub> O in discharged vapor, NaCl and Na <sub>2</sub> SO <sub>4</sub> in scrubber brine, and ferric arsenate
Efficiency	Data not available
Monitoring	Continuous monitoring for HCl, SO <sub>2</sub> , hydrocarbons, and NO <sub>x</sub> ; discontinuous monitoring for particulates and dioxins in vapor effluent and for sulfate and pH in scrubber brine
Disposal	Scrubber brine discharged into municipal waste water system; filtered arsenic sludge placed in old salt mine
Duration	Began 1980, continuing
Rate	About 70 metric tons/year, total agent; up to 350 kg/day
Cost/ton	DM 25,000
Comments	Highly automated operation (except for loading and unloading furnace wagons); urban facility

Source: Conference on Disarmament, CD/CW/WP.374, Geneva, 1991; Martens (1992).

TABLE 3-12 Former Soviet Union Experience with Agent Destruction

Destruction Method Characteristic	Site Data
Site	Shikhany Proving Ground and others.
Agent	GB, GD, and mustard
Amount	About 300 tonnes (including VX, see <a href="#">Table 3-13</a> )
Form	Munitions
Separation	Drilled and vacuum-evacuated
Neutralization	Batch-neutralized in ethanolamine at 100°C for 30-45 minutes with water or NaOH added to reduce viscosity
Incineration	Batch-incineration of neutralization reaction products without gas scrubbing
Effluents	CO <sub>2</sub> , HCl, NaF, NO <sub>2</sub> , PO <sub>x</sub> , SO <sub>2</sub> , and sodium salts
Efficiency	Reportedly 99.99999% (nerve agent)
Monitoring	Ionization detectors (with sensitivity 10 <sup>-2</sup> to 10 <sup>-3</sup> rag/cubic meter) and laboratory analysis
Rate	Reactor capacity 600 L; average 1980-1990 rate was about 20 tonnes/year
Cost/ton	Data not available
Comments	Use of ethanolamine reportedly reduces slag buildup and fouling of burners and incinerator; apparatus is mobile (known as a KUASI system)

Source: Conference on Disarmament CD/CW/WP 367, Geneva, October 7, 1991; SFIL-CMT (1992); Manley (1992b).

TABLE 3-13 Former Soviet Union Experience with VX Destruction

Destruction Method Characteristic	Site Data
Site	Shikhany Proving Ground and others.
Amount	About 30 tonnes (including GB, GD, and mustard, see <a href="#">Table 3-12</a> )
Form	Munitions
Separation	Munitions drilled and agent drained
Neutralization	Batch-neutralized with 1:1 mixture of ethylene glycol and phosphoric acid
Incineration	Batch-incineration of neutralization reaction products without gas scrubbing
Effluents	CO <sub>2</sub> , NO <sub>2</sub> , PO <sub>x</sub> , and SO <sub>2</sub>
Efficiency	Reportedly 99.99999%
Monitoring	Data not available
Duration	Data not available
Rate	Reactor capacity 600L; average 1980-1990 rate was about 20 tonnes/year
Cost/ton	Data not available
Comments	Mobile apparatus (known as the KUASI system)

Source: Conference on Disarmament CD/CW/WP.367, Geneva, October 7, 1991; SFIL-CMT (1992); Manley (1992b).

TABLE 3-14 U. K. Experience with Destruction of Mustard and World War I Gases

Destruction Method Characteristic	Site Data
Site	CBDE Porton, Wiltshire
Amount	Small, variable each year
Form	Old munitions from diverse sites (shells, grenades, mortars)
Separation	Overpacked, trucked, x-rayed, remotely cut, drilled and drained
Incineration	Batch-incinerated 2-3 seconds at 1200°C; quenched and then scrubbed flue gas with aqueous NaOH
Efficiency	>99.9999%
Monitoring	Analysis for CO, HCl, SO <sub>2</sub> , and trace organics in vapor', analysis for trace organics in brine
Disposal	After analysis transferred to effluent treatment plant of municipal sewer system
Duration	20 years and continuing
Rate	Incineration capacity 1-2 tons/day
Cost/ton	Data not available
Comments	Incinerator used for other hazardous wastes

Source: Manley (1992a,b).



TABLE 3-15 U.K. Experience with GB Destruction

Destruction Method Characteristic	Site Data
Site	CDE Nancekuke, Cornwall
Amount	About 20 tons
Form	Bulk agent
Separation	Vacuum transfer from bulk tanks
Neutralization	Batch-neutralized with aqueous 20% NaOH; diluted with water to <200 ppm fluoride
Effluents	Sodium isopropyl methylphosphonate, NaOH and NaF; final volume increase of effluents 4-5X greater than volume of agent destroyed
Efficiency	>99.9999%
Monitoring	For each batch, measurement of pH, fluoride, acetylcholinesterase activity, and toxicity to brine shrimp before disposal
Disposal	Discharge at depth into coastal sea
Duration	2 years, 1967-1968
Rate	250 kg/batch, 2-3 hours/cycle
Cost/ton	Data not available
Comments	Outside environmental review after completion; destruction carried out in converted GB production plant

Source: Manley (1992a, b).

TABLE 3-16 U. K. Experience with Mustard Destruction

Destruction Method Characteristic	Site Data
Site	Several sites within the United Kingdom
Amount	About 6,000 tons
Form	Bulk agent
Separation	Pumped from storage tanks
Incineration	Continuous, at well above 600°C; flue gas scrubbed with aqueous NaOH
Effluents	CO <sub>2</sub> and H <sub>2</sub> O in discharged vapor, NaCl and Na <sub>2</sub> SO <sub>4</sub> in scrubber brine
Efficiency	Not stated
Monitoring	Analysis for mustard
Disposal	Not stated
Duration	1958-1960
Rate	Data not available
Cost/ton	Not stated (pilot operation in 1956 estimated as 18 current pounds sterling per ton)
Comments	Data not available

Source: Toler (1990).

TABLE 3-17 U.N. Experience with Destruction of Mustard in Iraq

Destruction Method Characteristic	Site Data
Site	Al Muthanna
Amount	Estimated 400-500 tonnes with about 90% purity
Form	Bulk agent, aerial bombs, and 155-mm projectiles (some agent partly polymerized)
Separation	Vacuum-transferred from bulk storage tanks; munitions vacuumed drained through filling plugs or when necessary through holes creating by drilling or explosives charges
Incineration	Continuous, at 1100°C for 3-4 seconds; quenched and scrubbed flue gas with aqueous NaOH
Effluents	CO <sub>2</sub> , H <sub>2</sub> O, and SO <sub>2</sub> in discharged vapor, NaCl and Na <sub>2</sub> SO <sub>4</sub> in scrubber brine
Efficiency	Estimated >99.9999%
Monitoring	Continuous for CO, CO <sub>2</sub> , and O <sub>2</sub> in flue gas, as indicators of combustion efficiency; continuous for pH of scrubber brine; discontinuous for mustard in flue gas and scrubber brine
Disposal	Scrubber brine discharged to pit containing limestone (to be covered after evaporation)
Duration	Estimated 9 months for incineration, 1992-1993
Rate	360 kg mustard/hour (maximum)
Cost/ton	Data not available
Comments	Same incinerator to be used to destroy other agents, probably including GA

Source: Barrass (1992).

TABLE 3-18 U.N. Experience with Destruction of Nerve Agents in Iraq

Destruction Method Characteristic	Site Data
Site	Al Muthanna
Agent	GB and GB/GF mixture
Amount	Estimated 70 tonnes
Form	Bulk agent, aerial bombs, and ballistic missile warheads
Separation	Munitions vacuum-drained through filling plugs or through holes created by drilling explosive-shaped charges when necessary
Neutralization	Batch hydrolysis with excess aqueous NaOH in recirculating reactor
Effluents	Aqueous NaF and sodium salts of phosphonic acids with about 3% excess NaOH
Efficiency	<1 ppm
Monitoring	Continuous for temperature; continuous for reactor room ambient air for nerve agent; measurement of measurement of excess NaOH and analysis of each batch at end of reaction to verify agent level below detection limit of 1 ppm
Disposal	Spent reaction liquor discharged to impermeable lined pit (to be covered with concrete after evaporation)
Duration	Estimated six months for neutralization, 1992-1993.
Rate	One tonne/day
Cost/ton	Data not available
Comments	Data not available

Source: Barrass (1992).

Both of these above neutralization methods are discussed in [Chapter 6](#) . In both of the above cases, the products of the neutralization reaction were incinerated.

Another neutralization process of possible interest for its destruction of VX is the reaction of VX with a mixture of ethylene glycol and phosphoric acid, reported for the former Soviet Union ([Table 3-13](#)). However, few details of this experience were readily available.

In some of the cases reviewed, the amount of agent destroyed was comparable with or greater than that at small U.S. stockpile sites. In one U.K. case, the quantity of mustard destroyed was comparable with that at the largest U.S. site ([Table 3-16](#)).

In France, a novel method for opening old chemical munitions has been developed: the projectile or mine is conveyed to the bottom of a deep pool rifled with a water-alcohol mixture containing NaOH, where it is cut open by a sand blast apparatus (Froment, 1993). Any lethal chemicals released are rapidly neutralized by the NaOH. However, the method is not suitable for disposing of large quantities of munitions and agent as is required for the disposal of the U.S. stockpile.

### SUMMARY

Chemical neutralization methods followed by incineration have been used to achieve high levels of agent destruction. Different neutralization reactions have been successful primarily for GB, GD, and mustard agents (see [Table 3-8](#)). Incineration processes have generally been used to destroy mustard agent and are also being used to destroy VX and GB at JACADS.

## 4

# Requirements and Considerations for Chemical Demilitarization Technologies

As discussed in [Chapter 2](#), the U.S. chemical weapons stockpile exists in several forms. Some chemical agent is stored as bulk liquid in ton containers. Much, however, comes in weapons that are ready for transport to the battlefield and can be fired after relatively simple arming procedures. For such weapons, the current destruction or demilitarization baseline program includes reverse assembly, in which chemical agent is first separated from weapons containers and any explosives or propellants.

Technologies used for chemical agent destruction must entail a very low risk of agent release to the workplace and the environment. Because of the agents' extreme toxicity, the standards for their destruction (including the decontamination of weapons parts that have been in contact with agent) are much more demanding than the standards for the destruction of other chemicals. The serious consequences of any inadvertent release of agent near adjacent populations requires that the systems design for any disposal facility provide strict controls for the release of any substances to the environment. It may also be desirable to store waste streams for testing before releasing them to the environment. Stringent requirements are needed to protect worker safety and health. Finally, all effluents must also meet applicable regulatory requirements.

This chapter describes the major requirements and considerations relating to chemical demilitarization:

- chemical composition of agents and their breakdown products;
- waste streams resulting from chemical weapons destruction; including that from the reverse assembly procedure used to avoid complications in destroying explosive weapon components;
- processing rates required for chemical demilitarization;
- performance standards for all effluent air, liquid, and solid streams: standards are discussed for single-step operations in which full destruction and decontamination are accomplished by a single process, and for multiple-step

- operations that allow the transport of partially decontaminated wastes to other sites for full decontamination;
- general factors governing the probable applicability of any untested alternative technology to the destruction of waste streams and the decontamination of weapons and other metal parts;
- current monitoring capability for detecting residual chemical agent, including its methodology, accuracy, and time requirements;
- effluent retention time requirements and related process shutdown time requirements to certify the safety of effluents before their release to the environment;
- issues of development time and costs; and
- assessment criteria for alternative technologies.

### CHEMICAL COMPOSITION OF AGENTS AND THEIR BREAKDOWN PRODUCTS

Chemical agents in the U.S. stockpile are composed of carbon (C), hydrogen (H), oxygen (O), fluorine (F), chlorine (Cl), phosphorus (P), and sulfur (S). All these elements will be present in the waste streams, in type and quantity corresponding to agent inputs, independent of the choice of destruction technology. Most of the technologies that might be used would ultimately yield fully oxidized products, as discussed below, with the heteroatoms (noncarbon atoms F, Cl, S, and P) in the form of stable salts. For some alternative technologies, the final waste stream would be identical to that of the current baseline incineration technology.

A number of either low-or high-temperature oxidation processes could oxidize carbon atoms to carbon dioxide (CO<sub>2</sub>) gas; this CO<sub>2</sub> could be incorporated in a salt such as calcium carbonate. Biological reactions could be used to incorporate the carbon in a form of sewage sludge or a thermal reaction could be used to form both CO<sub>2</sub> and a tar or char suitable for disposal. In one special process (see [Chapter 7](#)), a reaction with sulfur vapor would form a carbon-sulfur equivalent of a solid char. The release of intermediate organic compounds to the liquid or gaseous waste streams at concentrations above those set by regulatory standards would be unacceptable.

Ideally, all hydrogen would be fully oxidized to water. The water would be released along with the CO<sub>2</sub> from the stack or it could be condensed, purified, and recycled. Solid organic compounds in any sewage sludge produced would also contain hydrogen.

The amount of oxygen present in the chemical agent is less than that required to fully oxidize the carbon and hydrogen atoms. It is assumed to appear as CO<sub>2</sub>, water, a carbonate or in solid organic compounds in disposable sludge.

The remaining elements of interest (fluorine, chlorine, phosphorus, and sulfur) will generally be converted to their acidic or oxidized forms, HF, HCl,  $P_2O_5$ , and  $SO_3$  ( $H_2SO_4$  in the presence of water), and ultimately to their related salts. Soluble salts would need to be disposed of in a hazardous waste site to prevent their leaching into groundwater. It is preferable to form the relatively insoluble calcium salts, such as  $CaF_2$ ,  $CaSO_4$ , and  $Ca_3(PO_4)_2$ . Unfortunately, all the alkali chlorides (which would form from Cl) are quite water soluble.

### WASTE STREAMS IN CHEMICAL WEAPONS DESTRUCTION

As discussed in [Chapter 2](#), chemical agents are stored as liquid in large containers or contained in weapons ready to ship to the field. Field-ready weapons contain explosive charges (burstors) that on detonation disperse agent as fine droplets. Burstors are detonated by fuzes that can usually be separated from the weapons. Land mines have burstors; their fuzes are stored with but disassembled from the mines. There are 105-mm projectiles configured both with and without burstors, fuzes, and cartridge cases containing propellant. Most 155-mm and 8-inch projectiles contain burstors but are not fuzed. In addition to fuzes and burstors, M55 rockets contain both rocket propellant and its igniter.

Because the presence of explosive components would greatly complicate the contained destruction of chemical agent, the baseline technology includes a reverse assembly procedure for these weapons before the agent contained is destroyed. Explosive components are completely removed from projectiles and land mines (except when mechanical resistance to removal may require special treatment). Liquid agent is then either drained or evacuated from the container, resulting in two process streams: (1) bulk liquid that is accumulated in a batch tank until enough is available for bulk liquid processing and (2) the drained but still contaminated projectile shells, mine casings, and ton containers, referred to as metal parts. Explosive components separated in reverse assembly, whether contaminated or not, must be destroyed in a system capable of withstanding their explosion.

M55 rockets were not designed to be disassembled but are contained within fiberglass tubes that make reverse assembly essentially impossible. As a result, individual rockets are fed to a rocket shear machine, which punches several vertical holes through the rocket and its encasing tube, drains the liquid agent into a storage tank, and shears the rocket into small pieces. With the current baseline technology, which has been tested at the Johnston Atoll Chemical Agent Disposal System (JACADS), the rocket drain and shear actions occur within rooms designed to contain and isolate any explosions ([Figure 4-1](#)). The stored agent is processed in bulk, and a deactivation furnace



system is then used to simultaneously destroy residual agent, explosives, propellants and decontaminated residual weapons parts. Subsequently, a heated discharge conveyer ensures the time and temperature requirements for thermal decontamination of the rocket pieces by carrying burned materials on an electrically heated conveyor for at least 15 minutes.

In addition to the above main component streams, additional solid wastes of the disposal process include wooden shipping and storage pallets, the protective clothing used by personnel, cleanup equipment, and other items potentially contaminated by chemical agent. These wastes are called dunnage and are combined for disposal with any compatible solid wastes from other processes in the system. The requirement to treat this waste stream is optional; experience at the baseline facility has shown that the contamination of these wastes is low and they can be chemically cleaned (e.g., with decontamination fluids) to a level that allows their transport and disposal in a hazardous waste landfill.

Any alternative process that fails to destroy the chemical agent completely or that creates new wastes that cannot be discharged to the environment may create additional process stream requirements. An example of such new wastes might be the scrubbing solution used in decontaminating equipment (and related salts, if the solution is reduced to a solid waste stream); in the baseline technology, these wastes are fed to the liquid incinerator.

Finally, all work spaces are normally ventilated with the air flow proceeding in the direction of increased probability of contamination, from the control room and analytical laboratories through the work areas. Each succeeding area is maintained at slightly lower pressure to ensure that this positive flow, and thus any leakage, occurs in the proper direction.

In all, therefore, six main process streams must be treated: (1) bulk liquid agent; (2) solids contaminated with agent without explosives or propellants; (3) solids with explosives or propellants contaminated with agent; (4) solid dunnage, such as packing materials and used protective suits; (5) decontamination fluids; and (6) ventilation air.

## PROCESSING RATES

The rate at which weapons and their resultant process streams must be destroyed is set by several factors. First, all weapons and agent at each site must be demilitarized by a target completion date. As noted in [Chapter 1](#), this



Source: PEIS (1988).

date was initially set by U.S. legislation and has been extended several times. To comply with international treaty, it was recently reset to December 31, 2004.

Second, only part of the time from now through 2004 is available for operations. There are many other necessary steps: technology selection; environmental reviews; congressional authorization; possible research, development, and demonstration of any alternative technology; design, permitting, construction; and testing of facilities. In addition, these times could be prolonged if multiple-step destruction processes required the transport of partially decontaminated materials to one or more centralized full-decontamination facilities.

One option discussed by the committee (see [Chapters 1 and 8](#)) might relieve the time pressure at some sites while allowing agent to be detoxified and weapons disassembled to meet treaty requirements. Final oxidation of all organic residues, destruction of energetics, and decontamination of metals could be deferred by local storage or transport of partially treated materials to other sites.

The processing rate for agents and munitions will probably be set by the mechanical operations in the reverse assembly process. This process will set both a maximum rate, due to mechanical limitations, unless the reverse assembly process is increased by multiple lines, and a minimum rate for performing these operations with a reasonable degree of efficiency. Significant delays between reverse assembly and later decontamination and destruction steps would add to internal inventory storage requirements as well as increase the probability of accidents.

The current program was designed so that the first disposal facilities would be constructed at sites with the largest chemical weapon storage inventories. The baseline technology would then be used at the sites with smaller inventories, resulting in shorter total operating periods. Processing rates for the largest continental site inventory at Tooele Army Depot (TEAD) are set to destroy the inventory in 4 to 5 years, with a specified flow rate of 1050 pounds of liquid agent per hour. This rate is about 50 percent greater than the collection rate from the simultaneous operation of two identical M55 reverse assembly lines, each having a nominal capacity of 35 rockets per hour (U.S. Army Corps of Engineers, 1987).<sup>1</sup> The 155-mm projectile processing rate, at 500 projectiles per day, is only 130 pounds of agent per hour. For the smaller stockpile sites, a nominal capacity of 100 pounds per hour of agent destruction is assumed in subsequent discussion of waste gas storage technologies.

---

<sup>1</sup> If two reverse assembly lines are used, each at a rate of 35 M55 rockets per hour, with 10.5 pounds of agent per rocket, the accumulation rate of drained agent will be 735 pounds per hour.

### **PERFORMANCE STANDARDS**

Chemical agent destruction technologies must meet various performance standards, including those for worker protection, ambient air quality control, and liquid and solid waste control. These standards are generated by several different regulatory agencies, including the Environmental Protection Agency, National Institute for Occupational Safety and Health, and U.S. Department of the Army, and by such laws as the Occupational, Safety and Health Act, the Resource Conservation and Recovery Act, and the Toxic Substances Control Act.

Special regulations are also imposed by the Army to meet the requirements necessitated by the especially toxic nature of the chemical agents. These special Army regulations are the main focus of the discussion below.

#### **Worker Standards**

Aside from protection against possible explosions and other industrial accidents, all handling processes are designed to preclude worker contact with chemical agent. This includes the requirement to use full-body, plastic protective suits, into which a worker is sealed (a Demilitarization Protective Ensemble, or DPE). The DPE includes a remote clean air supply for work in contaminated areas where the airborne exposure would likely exceed the maximum permissible level for workers (see [Table 4-1](#)).

#### **Air Quality Standards**

The Army has several air quality standards (permissible hazard concentrations) depending on the specific chemical agent and location. These and lethal dose estimates for agents are shown in [Table 4-1](#).

#### **Liquid Wastes**

State and community standards for water effluents and drinking water should be satisfied. As a practical matter, it is normally better to recycle the most contaminated water internally in the plant processes.

TABLE 4-1 Permissible Agent Hazard Concentrations in Air and Lethal Doses

Agent	Permissible Hazard Levels in Air(mg/m <sup>3</sup> )				Lethal Human Doses	
	Workers <sup>a</sup>	Stack Emissions <sup>b</sup>	General Population <sup>c</sup>	Skin (LD <sub>50</sub> , mg/kg)	Intravenous (LD <sub>50</sub> , mg/kg)	Inhalation (LCt <sub>50</sub> , mg—min/m <sup>3</sup> )
GA	0.0001	0.0003	0.000003	14-21	0.014	135-400
GB	0.0001	0.0003	0.000003	24	0.014	70—100
VX	0.00001	0.0003	0.000003	0.04	0.008	20-50
H/HD/HT	0.003	0.03	0.0001	100	—	10,000
L	0.003	0.03	0.003	—		100,000

<sup>a</sup> For 8-hour exposure.

<sup>b</sup> Maximum concentration in exhaust stack.

<sup>c</sup> For 72-hour exposure.

Note: The Army standards shown in the first three columns set the minimum level of performance required for gas release by any alternative process and are applicable to all four process streams. LCt<sub>50</sub> and LD<sub>50</sub> represent dosage that result in 50 percent lethality.

Source: U.S. Department of the Army (1974, 1975); PEIS (1988).

Solid Wastes

A major consideration at JACADS is the segregation of waste that may have been contaminated by agent from other hazardous and nonhazardous waste. Waste that is known never to have been contaminated is handled as simple hazardous or nonhazardous waste.

The Army has three self-imposed categories of chemical agent contamination of solid wastes:

- Level 1X is contaminated material that has not yet been processed or that still has detectable agent according to air monitoring above the material. This material must be controlled according to Army regulations and procedures.
- Level 3X was established primarily for worker safety to indicate potentially contaminated material or previously contaminated material that has been decontaminated to show zero residual contamination by air monitoring above the material. Such material includes wood pallets that have

held rockets that leaked and metal parts that contacted agent but have been decontaminated and verified by a monitor not to have agent. Worker contact with 3X materials is allowed under normal working circumstances, but release of these materials to the public for uncontrolled access or use is not allowed. (Some 3X waste salts and 3X dunnage are currently transported to hazardous waste sites for controlled landfill, i.e., a disposal method that presumably precludes public access and makes 5X treatment unnecessary.)

- Level 5X is fully decontaminated material with no detectable residual contamination that has had heat treatment of at least 1000°F for at least 15 minutes. 5X material can be released to the public for uncontrolled access or use. The high-temperature treatment is required to destroy any residual agent that may be inaccessible to chemical treatment.

To produce solid waste meeting the current 5X standard, any alternative technology would have to treat contaminated solids with 1000°F for 15 minutes. This requirement precludes several low-temperature alternative technologies. Consequently, the committee has assumed the acceptability of adding "or equivalent" to allow other treatment processes to be considered for meeting the 5X requirement. The equivalent could be, for example, treatment at a higher temperature for a shorter time. The "equivalent" capability would still have to be demonstrated, and the Army's self-imposed regulation would need to be changed to reflect the new conditions.

For decontamination purposes, the Army is considering a new alternative 5X standard for the destroying GA and GB nerve agents associated with local accidents, the resulting contamination, and the reoccupation of related housing. This alternative would require that any residual material be subjected to appropriate tests (not yet defined) to show that the air over the sample has an agent concentration of less than 3 ng/m<sup>3</sup> for 72 hours, that is, meets the air quality standard for the general population. However, the alternative standard would not apply to mustard agent (HD), because mustard is believed to be carcinogenic and no lower threshold (below which damage will not occur) has been established. The new standard is not intended to be applied to the primary operations at agent destruction facilities.

#### **GENERAL CONSIDERATIONS IN ASSESSING UNTESTED ALTERNATIVE TECHNOLOGIES**

Most potential alternative technologies have not been tested with the chemical warfare agents in the U.S. stockpile. It is therefore necessary to judge whether such technologies will likely meet the very stringent destruction requirements when tested. An initial judgment can be made about a technology's probable success in destroying bulk chemical agent by considering the technology's success in destroying similar bulk chemicals. A

further judgment must be made about the ability of any alternative technology to decontaminate metal parts, explosives, propellants, dunnage, and other components. (It may be possible to deal with dunnage by disposal in hazardous landfills.)

### Decontamination Standards

The Army has developed data over a number of years in support of the current 3X and 5X criteria (see [Appendix H](#)). This work has included a variety of tests on the liquid forms of all agent types, at various temperatures and times, and with and without oxygen present. Tests have also addressed the decontamination of solids containing the different agents.

Previous Army experience showed that past chemical treatment processes left residual agent contamination on metal parts that was detectable on subsequent thermal treatment.<sup>2</sup> However, these activities have not included the use of somewhat more reactive chemicals, such as ammonia gas or corrosive acids, at elevated temperatures and for longer times. In principle, with further research and proper choice of reagents, it may be possible to chemically decontaminate metal parts. New ways to certify such decontamination would have to be developed. In conjunction with a development program to chemically destroy agent from ton containers, research to identify low-temperature chemical processes that would match the 5X thermal treatment decontamination would be useful. These results suggest that some consideration should be given to the fundamentals of the problem to indicate the likelihood that similar alternative technology could achieve the equivalent of full 5X decontamination.

Current analytical techniques can measure  $0.6 \text{ ng/m}^3$ . For GB, with a molecular weight of 140, this is equivalent to  $2.6 \times 10^{12} \text{ molecules/m}^3$ . The typical solids waste debris box being sampled holds about 1 to 2  $\text{m}^3$  of solid wastes. Because GB has a molecular diameter of roughly 10 angstroms, the detectable number of molecules in such a debris box, if spread out into a monomolecular layer, would have a surface area of only a few square millimeters. GB readily wets metal surfaces, and thus only a few small cracks or crevices would be required to contain more than the allowable residue of GB. Further, removal of agent from crevices is likely to be much slower than from an exposed flat surface, because of the limited surface area at the opening of a crevice, the possible blocking of the opening by reaction by-products, and the reduced vapor pressure of the liquid in a crevice. The incomplete reaction observed with decontamination solution is probably due

---

<sup>2</sup> U.S. Army Program Manager for Demilitarization, presentations to the committee at its March 9-10, 1992, meeting.

to a diffusional limitation, a limitation that would also probably limit the use of microbial organisms or their related large molecule enzymes. The diffusion of heat in solids, liquids, and gases occurs at a much higher rate than molecular diffusion. Thus, the ability of heat to reach and destroy isolated pockets of agent makes heating the process of choice to date for decontaminating residual agent from the surface of solids.

### **Chlorinated Dioxins**

In addition to providing for the complete destruction of the chemical agent, any alternative process must not inadvertently create other harmful waste products. Of special regulatory concern is the possible production of chlorinated dioxins by recombination of the components produced in the primary agent destruction process. Chlorinated dioxins can be formed in waste gas streams where the temperature is 180 to 400°C and where chlorine and reactive hydrocarbons are present. The reactions take place on the surface of inorganic particulate matter. Salts of iron, copper, and aluminum, as found in fly ash from coal combustion, catalyze this reaction.

Subjecting chemical agents to high-temperature pyrolysis or oxygen-deficient combustion will also produce hydrocarbon fragments, which, if not destroyed in an afterburner before cooling to below 400°C, can lead to chlorinated dioxin formation if chlorine is present. The agents GB and VX contain no chlorine; however, HD can be a major source. Nonetheless, because the concentration of allowable chlorinated dioxins is extremely small, even small quantities of chlorine (such as may be present because salt in the air used in oxidation processes) may be sufficient to produce significant quantities of chlorinated dioxin if the proper conditions for the recombination reactions exist. Thus, all processes should be selected and designed to minimize the time spent in the critical 180 to 400°C temperature range and to have subsequent process steps for adequately removing any chlorinated dioxins that are formed.

Although the 5X decontamination equilibrium conditions of 1000°F (538°C) for 15 minutes are somewhat above the recombination temperature range, they may allow some synthesis of chlorinated dioxins. More important is that the decontamination of metal parts is inherently a batch process with a substantial heat up time (minutes). Because volatile organic compounds will be released during this heat up period, some chlorinated dioxins may be formed as the heat up progresses through the critical 180 to 400°C temperature range.

Further, although subsequent afterburning of any off-gases may destroy these chlorinated dioxins, they might again be produced in the subsequent cooling of the gas if adequate hydrocarbon and catalyst surface still remain



and if the cooling is slow enough to allow the reaction to take place. The same is true for all bulk liquid agent destruction processes that use high temperatures and then provide for cool down of the reaction products to ambient temperatures.

A measure of the significance of these considerations may be gained by reviewing the JACADS operating experience. Although the level of production inside the current JACADS furnaces and related afterburners is not known, the immediately downstream pollution abatement systems are designed to minimize subsequent chlorinated dioxin production conditions by using a water quench to rapidly cool the gases to about 60°C and then remove both HCl and Cl<sub>2</sub> by contact with a sodium carbonate solution.

Analysis of the exhaust gases from the JACADS systems has shown little evidence of significant residual chlorinated dioxins. However, traces of chlorinated dioxins were found in the stack emissions when projectiles containing high residuals of HD were heat treated in the metal parts furnace. Under these conditions the quantity of chlorinated dioxins varied from 0 to 0.16 ng/m<sup>3</sup>, more than an order of magnitude less than emitted from municipal incinerators (MITRE Corporation, 1993).

The low-temperature chemical and biological processes are not expected to form chlorinated dioxins because the recombination temperature conditions will never exist.

Subsequent filtering for particulate removal or storage of effluent gases at approximately 120°F, such as would exist after passing through a water-scrubbing pollution abatement system, is not expected to form additional chlorinated dioxins. In fact, the use of activated charcoal filters would be an effective method for further removal of chlorinated dioxins.

While the production of chlorinated dioxins should be minimized, and subsequent removal methods should be provided, periodic monitoring for their presence would also be prudent.

## MONITORING

The detection of chemical warfare agents at extremely low concentrations is difficult in practice for several reasons (NRC, 1993):

- There are several agents in the U.S. stockpile, GB, VX, and HD (mustard), with different characteristics.
- All are complex organic compounds without an identifying characteristic that allows easy and rapid identification.
- The agents may be masked by, as well as mistaken for, other organic compounds that happen to be present in higher concentrations.

In the current Army method of analysis, air samples are collected by withdrawing a small air stream from the process stream, the atmosphere, or air adjacent to potentially contaminated material. This air stream is then passed through a sample collection robe, where organic components are deposited on an absorbent medium. For quick analysis of limited sensitivity, sample collection time may last only a few minutes. For the detection of smaller quantities of agent, the amount of sample collected must be larger, and the collection time may be several hours. This sample is then desorbed into a gas chromatograph with a flame photometric detector.

The minimum level of detection now used for all agents is very small, about 20 percent of the maximum allowable concentration for uncontrolled access (Table 4-1). Although the maximum allowable concentration of agent is 3 ng/m<sup>3</sup>, the minimum detectable amount for several hours of collection time is about 0.6 ng/m<sup>3</sup>. As noted above, for GB this is equivalent to about  $2.6 \times 10^{12}$  molecules/m<sup>3</sup>. The Army requirement to detect these very small quantities (Table 4-1) leads to many false positives, more than found with less sensitive measures, because the instrumentation detects other similar organic compounds that emerge from the chromatographic column at the same time as agent.

Especially for future operations in the continental United States, false alarms should be minimized because of the delays for retesting and other associated problems. The storage of gas emissions will allow time for the analysis required for certification (see Chapter 5). However, improved test reliability as well as sensitivity is highly desirable. The NRC recently discussed with the Army the conduct of further R&D on the use of agent-specific mass spectrometry, which should decrease both false positives and analysis time (NRC, 1993).

The existing gaseous-waste monitoring equipment was developed for use on well-oxidized gases saturated with water vapor. Selection of any alternative technology would require further development of early monitoring equipment if other components, such as incompletely oxidized hydrocarbons or sulfur compounds, are present to any significant degree. In addition, any alternative technology will need to have its own monitoring capability for process control, the nature of which must match the chemistry and physics of the specific internal process steps needing control. Although these are readily available for many measurements, a review of the specific requirements and equipment availability should be made before any selection is finalized. Any requirement for invention of monitoring equipment would involve a high risk.

### **EFFLUENT RETENTION TIME REQUIREMENTS**

Further reduction of the risk of potential releases of agent or air toxics to the atmosphere could be accomplished in three ways: store and test gaseous waste streams before release, use activated-carbon beds (charcoal filters) to capture organic matter contained in the gaseous effluents, and reduce gaseous effluents by conversion to solids.

The baseline system does not currently store and test (storage and certification) gaseous effluents before release to the environment. To ensure that an effluent waste stream is safe for disposal requires a retention time including time required for analyses and certification plus time to shut down all inputs to the effluent stream safely if the analyses determine that the waste stream exceeds specified standards.

It takes several minutes to perform normal operational analyses (up to 20 minutes if repeat analyses are required) and several hours to collect and analyze samples from the site boundary. Although more nearly real-time analyses may be possible in the future, the times cited reflect actual current baseline capability.

The time required to terminate process operations and to stop the effluent stream varies depending on the operations involved. Some processes may be shut down almost instantaneously, but most will require more time. For example, any thermal process may be shut down instantaneously by shutting off the agent feed stream, rapidly removing the greatest contamination source.

However, if the system design requires the feed system to be kept hot, and if doing so requires the continued feeding of an alternative (if innocuous) fuel in place of chemical agent, there will be continuing flow of material through the contaminated system, which may take tens of minutes or longer to stop production of additional contaminated waste stream. Because combustion chambers and gas cleanup systems are both potential contamination sources, the continuing gas waste stream will also require analysis before its release. Using the existing metal parts furnace to evaporate and pyrolyze agent that has been polymerized and cannot be drained from the ton containers or projectiles continues to produce contaminated wastes until all of the agent is destroyed because the system remains hot for hours.

Should storage and certification be implemented, all process waste streams should be retained for at least 1 hour (preferably up to 8 hours),-to provide adequate time to certify their acceptability for uncontrolled release to the atmosphere (see [Chapter 5](#)). Charcoal beds could be used to capture any organic materials, including agent, that might be in the gaseous waste streams. These charcoal filters would in effect store such compounds.

An alternative to storage and certification would be to convert the waste stream to a form easily stored for long periods of time. For example, all

carbon atoms might be converted to CO<sub>2</sub>, which could be liquefied and stored or converted to a salt (calcium carbonate).

### **TIME REQUIRED FOR TECHNOLOGY DEVELOPMENT AND DEMONSTRATION**

Any use of an alternative technology for chemical weapons destruction would require that it be fully developed and demonstrated, requiring a corresponding extension of the current destruction schedule. No alternative technology was eliminated from consideration here because of the time required for its full development and demonstration. Time estimates are presented below for any technology to go from concept through demonstration stages. Each technology was evaluated for its current status with respect to this standard. Although generic time estimates are useful in assessing the technological options, the actual development time required for any option would depend strongly on such variables as the difficulties encountered, the level of effort, and the capability of the group carrying out the program, as well as other factors discussed below.

The following steps must be taken in developing any new destruction technology:

- Concept development. Time required for concept development is an unknown, often depending on invention. No time is estimated in this report for any technology still in concept development.
- Laboratory data development. Bench-scale tests and experiments are required to determine chemistry and kinetics.
- Concept design. This phase includes the development of flow sheets, heat and material balances, equipment design and selection, and schedule and cost estimates.
- Pilot plant. Test needs and plans are developed for a pilot plant. This step requires time to design, obtain permits, construct, test, operate the pilot plant, and evaluate performance data.
- Demonstration. Demonstration entails design, obtaining permits, constructing a facility, and conducting tests equivalent to the Operational Verification Testing (OVT) recently completed at the Johnston Island facility. Such tests, with agent, would be conducted in a special facility, such as the Chemical Agent Munitions Disposal System (CAMDS).
- Production (destruction) facility. Bringing the final destruction facility on line will require design, obtaining permits, construction, start-up, and the beginning of operations.

Table 4-2 presents estimates of the time required for these steps on the basis of input from various outside sources, including Army estimates made at the committee's request (Baronian, 1992a,b; see Appendix C) and the experience of committee members in industrial applications. The development of a major new technology from the stage of lab data development through demonstration would likely take 9 to 12 years. Development times could be delayed or accelerated by a number of factors beyond those noted above. The development schedule might be delayed by the absence of DOD pilot testing facilities, delays in obtaining permits, and additional requirements associated with the handling of chemical warfare agents, including personnel training. Thus, development time would not be so much a question of technology limitations; these further time delays might also raise issues of public acceptance and obtaining permits for pilot processes that have not been previously demonstrated. The time to produce a production facility would probably be similar to that for the existing program, with design, construction, and systematization requiring about 5 years (see Table 1-1).

The time requirements indicated in Table 4-2 are typical for a new technology with a separate stand-alone development program and no program overlapping. Development times could be shortened if any of several conditions is met:

- The technology is only a small modification of an existing, fully developed, commercial technology. Use of a modified JACADS might be possible, but only if it did not interfere with production run requirements.
- For a demonstration, only minor changes are required to an existing facility.
- The Army is willing to overlap some steps that might normally be done sequentially (probably at substantial additional cost risk).
- The required scale of the destruction facility is small enough that a decision could be made to omit intermediate-scale, pilot plant studies and to proceed directly to full-scale development and demonstration.

As Table 1-1 suggests, the Army expects to begin construction of the last planned facilities in January 1995. However, reaching agreements with local communities, design, and obtaining permits could easily consume the 2 years from the time of this writing until then. Even though 2005 is the completion date for stockpile destruction, there may not be enough time for new technologies to replace the current baseline technology and meet the destruction target date.

TABLE 4-2 Time Estimates for Development and Demonstration of Alternative Technologies

Development/Demonstration Stage	Approximate Time Required
Laboratory data development	A minimum of 1 to 2 years if major problems not encountered; longer if related data not available
Conceptual design	0.5 years (could overlap laboratory work)
Pilot plant	0.5 to 1 year for design 2 years to apply and obtain permits 0.5 years to construct 1 to 2 years to operate 0.5 years to evaluate
Demonstration	1 year (or more) to design and permit 1 year to procure 1 year of OVT
Total time	9 to 12 years (if related data available at concept development stage)

TECHNOLOGY DEVELOPMENT AND DEMONSTRATION COSTS

The use of an alternative technology would incur additional program costs both to complete development and demonstration of the technology and to account for delays in the current program. The cost of laboratory and pilot plant development will likely be significantly higher for an alternative chemical demilitarization technology than for an industrial process not involving lethal chemical agent. Special training and facilities are obviously required to work with such toxic chemicals. Furthermore, it is unlikely that

test work will be performed in university, national, or commercial development laboratories not currently equipped to work with agent.<sup>3</sup>

Note that the greatest part of facility costs is accounted for by the frontend reverse assembly function and related safety concerns. The costs for the actual destruction process equipment are a relatively small part of total system costs. Thus, the functional capability of any unit process to destroy chemical agent, without introducing new waste problems, is likely to be much more important than the equipment costs.

Some potential alternative technologies would require the use of large amounts of energy, such as for the production of a plasma arc and the heat to dry salts. These energy requirements are very important to the economic viability of other waste disposal methods when disposal costs are measured in terms of a few dollars per pound. However, the cost for the total program to destroy chemical agents amounts to about \$120 per pound (or \$6 billion to destroy 25,000 tons). Thus, energy costs will be much less important than the capability to destroy agent.

Finally, it is possible that useful by-products from chemical weapons disposal facilities could be collected and sold to reduce program costs. The committee believes this consideration to be of secondary importance: buyers would not pay normal market prices because of potential liability and public perception problems, and the income generated would at most pay only for the disposal of these specific materials, allowing for no profit.

### ASSESSMENT CRITERIA FOR ALTERNATIVE TECHNOLOGIES

The committee evaluated potential alternative technologies on the basis of development status, functional performance, and engineering factors.<sup>4</sup>

*Development status.* As discussed previously, level of development is an important criterion in this technology assessment. Also of importance is whether a technology has ever been applied to chemical agent. Categories used in the committee's analysis are the following:

---

<sup>3</sup> As for estimates of development time, the Army has suggested a generic approach to estimates of program costs (Baronian, 1992a,b). This Army approach assumes the use of an already well-developed technology, further laboratory and pilot testing at the CAMDS facility, no demonstration, and construction of full-scale destruction facilities. The Army estimate is approximately \$880 million dollars but does not include savings from elimination of the baseline technology. It is not specific to any given technology.

<sup>4</sup> In some cases, where information is common to closely related technologies or where data are not available, only a summary statement may be made without reference to each technology developer listed in [Appendix E](#).

- concept only: adequate data base does not exist;
- laboratory stage: initial data encouraging but not complete;
- pilot plant stage: small plant operative with data collected for scale-up;
- in commercial operation for similar applications; and
- prior experience in destroying one or more agents.

*Functional performance.* It is important to assess a technology's capability to perform one or more of the functional steps needed to destroy chemical weapons.

- treatment capability and attributes (for each chemical agent)—The assessment must include consideration of the ability to treat liquid agent, metal parts, propellants and explosives, dunnage, and air streams. It also must determine the technology's likely level of agent destruction (whether it is useful for pretreatment or for other degrees of destruction).
- waste treatment requirements—Each technology should be assessed for the likely solid, liquid, and gaseous waste streams it would generate and the requirements for further treatment.

*Engineering factors.* Various engineering factors must be considered that may significantly influence the effectiveness of a technology, its potential for failure in development, and its safety or hazard potential under operation. Such engineering factors include pressure, temperature, corrosion, stability of operation (rate, control), explosion potential, inventory requirements, and potential for human error during operations.



## 5

# Thermal Treatment and Preprocessing and Postprocessing Operations

Technology often means different things to different people. The Army's current baseline program uses what is often called incineration technology. When used in this general sense, technology refers to a system with component elements or steps that are referred to as processes or unit operations. The baseline incineration technology system includes such processes as combustion and flue gas cleanup and, as parts of these processes, such unit operations as liquid storage, liquid pumping, air compression, agent and fuel atomization, combustion, flue gas cooling by water quenching, flue gas scrubbing with decontaminating fluid (and its recycle or destruction), flue gas dewatering, and gas blowing to carry the effluent gas to the stack.

Thus, an evaluation of alternative technology systems must consider first the availability and capabilities of alternative processes and unit operations and then the effectiveness of combining them in an operating technology system. This kind of analysis is especially important in cases where available unit operations will only partially detoxify the chemical agent rather than fully destroy it and where they will convert chemical agent to other organic forms but will not convert all the carbon waste to acceptable wastes, such as CO<sub>2</sub>, sodium carbonate, or material roughly equivalent to sewage sludge.

Chapters 6 and 7 address a number of the principal alternative unit processes and technologies that might be used to destroy chemical agent and energetics and decontaminate metal parts and containers. Chapter 8 considers possible combinations of these elements as potential alternative technology systems. However, before a destruction technology is used, weapons must be prepared for subsequent destruction. For example, munitions must be disassembled to separate agent from propellants and explosives; ton containers must be drained of agent. In addition, the destruction processes result in gas, liquid, and solid waste that must be processed before being released to the environment.

This chapter covers some optional processes that might be used at the front end of the system to preprocess feed materials and at the back end of the system to treat, temporarily retain, or further prepare waste streams for

off-site shipment. It also addresses thermal treatment that could reduce waste gas volumes.

The following types of operations are reviewed in this chapter:

- preprocessing unit operations: cryoprocessing and mechanical removal of energetics;
- heat treating of contaminated parts: pyrolysis and oxidation; and
- postprocessing and pollution control unit operations: drying, activated-carbon adsorption beds, and stack gas holdup.

The postprocessing and pollution control operations examined here are more demanding than normal industrial applications because chemical weapons destruction must consider the potential extreme toxicity of any residual chemical agent in the waste stream. Commercial preprocessing and postprocessing liquid and solid handling, holdup, and pollution control processes do not need special evaluation to be considered for use. (The pollution abatement system that removes acid gases and particulates was examined at a pollution abatement workshop held by the National Research Council's Committee on Review and Evaluation of the Army Chemical Stockpile Disposal Program on May 15-17, 1991.)

### **PREPROCESSING OPERATIONS**

Although the development of alternative approaches has generally assumed the use of a front-end reverse assembly facility similar to that now being demonstrated at the Johnston Atoll Chemical Agent Disposal System (JACADS), certain variations of this front-end operation are possible.

#### **Cryoprocessing**

There are several possible cryogenic processes that would use liquified nitrogen to cool the still-assembled weapon below its brittle fracture temperature, which would be followed by the use of a mechanical method to break up the weapon. The resulting mixture of frozen agent and fractured metal parts and energetics would then be fed into a single rotary kiln incinerator.

The NRC recently completed a separate study on this technology (NRC, 1991). One conclusion was that "...although there exists a reasonably good chance that the cryofracture process can eventually be made to operate satisfactorily, the start up time for the proposed full-scale facility at Tooele might be extended over several years, and major modifications or even a

complete replacement of the currently designed incinerator and pollution abatement system might well be required."

### **Mechanical Disassembly of Explosives, Propellants, and Solidified Agent**

The baseline reverse assembly process punches and drains chemical agent from the M55 rockets but does not separate the explosives and propellants from the contaminated metal parts. If explosives or propellants are left in place, any subsequent process must be able to withstand potential explosions of these components. In artillery projectiles and mines, explosives are removed and the agent is then drained. Ton containers are punched and drained; however, mustard gels and solids sometimes adhere inside the containers.

Similar problems are presented in many other weapon demilitarization programs in which used explosives and propellants must be removed to avoid explosive conditions. The methods used in these programs to remove explosives and propellants from missile casings do add a data base that could be further developed if needed. For example, one such method uses a high-velocity water jet to break the explosives and propellants into small pieces that are then flushed from the system by the returning water stream (Fossey et al., 1991). This method is of interest because some of the alternative technologies can process slurried energetics (a watery mixture) and because it might be used to remove undrained agent.

In this method, a high-pressure pump, operating near 15,000 psi, feeds a jet nozzle located on the end of a moveable lance. The lance is inserted into the open end of a rocket casing and is rotated to direct the high-velocity water jet to the surfaces of the propellant, causing it to break into small pieces, which are flushed from the system. Considerable work has been done on critical water velocities (high-velocity water jets have sometimes added too much energy, inadvertently igniting the explosive), the best water jet angles, the resultant forces acting on the lance, and the degrees of freedom in aiming the jet with existing equipment. Such an application of a water jet would result, in most cases, in water contaminated with agent that would need to be handled accordingly. In some circumstances, use of decontamination solution instead of water might be used to achieve decontamination of the remaining metal parts and containers and would reduce the problems of dealing with water contaminated with agent.

## THERMAL TREATMENT

Many processes require heating or cooling steps before or after the destruction operation. Conventional heat exchange methods are assumed to be available for most of these needs. Chemical agents can be destroyed by simple thermal decomposition through indirect heating without their reaction with oxygen in combustion or with other chemicals.

Simple thermal decomposition results in the release of less exhaust gas, representing only the products of agent decomposition without the larger volume of additional fuel combustion products, excess oxygen, and nitrogen present in the baseline processes. However, the products of thermal decomposition would still require oxidation (in an afterburner) before release.

This alternative approach is clearly applicable to the treatment of energetics and contaminated metal parts and containers. For bulk agent, the use of combustion heat provides a self-sustaining flame, and there appears to be less advantage to the two-step process of thermal decomposition followed by oxidation.

Several indirect heating methods are available for heating contaminated metal parts to the required time and temperature conditions for achieving the 5X level of decontamination (i.e., 1000°F for 15 minutes; see [Chapter 4](#)). These methods include indirect gas firing and electrical resistive heating. (Plasma arc and molten-metal heating are discussed as principal alternative processes in [Chapter 7](#).) Gas burners, electric heating elements, and heating chamber equipment are commercially available, although special designs would be required for chemical demilitarization.

Special factors that would require consideration for the use of indirect heating include the following:

- remote operation: required for solids handling because of the presence of both agent and explosives;
- uniform heating: distribution must be ensured to treat all material to 5X criterion time and temperature;
- molten aluminum: provisions would be required to handle molten aluminum when decontaminating M55 rockets; and
- decomposition products: available data on the thermal decomposition of agents do not describe the quantities or nature of by-products. However, if oxygen is not present, the decomposition products must include a variety of only partially oxidized hydrocarbons (only two atoms of oxygen are present in the molecule of the agent GB). A subsequent oxidation process (afterburner) will still be required to transform the decomposition products, which can include hazardous organic chemicals, into wastes that are suitable for disposal.

A subsequent oxidation process could probably be easily incorporated into a combined thermal decomposition and oxidation system, because decomposition products of concern are likely to be gases under 5X treatment conditions. Such a system would have the advantage over an incinerator of a substantially lower rate of gas production. Equipment required for temporary gas storage and certification would be correspondingly smaller.

## POSTPROCESSING OPERATIONS

Because any process can only transform agents from one chemical form to another, all processes have waste streams. These waste streams must be suitable for disposal to the environment or for reuse.

Although many conventional processes are available for use in waste treatment, the nature of chemical agents invokes some special considerations and requires the use of protective measures that go beyond those of normal industrial practice. [Chapter 4](#) addressed the need for effluent retention systems for dynamic processing units to certify the suitability of all effluents for disposal. Other postprocessing operations that could be used in a system for chemical demilitarization are described below.

### Solid Wastes

The two major solid waste streams in chemical demilitarization are decontaminated metal and salts formed from neutralization of the acidic products of oxidation (HF, HCl,  $\text{H}_2\text{PO}_4$ ,  $\text{H}_2\text{SO}_4$ , and  $\text{CO}_2$ ). There are proposals to solidify organic wastes from chemical processes for subsequent disposal, thus avoiding the necessity for complete oxidation (Kalyon, 1992).

*Metal wastes.* [Chapter 4](#) discussed the need to use high temperatures to achieve full decontamination of metals (i.e., to the 5X level). The baseline process is designed to meet the 5X requirement of treatment at 1000°F for 15 minutes. The ability of alternative technologies to carry out this step is discussed in [Chapters 7 and 8](#).

Chemical decontamination to the 3X level would allow transportation and storage, but it is not currently believed capable of reaching the 5X level required for release of materials to the general public. If materials decontaminated to the 3X level can be disposed of in central hazardous waste facilities, the high-temperature 5X treating requirements could be modified, making construction and operation of the baseline traveling-grate metal deactivation furnace for large metal parts or any similar alternative unnecessary. Small metal parts would still require, along with energetics, a

high temperature for destruction and deactivation to meet the 5X criterion as currently carried out in the rotary kiln in the baseline technology.

*Salt wastes.* The quantities of waste salts produced will vary with the agent feed rate and the processes used. As a theoretical minimum, if all carbon atoms are converted to  $\text{CO}_2$ , the only salts produced would be those resulting from oxidation of fluorine, phosphorus, sulfur, chlorine, and nitrogen to acids, which could be neutralized by NaOH or  $\text{Ca}(\text{OH})_2$ .

Table 5-1 presents the weight of salts formed from  $\text{Ca}(\text{OH})_2$  neutralization of GB. If  $\text{CO}_2$  is discarded as a gas, the minimum produced would be 2.3 pounds of salts per pound of GB, with calcium phosphate representing the largest component (65 percent). For most systems, some  $\text{CO}_2$  will also be captured. If all the  $\text{CO}_2$  generated by agent oxidation was captured, calcium carbonate would be the major component; the total salt weight would approximately double to 5.1 pounds of salts per pound of GB. A process to capture all the  $\text{CO}_2$  would probably require excess base, and any  $\text{CO}_2$  from fuel combustion would also increase the total amount of salts. Decontamination fluid, when oxidized, would also add to total salt loading, as would the use of organic solvents such as alcohol or organic reagents such as ethanolamine. Total dry waste salts for GB, then, would probably be from 5.1 to perhaps 20 pounds per pound of agent.

The character of the waste salts will influence their ultimate disposition. Notably, their solubility will be a major determinant of their acceptability for land disposal. If NaOH is used as the reactant to destroy agent, then the fully oxidized reaction products would be sodium carbonate, sodium fluoride, sodium phosphate, sodium sulfate, sodium chloride, and sodium nitrate. Although most of these sodium salts are relatively innocuous, all are quite soluble, requiring that land disposal methods take into account potential groundwater contamination. (There would be a greater potential for contamination by the more soluble chlorides if a destructive reagent containing chlorine atoms was used.) Sodium fluoride is considered a toxic waste and might present a special problem. Calcium fluoride, which has low solubility, would probably be a more acceptable waste product. Metals used as catalysts or in small metal parts, which might be mixed with the salts, could also require special handling.

An alternative approach would be to produce the generally less soluble calcium salts, by substituting  $\text{Ca}(\text{OH})_2$  for NaOH as the reagent when possible. The same result could be achieved by a later reaction step in which calcium ions would be substituted for the sodium ions in the waste salts. Such a method would convert the salts to generally less soluble forms and also regenerate the sodium ions for reuse in agent destruction. However, it would not solve the problem of generating soluble calcium chloride when mustard is destroyed.

TABLE 5-1 Salt Formation from GB Oxidation Products

Management of CO <sub>2</sub>	Salt	lb/lb GB
CO <sub>2</sub> release as gas	CaF <sub>2</sub>	0.8
	Ca <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub>	1.5
	Total	2.3
All CO <sub>2</sub> captured	CaF <sub>2</sub>	0.8
	Ca <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub>	1.5
	CaCO <sub>3</sub>	2.8
	Total	5.1

*Drying of solids.* Most chemical processes, such as the various forms of hydrolysis, will produce a wet, dilute slurry of salt that can then be converted to a wet cake by appropriate precipitation and/or filtering. The storage volume required to retain these more concentrated salts for certification for release is not usually excessive, but the residual moisture content is often sufficiently high so that it is economical to dry the material further before shipping it to its disposal destination.

Standard commercial drying equipment (e.g., spray dryers) can be used but usually depend on mechanical techniques to bring the wet waste into contact with warm, dry, fresh air that is then released to the atmosphere. However, such a release is also an effluent stream, and if the material being dried has only been treated to the 3X level, the moist air discharge must also be treated as potentially contaminated. Thus, for present purposes, such systems might have to be modified to recycle the air through indirect heat exchangers, which would cool the air, condense the bulk of the water, and recycle the dried air stream to the dryer or send it to an afterburner. The condensed water stream would then also have to be treated as potentially contaminated and be recycled, preferably as part of the feed stream. The equipment and technology to perform these additional functions is readily available, but they would involve added complications to integrated system operations as well as added costs.

*Methods of shipping of by-product 3X salts.* The standard method of shipping contaminated wastes involves packaging them in barrels or in larger

approved containers. The salts may be premixed in a matrix to further minimize the risk of leakage during and after transport. Various methods are possible, including mixing salts in concrete or plastic matrix material. As a further extension of this approach, it might be possible to use a chemical matrix that contains the reactive hydrolysis detoxification reagent.

### **Control of Nitrogen Oxides**

Various oxides of nitrogen ( $\text{NO}_x$ ) are generated in high-temperature oxidation processes, both from the oxidation of nitrogen from the air and from nitrogen contained in the materials being oxidized. For agent disposal, the largest sources of nitrogen are VX and the propellants and explosives that are being destroyed. GB often contains small amounts of nitrogen compounds as stabilizers, but HD contains nitrogen only as minor impurities if at all. The operations at JACADS (MITRE Corporation, 1993) produced  $\text{NO}_x$  concentrations of 200 to 500 ppm, which is within the applicable federal regulations but may exceed local or future limits.

Several methods for controlling  $\text{NO}_x$  are available and currently used with combustion systems. The most important is to reduce the temperature and residence time used for high-temperature oxidation process. However, doing so in equipment such as afterburners may also reduce the operability of the process and/or decrease the degree to which combustible air pollutants are destroyed, depending on the choice of destruction technologies. Thus, it may be necessary to add to the pollution control system one of several available processes for  $\text{NO}_x$  destruction.

### **Water Recycle**

Water is used in some alternative processes, as well as in the current pollution abatement systems; in any event, it is a by-product, along with  $\text{CO}_2$ , of the final oxidation steps necessary to destroy all organic carbon. Thus, water must be discharged from the plant by some method. In current pollution abatement systems involving aqueous scrubbing, a significant quantity of water is usually discharged as water vapor along with any other effluent gas. If the gas is cooled for chemical adsorption or storage, the amount of water vapor that is discharged with gas emissions to the atmosphere is less than the water generated by the oxidation of the chemical agent. Thus, water discharge by some other method might also be required.

Numerous commercial systems are available for the adequate cleanup of this kind of wastewater stream that allow the wastewater to be recycled to the feed streams for the destruction processes or to general use on the site.



Thus, it should be possible to use systems that recycle all water not discharged with other gases.

### **Reduction of Waste Gas Volume**

Reduction of the volume of gaseous waste streams has certain advantages, especially if storage and certification of such streams is desirable. Any process or group of processes that oxidizes all the carbon compounds in chemical agents to  $\text{CO}_2$  and water requires a supply of oxygen. If this oxygen is supplied as air, about four volumes of inert nitrogen will also be present for each volume of oxygen. This nitrogen and the extra fuel (and air) to heat the nitrogen will increase the volume of the gas waste stream. If the water that is formed by the oxidation is condensed, the gaseous waste stream consists of only  $\text{CO}_2$ , nitrogen, and minor gas impurities; the volume of waste gas volume is reduced substantially.

Alternatively, most processes could use air enriched with oxygen or pure oxygen. Oxygen-enriched air and (essentially) pure oxygen are both commercially available, are transportable or producible on site, and would represent relatively insignificant cost in the scheme of overall program costs. Thus, tradeoffs of using oxygen versus air are determined largely by the impacts on selected processes and by the gas storage volume required to certify the gas for release.

Generally, the processes that benefit the most from the use of more concentrated oxygen are those that rely on more expensive equipment; with smaller gas volumes, less equipment is needed. For example, wet air oxidation might use a 50:50 mixture of air and oxygen, whereas supercritical water oxidation is designed to use pure oxygen. However, other processes would also benefit substantially if the volume of stored waste gas could be substantially reduced.

Other technical factors must also be considered when substituting oxygen for air. For example, the nitrogen in air provides a dilution that usually aids in avoiding hot spots in oxidation equipment. It may provide additional mass and energy to assist in the initial atomization or dispersion of the agent and any supplemental fuels, and it provides a larger gas volume that acts as a cushion in the event of puffs caused by the nonuniform oxidation of explosives or propellants.

One method tested at the pilot stage for the use of oxygen in combustion furnaces involved substituting recycled flue gas for the nitrogen eliminated from the oxygen feed stream (MRK, Incorporated, 1992). This approach requires additional equipment for temporary flue gas stream surge capacity, recycle blowers and ducting, and redesign of the burners and furnace to reflect the different characteristics of the recycled flue gas, which is primarily

CO<sub>2</sub>, water vapor, and nitrogen. However, flue-gas recycle does provide a solution to problems that might occur if pure oxygen were used.

A modification of the flue-gas recycle method was commercialized recently (Ho, 1992). In this method, a modified fuel-and-oxygen burner injector uses the kinetic energy of the oxygen feed stream to induce internal burner-gas recirculation by aspirating internal combustion gas through the burner nozzle head. This method is reported to avoid hot spots and could presumably be used to atomize liquid agent (atomization is not done currently by pressurizing the agent, to avoid various pressure-related agent contamination problems). Heat extraction to control flame temperature is necessary in this approach. This function is normally achieved in demilitarization systems through the design of furnace and boiler combustors. The lower gas flow in the alternative approach would provide less dilution to manage puffs, but capture of puffs of organic compounds in the waste stream on activated carbon or in gas storage would still be effective.

An additional consideration is that although oxygen is produced and used in many commercial operations, the production, transport, storage, and feed introduction steps all involve a degree of additional hazard until the oxygen has been diluted. Pure oxygen significantly changes the combustion characteristics of many materials compared with their combustion in air, requiring special organic-grease-free valves and other precautions against combustion conditions. Additional worker hazards include oxygen being easily trapped in the void spaces of woven clothing and contributing to clothing fires that would not normally be expected. Standards for these requirements are well developed and available but must be rigorously implemented for safety.

### **Waste Gas Storage Requirement**

Although the retention of liquid and solid waste streams until they are certified for disposal should not generally be a technical problem, the retention of large-volume gas waste streams is common practice. However, the extreme toxicity of the chemical agents and the proximity of some stockpile sites to highly populated areas prompts consideration of storing waste gas until analyses establish that agent and other toxic materials in air are suitable for discharge. All alternative technologies in which oxidation to CO<sub>2</sub> occurs will produce some gas waste stream, so the need for storage and certification is universal. If all gas waste streams must meet the same requirements, the choice of storage technology will depend on the ability to meet the specifications for gas composition reliably and efficiently. In all cases, afterburners should be used to ensure that toxic materials in air are below permissible concentrations under normal operating conditions. However, gas volumes can vary over a wide range. The smallest volume results when oxygen

is used and  $\text{CO}_2$  is removed by lime and the greatest volume results with the baseline design, in which air is used to burn agent and to burn the fuel added to the process stream to heat the furnaces and afterburners. Minimizing gas volume, and thereby reducing storage volume requirements, results in higher concentrations of toxic material for a given fractional destruction (such as 99.9999 percent destruction of original material), which would provide some improvement in the reliability of detecting residual toxics. Atmospheric dispersion of the leaving gas stream would depend on use of a large gas jet, and mixing with additional air might be needed. Gas reheat may also be required to ensure that the effluent stream is buoyant and will rise to an effective dispersion altitude in the atmosphere.

The volume of gas that must be stored depends on many factors, including the plant processing rate, the amount of gas produced per unit of agent processed, and the certification and plant shutdown time (see [Chapter 4](#)). A genetic unit gas storage volume has been developed based upon the following assumptions:

- consideration of the liquid agent stream only: separate calculations will be required for those processes that treat the metal parts or other components;
- a liquid GB agent destruction rate of 100 pounds per hour (see [Chapter 4](#)): greater or lesser rates of operation can be scaled directly from this number;
- full oxidation of all carbon to  $\text{CO}_2$  assuming 20 percent excess air and no supplemental fuel used internal to the process: the water formed by oxidation of the hydrogen in agent is condensed so that it is in equilibrium with an exit gas stream that has been cooled to 120°F; and
- a minimum 1-hour storage time for certification and plant shutdown, if needed: use of longer storage periods would proportionately increase the amount of gas to be stored.

The above assumptions result in an estimated total gas volume for temporary storage of approximately 11,500 cubic feet. Use of an 8-hour storage cycle, which would allow more time for detailed analysis and operating decisions, would increase this volume to 92,000 cubic feet. In the event that pure oxygen rather than air is used as the oxygen supply, the similarly derived estimate is about 1,150 cubic feet for a 1-hour cycle. For the JACADS liquid incinerator, the storage volume for a 1-hour cycle would be 350,000 cubic feet. This larger volume results from the high feed rate (of 750 rather than 100 pounds per hour), the use of almost 300 percent excess air, and the use of some air to burn fuel for additional heat (SRI, 1992).

### Storage and Retention Technologies

Several such gas storage or retention technologies are possible, including large atmospheric gas holders, smaller pressurized tanks, and systems that either absorb or solidify the CO<sub>2</sub> with separate CO<sub>2</sub> storage in solution or as a solid. If the captured gas does not meet requirements for concentration of toxic materials in air and agent, it would be recycled to the afterburners or to a charcoal filter. If agent contamination occurs in the gas holding system, decontamination will be needed. Facilities for this purpose must also be provided. Care must also be taken to provide good mixing of the captured gas to ensure representative sampling; this mixing could be accomplished with fans. Thus, although such technologies are commercially available, they would need to be carefully analyzed for this storage application, especially regarding cleanup of the storage system, including its piping and valves, if it became contaminated through the storage of a contaminated gas waste stream.

*Near-atmospheric gas-holding tanks.* Very large, near-atmospheric-pressure gas holders are proven technology. They were used by the natural gas and related industries for many years before becoming popular for use in other gas storage. These systems use concentric vertical cylinders that telescope to expand or contract the tank volume as needed. Because the bottom cylinder is stationary on a flat foundation, systems using only two concentric cylinders are called single-lift systems, and systems using three or more are called multiple-lift systems.

The movable cylinders, or lifts, are usually partially supported by counterweights to adjust the internal pressure relative to atmospheric pressure (usually a few inches of water difference). Several types of seals have been used between these moving cylinders. Two positive seal systems are described here for possible use in chemical demilitarization, the water seal and Wiggins (bellows) seal types.

The water seal type uses an inverted tub with sides extending down into the water-filled space in between the two walls of a double-walled bottom cylinder. The water makes the seal. The largest such single-lift unit has a usable capacity of 350,000 cubic feet (10,000 m<sup>3</sup>). One such unit is currently being constructed for a chemical manufacturer. Multiple-lift units have been built with usable capacities of up to 10 million cubic feet. These units are reportedly reliable and do not leak. However, they may result in contaminated water, requiring a water purification system, depending on their use (Bronson, 1992).

The Wiggins (bellow) seal type uses two vertical concentric cylinders with a large connecting membrane of rubberized canvas that allows the inner cylinder to rise as gas is added. The top section is counterweighted to control

gas pressure. Patent rights are held by Brown Minneapolis, which sells units of up to 2 million cubic feet capacity (Liljegren, 1992).

The maximum sizes mentioned above are more than adequate for use in demilitarization facilities.

*Gas holder safety.* Gas-holding tanks were safely used for many years to temporarily store town gas (mostly CO and H<sub>2</sub>) for both residential and industrial uses. They were then used to store natural gas (CH<sub>4</sub>) until natural gas storage in pipelines or underground storage became more economical. Today, these tanks are still used to store industrial gases.

Although there is the potential hazard of releasing the stored gas through an accident such as an airplane crash or catastrophic tank failure, the relative hazard from the sudden release of warm flue gas, with its large nitrogen content, is likely to be significantly less than for similar releases of town gas or methane. The hazard that gas containing chemical agent would be released is quite remote, being dependent on the simultaneous occurrence of a major external accident and an internal plant failure.

*Pressurized gas storage.* Large tanks capable of holding five atmospheres of pressure (75 psig) are common in industry. Under these circumstances, the gas storage volume needed for chemical demilitarization would be reduced by 80 percent.

*Gas absorption and solidification.* If oxygen is used instead of ordinary air (with essentially complete oxidation of carbon compounds to CO<sub>2</sub>) and all acid gases are removed from the flue gas with a water scrub that also condenses the newly formed water to the saturation level of a normal cooling tower system, then the flue gas should consist primarily of CO<sub>2</sub> saturated with water vapor. The water vapor can be further reduced by refrigerant cooling, and the CO<sub>2</sub> can be removed by conventional CO<sub>2</sub> absorption or solidification processes used by the CO<sub>2</sub> manufacturing industry. The CO<sub>2</sub> can also be reacted with lime, Ca(OH)<sub>2</sub>, to form calcium carbonate, which would be suitable for landfill disposal.

### **Activated-Carbon (Charcoal) Adsorption Systems**

The above-described methods store effluent gases from dynamic process systems to allow certification of the suitability of the gases for discharge to the environment. An alternative solution to ensure such suitability would be to use one or more static systems in a final gas cleanup step before gas discharge. One such system would be to pass all effluent gas through a charcoal adsorber (the method used in gas masks) before discharging the gas.

Charcoal filters are in commercial use and have been used at Army facilities to remove trace quantities of impurities, including chemical agent, from building ventilation air. This technique is sometimes used in inlet air systems to ensure a dean air supply to the control room and other critical working areas if an accident contaminates incoming ventilation air.

Charcoal filters usually are box-like structures that hold beds of granulated charcoal (or other activated carbon) through which a gas waste stream is forced. Several sequential beds are generally used to provide backup for when the first beds are saturated with impurities and to allow replacement of beds without disturbing the backup beds. Flexible piping and valves may also allow bed switching. This sequence of beds provides adequate time for chemical analysis and certification of the leaving gas stream before saturation results in breakthrough of contaminants, a feature in common with the gas storage system discussed earlier.

The charcoal or activated carbon selectively adsorbs certain types of molecules onto the internal surfaces of tiny pores and interstices of the granules, with the type and amount of such adsorption depending on the method of charcoal production and/or activation and on the concentration of the impurity being adsorbed. Typically, activated carbon will not strongly adsorb oxygen or nitrogen but will adsorb polar compounds, hydrocarbons, water vapor, and CO<sub>2</sub>. Although the presence of large quantities of water vapor and CO<sub>2</sub> will tend to saturate the adsorption surfaces, they are displaced by larger molecules. (The gas must be dried to avoid the presence of liquid water or condensation.) The chemical agent will be strongly adsorbed in the first section until saturation is reached and breakthrough occurs. Replacement of sections is necessary when breakthrough is observed in the backup sections (Ward, 1992).

The disposal of contaminated filter sections can be accomplished either by combustion or by direct burial in a landfill. The baseline metal parts and metal deactivation kilns might, with some modification, be used for this purpose. Entrainment of partly burned charcoal is expected to be a problem in the rotary kiln; however, severe heat treating and at least partial combustion of spent charcoal in trays passing through the traveling-grate metal parts kiln may be feasible. Any remaining charcoal would qualify for a 5X rating and landfill disposal.

Disposal of the spent charcoal would involve the following (Ward, 1992):

- The beds would be removed by methods that assume their contamination with chemical agent.
- The beds would be tested for agent by bubbling air through the spent section to see if any agent could be detected in the air stream. Normally none is detected because the agent is tightly bound to the adsorption surfaces of the charcoal.

- If no agent was detected, the spent charcoal would meet the 3X criterion and be bagged, transported to, and buried in a commercial hazardous waste landfill. A hazardous waste landfill would be required because the charcoal would be expected to contain small amounts of chemical agent, even though it could not be detected by air sampling techniques.
- Procedures would still need to be developed for handling any material that did not meet the 3X disposal criterion. These would include temporary storage with a slow flush of air (vented through the newly installed charcoal filters) to allow slow decomposition of the agent in the filters. This approach is reported to be effective for small quantities of nerve agent but has not been tried for mustard.

Charcoal filters could be used with both the baseline and alternative technologies. The Army and the NRC are now reviewing the possibilities and implications of using these filters on the gaseous waste streams generated by the currently used incineration technologies at the various chemical weapons storage sites.<sup>1</sup>

---

<sup>1</sup> This activity is being carried out by the NRC Committee on Review and Evaluation of the Army Chemical Stockpile Disposal Program.

## 6

### Low-Temperature, Liquid-Phase Processes

This chapter reviews several chemical, biological, and other processes designed to destroy chemical agents under low-temperature conditions, those from about 20°C to less than 100°C. The lower value is room temperature. The upper value allows the use of aqueous systems at atmospheric pressure to minimize the risks of leakage of high concentrations of agent from pressurized autoclaves.

Three main types of low-temperature, liquid-phase processes are reviewed below: processes for detoxification, processes for oxidation of organic residue, and biological processes.

Detoxification processes have been the most intensively studied. They offer promising approaches for all three major agents in the U.S. stockpile (GB, VX, and H). This set of processes includes chemical processes and the use of ionizing radiation for detoxification.

In addition to detoxification by conversion of agent to other compounds, demilitarization requires the process to be essentially irreversible (see [Chapter 1](#)). This requirement will, in some cases, require a two-step sequence of initial detoxification followed by further chemical processing, which could be accomplished with additional chemical reaction but would not require complete oxidation to carbon dioxide. Detoxification reactions that produce irreversible products are therefore of most interest.

Relatively little effort has been directed to achieving complete oxidation at low pressure and temperature. However, there are several leads in this direction, arising from studies of chlorinated hydrocarbon destruction and agent decontamination. In view of recent advances in synthetic and catalytic chemistry, the discovery of improved oxidation processes seems possible. The time pressure to develop these processes is less than for detoxification processes, because material detoxified to meet the treaty demilitarization requirements can be stored safely and in compliance with the international treaty, until an improved oxidation process is developed and tested.

Biochemical processes to destroy chemical agents have received relatively little study, and if they are to be used, both exploratory and basic



research will be required. The discussions of the three types of processes below reflect their developmental differences.

An advantage of these technological alternatives is that they generally permit highly controlled, dosed environments. Most of these approaches will involve minimal gas emissions, and are suitable for in situ analysis of the progress of the course of agent destruction. A variety of toxicological tests has indicated that the chemical hydrolysis products have very low toxicity, making it possible to effectively manage the waste streams resulting from most of these processes. There has been extensive study of the alkaline hydrolysis of nerve agent GB, and the chemical products have been identified.

Although the chemical and biological systems have a certain, inherent technological simplicity due to their mild environmental requirements, there are several important considerations common to all of them:

- There are various chemical specificities in the nature of the chemical or biological reactions that may limit their applicability to some of the contaminating ingredients of many stockpile elements.
- The gelatinous or insoluble nature of some of the stockpile material configurations may hamper their conversion.
- Each approach will result in a variety of process-specific reaction products with various levels of hazard that must be handled as separate waste streams in many cases.
- It may be necessary to sequence several processes, in some cases integrating chemical and biological technologies to adequately manage all of their reaction products.
- These low-temperature processes are generally not applicable to dunnage or the 5X decontamination of metal parts. Therefore, other processes would still be needed to handle these streams in the overall demilitarization system.

The implication is that alternative demilitarization chemical processes must be carefully tailored to meet the requirements for each agent. A readily available low-temperature, liquid-phase technology is unlikely to be appropriate for all of them.

### **CHEMICAL DETOXIFICATION PROCESSES**

A number of chemical processes that are known conceptually, experimentally, or in practice to destroy agent will (or can) run at moderate temperatures (between room temperature and 100°C) and at atmospheric pressure. Most of these processes are relatively simple to carry out and can be used in reactors commonly used in the chemical industry. Although no

single chemical treatment appears to destroy all three agents (GB, VX, and H), reactions to destroy all three could probably use the same basic equipment. However, parallel sets of some components may be desirable for each process because of differences in reaction rates, mixing conditions, and heating and cooling requirements.

A distinct advantage of these chemical processes is that they can be operated in batch mode, with complete containment during the process and opportunity to verify satisfactory agent destruction. The destruction level should satisfy treaty requirements and hazardous material requirements for subsequent on-site storage and transportation to another site. Alternatively, further on-site treatment could be used to complete oxidation. A small gas evolution is expected for acid chlorinolysis and other processes that use oxidizing agents. A further advantage of these low-temperature, atmospheric-pressure, liquid-phase processes is that leaks of lethal agents are less likely to occur than from pressurized equipment.

Although all these methods are generally effective for destroying the chemical agents of chief interest, they generate different waste streams. Some might yield chemicals now used in the civilian economy, but economically viable recovery is not expected.

By using some of the processes, relatively simple operations at each Army storage site could convert lethal chemical agents into material that meets demilitarization requirements. Such material could be managed according to standard practices for chemical waste. This approach would permit local storage or transport of the demilitarized material, of hazard no greater than that for industrial chemicals regularly shipped, to a central location where it could be processed by conventional waste treatment technology.

In the United States, research on the chemical detoxification of bulk agent for demilitarization was mostly discontinued in 1982, when the decision was made to use incineration. Fortunately, a research and testing program on decontamination techniques for battlefield use has continued and produced many advances in understanding and applying chemistry relevant to detoxification. An informative review was recently published (Yang et al., 1992).

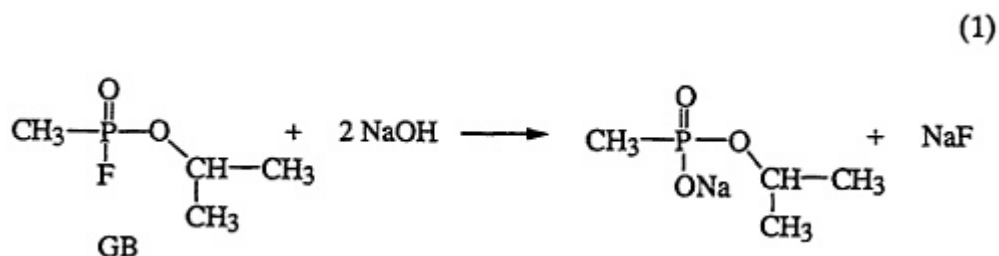
Battlefield decontamination systems face a number of constraints not directly relevant to demilitarization of bulk agents. They are restricted to ambient temperatures and the need to minimize damage to surfaces. In addition, speed and ease of operations are essential.

For bulk agent demilitarization, minimizing disposal problems is more important than for battlefield decontamination. Also, some chemical reactions that have not been found useful for battlefield decontamination might, under conditions of intense mixing and higher temperature, be useful for bulk agent detoxification.

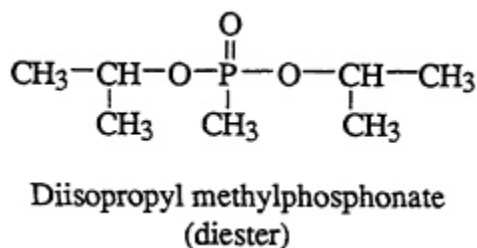
The following sections address the applicability of specific chemical processes to the agents of greatest interest.

### GB (Sarin)

*Reaction with sodium hydroxide in water.* The hydrolysis process in which GB (isopropyl methylphosphonofluoridate, or Sarin) is reacted with sodium hydroxide (NaOH) in water, a process often called neutralization, was studied intensively by the Army a decade ago (Eq. 1). Trial runs, including some at full scale, were conducted. On the basis of that experience, the process was abandoned in 1982 in favor of the current incineration technology. Major considerations were the large residue of hydrolysis products and problems encountered in scaling up the mixing of GB with aqueous NaOH solution (Flamm et al., 1987; Coale and DePew, 1992).



Large quantities of residual salts were formed because of the use of excess NaOH, which was used in an attempt to destroy GB completely. Although it is now evident that apparently incomplete reactions were analytical artifacts related to a diester impurity in GB, acceleration might be achieved by use of small amounts of catalysts, especially *ortho*-iodosobenzoate salts. The latter accelerate reactions of structural analogs of GB with sodium hydroxide (Moss et al., 1984). As to the problem of residual salts, use of just slightly more than enough NaOH to satisfy the requirements of the balanced equation (Eq. 1 above) should be sufficient.



In view of the high reactivity of GB with hydroxide ion in water (rate constant,  $k=23.7$  liter/mole/second), it is probable that solutions of ammonia or low-molecular-weight amines in water would effectively detoxify it (Gustafson and Martell, 1962). This would need to be verified by research. Note that use of  $\text{NH}_4\text{OH}$  instead of  $\text{NaOH}$  would change the nature of the waste stream from the process.

The products from reaction of GB with aqueous  $\text{NaOH}$  are only slightly hazardous and are suitable for shipment, storage, or further processing. They will contain some of the mentioned diester, a substance not very hazardous itself and a contaminant in stockpiled GB, but convertible to GB on reaction with hydrofluoric acid ( $\text{HF}$ ). Maintaining an excess of  $\text{NaOH}$  is therefore indicated. Although discontinued by the Army in favor of incineration (Flamm et al., 1987), this process has been used in the United Kingdom and other countries to destroy relatively small stocks of GB (see [Chapter 3](#); Manley, 1992a, b).

The hydrolysis of VX and GB by  $\text{NaOH}$  and  $\text{Ca}(\text{OH})_2$  is further discussed below.

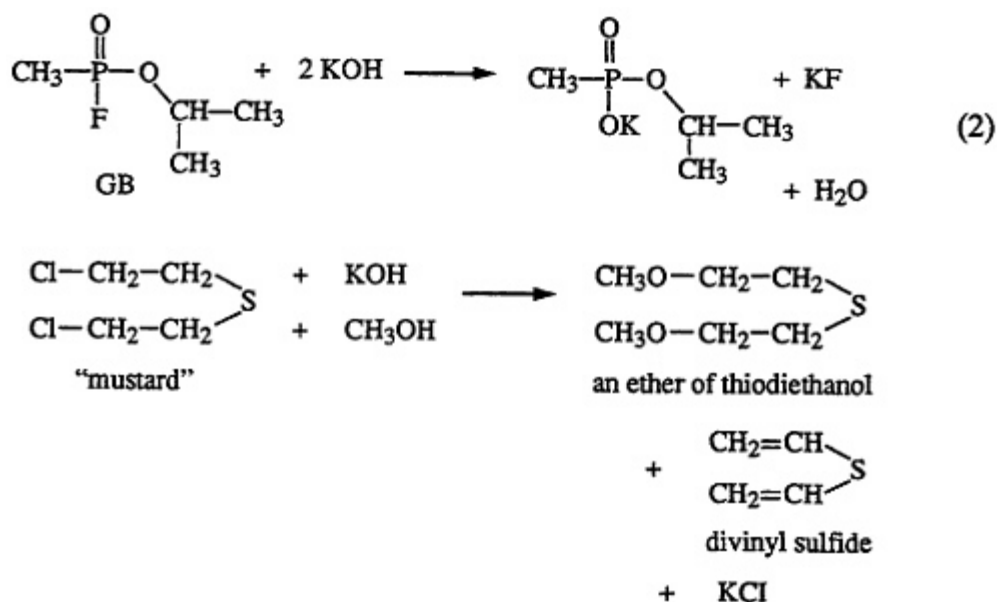
*Reaction with alkali in an alcohol* The process of reacting agent with alkali in an alcohol may also be called neutralization. In this process, agent is combined with a solution of  $\text{NaOH}$  or potassium hydroxide ( $\text{KOH}$ ) in an alcohol solvent. The alcohol may be methanol (McAndless, 1992a), 2-methoxyethanol (EPA, 1991), polyethylene glycol (Picardi et al., 1991), or (in principle) ethylene glycol. In Canadian experience, the solutions remaining after destruction of agents with  $\text{KOH}$  in methanol were then incinerated (McAndless, 1992a).

Equation 2 shows the reactions that occur in this process. For H, or mustard, its reactions with  $\text{KOH}$  in methanol are shown; in other alcohols, the alkyl group in the ether (instead of  $\text{CH}_3$ ) would be that contributed by the structure of the alcohol.<sup>1</sup> The ratio of the ether product to divinyl sulfide will depend on conditions. In the case of GB, probably some replacement of fluorine by the alkoxy group of the alcohol (e.g., minus  $\text{OCH}_3$  with methanol) occurs, forming an intermediate that reacts further to form products of the type shown.

This type of process is suitable for destruction of GB and H. There are doubts about its suitability for destruction of VX. Although reactions with VX are fast (Durst, 1992; Yang, 1992a-d), it appears that a by-product is a highly toxic compound also obtained from reaction of VX with  $\text{NaOH}$  in water

---

<sup>1</sup> Most alcohols are composed of a hydroxyl group ( $\text{OH}$ ) attached to a group composed of carbon and hydrogen atoms, such as  $\text{C}_2\text{H}_5$  in the case of ethyl or grain alcohol. Thus, ethyl alcohol is  $\text{C}_2\text{H}_5\text{OH}$ .



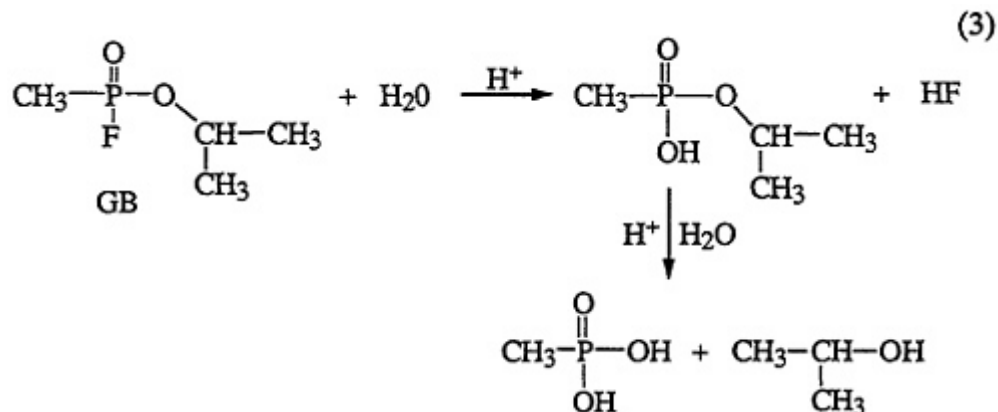
(Epstein, 1992a,b). This compound is described below in the discussion of VX hydrolysis.

Energetics such as TNT are expected to react with methanolic NaOH or KOH, to yield azoxy compounds (Hickinbottom, 1957). Similar reactions are expected with solutions of these alkalis in the other alcohols mentioned. Other energetics may also react, depending on their chemical structures.

The U.S. Army decontaminating agent DS2 is a solution of NaOH (2 percent) in 2-methoxyethanol (28 percent) and diethylenetriamine (70 percent). Its action is based on hydrolysis chemistry like that described here. KOH in 2-methoxyethanol is the active reagent in the proprietary DeChlor/KGME process (EPA, 1991), which, although intended for destruction of polychlorinated biphenyls (PCBs), should also be effective with GB and H. Solutions of KOH in polyethylene glycols are used in other proprietary processes to destroy PCBs and dioxins, such as the Galson and General Electric KPEG processes (Picardi et al., 1991). The reagents were developed to manage toxic materials (aryl chlorides) far less reactive than the agents H, GB, and VX. The general class of processes described here appears to be broadly applicable to agent destruction. A disadvantage common to these processes is the relatively large quantity of organic waste produced.

*Acid-catalyzed hydrolysis.* The rate of acid-catalyzed hydrolysis depends on the concentration of hydrochloric acid (HCl) or sulfuric acid and on the temperature. At a hydrogen-ion concentration of 1 mol/L (about 4 percent HCl in water), the half-life of agent is 138 minutes, which implies 99.9999

percent destruction in 27.6 minutes at 25°C (77°F) (Epstein, 1992b). This rate pertains to the first stage of reaction shown in Equation 3; the second stage is thought to be slower. (Its rate constant needs to be determined.) The products of the first step lack the enormous toxicity of GB. In principle, hydrolysis of diisopropyl methylphosphonate (the diester of structure shown above) should also be catalyzed by acids, but the actual reaction rate appears not to have been measured.

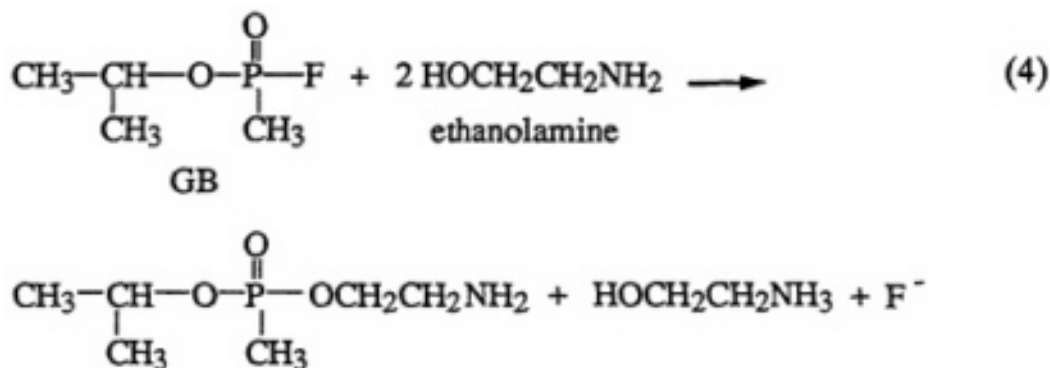


GB undergoes some spontaneous hydrolysis in water. The acid product, HF, would be expected to accelerate the hydrolysis. It is therefore conceivable that dissolving GB in water and letting it stand for considerable time would allow the spontaneous reaction and ensuing autocatalysis to completely destroy the GB. A preferred alternative would be to recycle the HF-containing hydrolysis products to eliminate the need for adding other acids. A second reactor would be needed to serve as a source of acid and to attain the desired level of agent conversion. A possible disadvantage of acid-catalyzed hydrolysis is that corrosion of process equipment is likely to be more severe than for reaction of GB with aqueous NaOH.

The chemical reaction described in Equation 3 is well known from laboratory studies (Epstein, 1992a,b). Additional laboratory work should be conducted to determine rate constants for diester hydrolysis and the second stage of GB hydrolysis, to allow comparison with the rate constant for reaction with NaOH and to form a basis for pilot plant work if this alternative is to be pursued.

*Reaction with ethanolamine.* When dissolved and heated with ethanolamine (a commercial product), GB reacts to form products of lower toxicity that are suitable to store or ship for further processing (Eq. 4). Because the products contain a diester, further processing to destroy the

diester or to remove HF is necessary to prevent formation of GB from reaction of HF with the diester.

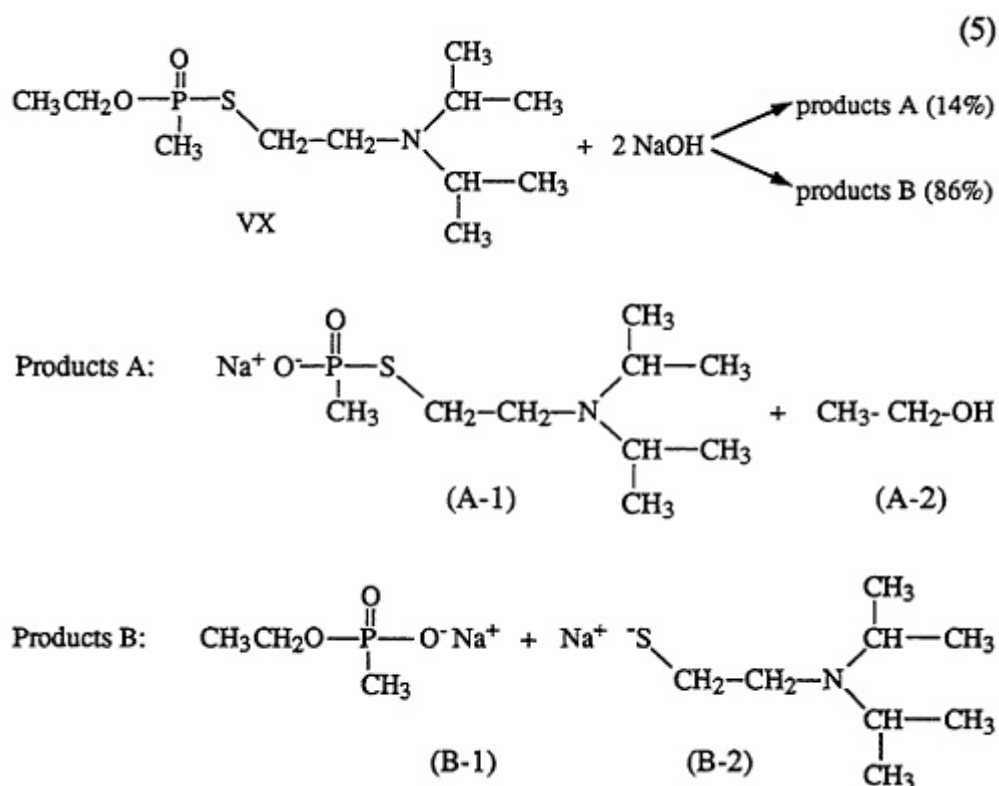


Advantages of this process are that the volatility of GB is much reduced when GB is dissolved in ethanolamine, that the reaction occurs cleanly as depicted (Greenhalgh and Weinberger, 1967), and that the corrosion of process equipment is minimal. Its principal disadvantage is the total amount of organic material produced, which will require further treatment. The nitrogen content is expected to increase the production of nitrogen oxide compounds on final oxidation.

This methodology was used by Soviet authorities to destroy about 200 tons of nerve agents in faulty chemical munitions that contained no explosives (Leonov, 1991). The committee is unaware of any American pilot plant studies. It has also been found useful for HD detoxification (see later section on mustard).

## VX

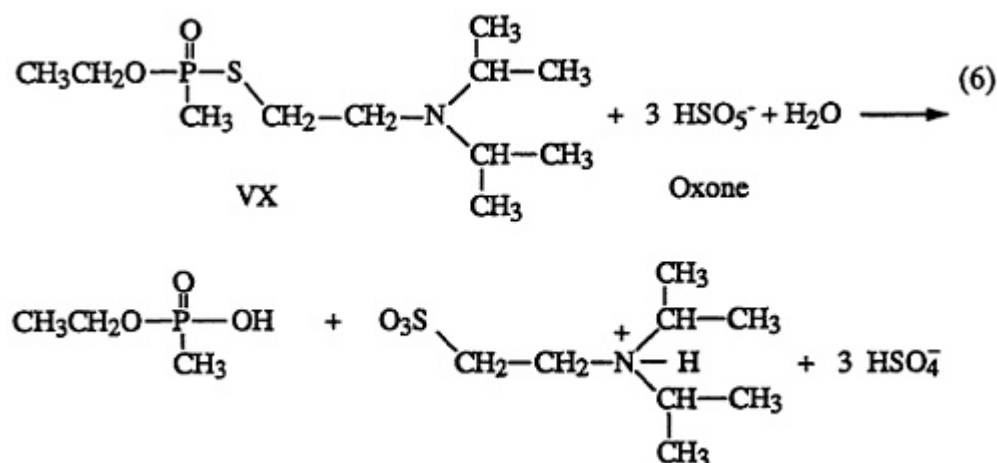
*Reaction with NaOH with and without hydrogen peroxide, in water.* VX reacts with aqueous NaOH (Eq. 5), but the resulting product A-1 is very toxic—nearly as toxic as VX—when administered intravenously to rabbits (Yang et al., 1990b). Further hydrolysis of product A-1 should be achievable, possibly at more severe conditions or through use of catalysts or improved hydrolysis systems. Addition of hydrogen peroxide ( $\text{H}_2\text{O}_2$ ) to aqueous NaOH was recently found to avoid formation of product A-1 and to give the same products shown for reaction of VX with the commercial product OXONE® (Eq. 6) followed by neutralization by the NaOH present (Yang, 1992c). The combination of NaOH and  $\text{H}_2\text{O}_2$  reagent might be effective for the detoxification of GB, but the committee does not know of any research specifically on this subject.  $\text{H}_2\text{O}_2$  is relatively inexpensive and its residue after reaction is water.



*Reaction with oxidizing agents in acid solution.* VX is rapidly detoxified by several oxidizing agents, of which chlorine in aqueous acid (acid chlorinolysis) and OXONE are of interest for demilitarization purposes. Equation 6 shows the reaction of VX with OXONE, which is a mixture of  $\text{KHSO}_5$ ,  $\text{KHSO}_4$ , and  $\text{K}_2\text{SO}_4$  in 2:1:1 molar proportions (Yang et al., 1992a). The reactions in acid chlorinolysis and in oxidation with  $\text{H}_2\text{O}_2$  in aqueous NaOH share an important characteristic with the OXONE reaction, namely, that the P—S bond is broken and products of reduced toxicity are formed.

Although these oxidative methods can all be effective for demilitarization, they differ in some attributes. Acid chlorinolysis and treatment with OXONE are conducted in a strongly acidic solution, which may encourage equipment corrosion. Chlorination involves use of chlorine gas, the first poison gas used in World War I but a common substance in most American communities, where it is used for chlorination of swimming pools and drinking water supplies. OXONE is a mixture of salts that, when combined with the salts of the acidic products of reaction with VX, would increase the waste stream for ultimate disposal.





### H (Mustard)

For H and other mustard agents, insolubility, inclusion of thickeners, and the formation of gels and solid deposits during long storage present problems in carrying out chemical detoxification. Possibilities for overcoming these problems will be discussed after the chemistry is considered.

*Hydrolysis of mustard.* Mustard agent in water solution hydrolyzes rapidly, but for demilitarization purposes the reaction is impaired by both physical and chemical factors. The physical problem is the extraordinarily low solubility of mustard in water. Investigators who have determined rate constants for mustard hydrolysis carried out their studies in mixed solvents, such as aqueous acetone (Bartlett and Swain, 1949; Yang et al., 1990c) or aqueous ethanol (Yang et al., 1987). The chemical problem is that the intermediate products are cyclic or oligomeric sulfonium salts, which are relatively unreactive and which moreover have the potential for slowly reforming mustard (Yang et al., 1990c).

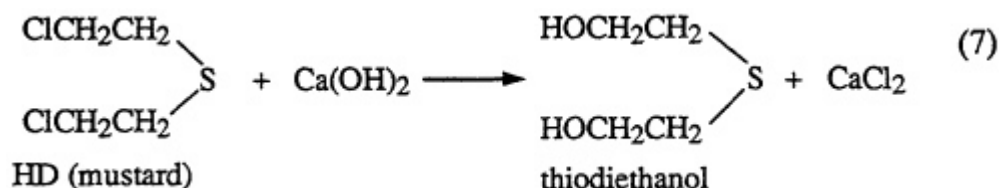
An estimate for the mustard hydrolysis rate constant at 90°C can be made, based on the enthalpy of activation ( $\Delta H^\ddagger$ ) of 18.5 kcal/mol reported by Yang et al. (1987) and on the rate constant  $0.261 \text{ min}^{-1}$  at 25°C tabulated by Ward and Seiders (1987). (They pointed out reasons to consider this value as being of uncertain quality.) The estimate is  $18.1 \text{ min}^{-1}$  at 90°C, or half-life 2.3 seconds. The actual hydrolysis reaction is thus very fast; if the solvent is just water, the rate-limiting step is the dissolution of mustard in water rather than the hydrolysis.

Formation of the troublesome oligomeric sulfonium salt can be avoided if a strong nucleophile is present in the water; hydroxide ion fulfills this role. In principle, it can be supplied either as NaOH or calcium hydroxide  $\text{Ca}(\text{OH})_2$ .

In NaOH solutions, mustard reacts with an initial (rate-limiting) internal displacement to form a cyclic sulfonium salt (Bartlett and Swain, 1949; Ward and Seiders, 1984). This reaction is then followed by further reaction with NaOH. However, the surface reaction of water on liquid mustard agent is reported to form a complex set of ionic products, which then diffuse into the bulk phase. Overall performance of this system has been rated as unsatisfactory for demilitarization purposes (Durst et al., 1988).

In contrast, reaction of mustard with  $\text{Ca}(\text{OH})_2$  in water at  $90^\circ$  to  $100^\circ\text{C}$  was reported (Reichert, 1975), although this reaction seems not to have been used for large-scale demilitarization. It was used in England to convert 125-gallon batches of HD (mustard) to thiodiethanol in an apparatus not much more complicated than a tub (Eq. 7).

The committee considers this method to be very promising but advises further study before any use is made of it.



*Reaction with oxidizing agents.* HD can be oxidized in the liquid phase by several strong oxidizing agents. All of these reactions are limited by HD's low solubility in water. Approaches to increasing the contacting between reactants include improving the physical dispersion and forming microemulsions of HD.

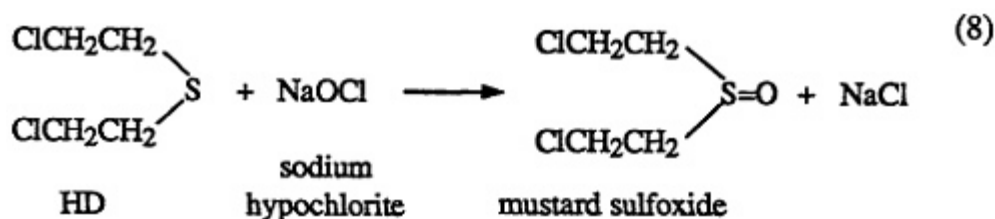
As discussed above, the rate of reaction at the HD surface appears to be fast enough to prevent significant diffusion of HD into the aqueous phase. Even though HD solubility may increase with temperature, corresponding increases in reaction rates may still prevent penetration into the aqueous phase of dissolved HD. Regardless of the specific mechanism, overall reaction rate will be controlled by the HD-liquid surface area.

Mechanical emulsification (as in milk homogenization) can reduce droplet size to a few micrometers, forming a very large surface area (about  $5 \text{ m}^2/\text{gram}$ , for a droplet of  $1 \mu\text{m}$  in diameter). Work on physical dispersion should be an important component of a program on liquid-phase detoxification of HD. The need for dispersion with gelled or solidified agent should also be included in such a program.

A surfactant and a cosurfactant (such as butyl alcohol) in proper proportions, along with a hydrocarbon, readily form an emulsion with HD so freely dispersed that it appears clear. A compound less toxic but very similar to mustard ( $\text{CH}_3\text{CH}_2\text{SCH}_2\text{CH}_2\text{Cl}$  instead of  $\text{ClCH}_2\text{CH}_2\text{SCH}_2\text{CH}_2\text{Cl}$ ) was found

to react rapidly with sodium hypochlorite in microemulsion (Menger and Elrington, 1991). The half-life of reactant was about 3 seconds at room temperature. This method for bringing mustard into effective contact with sodium hypochlorite suffers a disadvantage in that the amount of the waste streams generated is increased. A typical microemulsion is composed of about 50 percent water and 50 percent organic compounds.

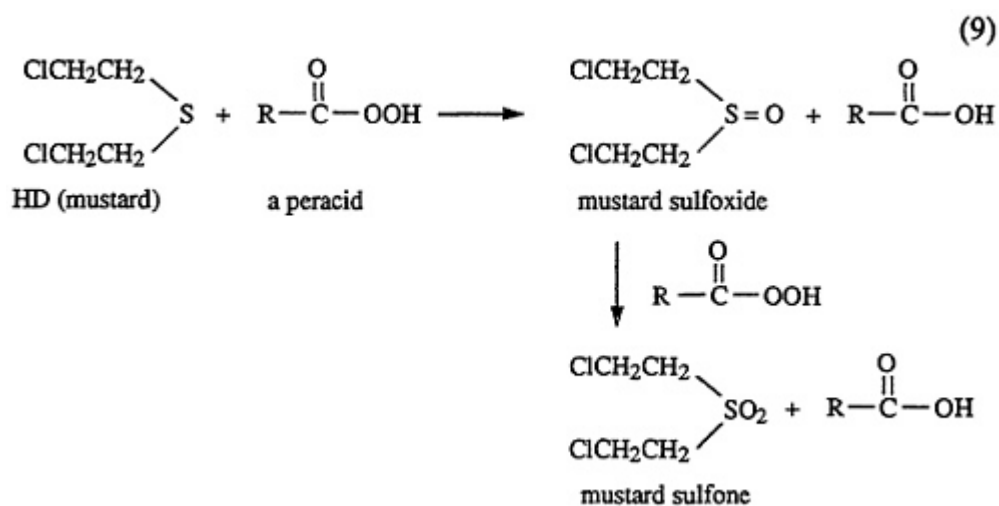
*Reaction with sodium hypochlorite.* Mustard reacts readily with hypochlorite ion to form oxidation products of reduced toxicity. This chemistry has been used for decontamination since World War I (Eq. 8). As in NaOH hydrolysis, an impediment is the low solubility of mustard in water. Although hypochlorite salts are water soluble, a water solution of sodium hypochlorite, although good for decontamination of thin layered spills, can make such poor contact with bulk HD that very little reaction occurs.



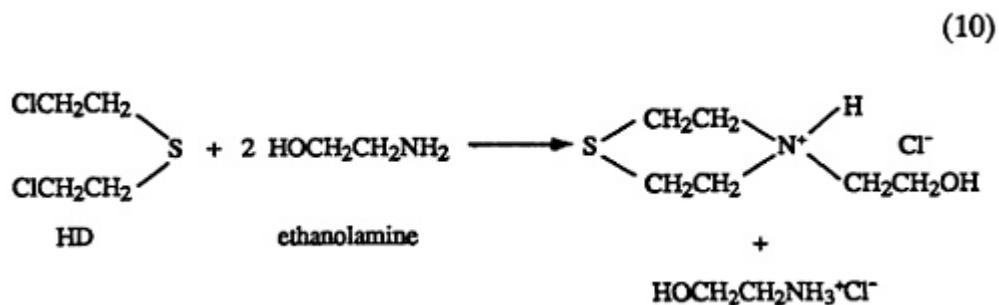
*Reaction with peracids.* Mustard is very rapidly oxidized by *m*-chloroperbenzoic acid, at a rate described as "too fast to measure" (Yang, 1992c). The products are both mustard sulfoxide and mustard sulfone (Eq. 9; in the equation, R is generalized notation for part of a molecule). However, *m*-chloroperbenzoic acid is a moderately expensive laboratory chemical; moreover, if it were used, the by-product RCOOH would be *m*-chlorobenzoic acid, a product requiring further conversion.

The use of ammonium peroxydisulfate in strong acid at 100°C for complete oxidation of the mustard surrogate thiodiethanol was reported (Cooper, 1992). This treatment would probably detoxify HD as would OXONE. Operation at 100°C, as for calcium hydroxide hydrolysis, may greatly increase the effectiveness of these and other reactions involving oxidizing agents.

Other oxidizing agents of interest include a variety of peroxy acid salts and H<sub>2</sub>O<sub>2</sub>. H<sub>2</sub>O<sub>2</sub> is of special interest because it is inexpensive and has water as its sole by-product. OXONE, persulfuric acid, and other peracids are commercially available and could probably also be used. Safety and performance need to be established.



*Reaction with ethanolamine.* HD reacts rapidly with ethanolamine (Eq. 10) to give products of reduced hazard (Durst et al., 1988). Ethanolamine has been praised by these authors for its numerous advantages: "relatively high flash point, relatively non-toxic..., non-corrosive to metals, inexpensive, relatively stable." It will, however, also increase the oxidation load for final destruction and might generate undesirable quantities of nitrogen oxides in subsequent combustion processes.



#### Reduction Methods Conceivably Applicable to GB, VX, and H

Prominent among methods reported here are some that would effect reduction of GB, VX and/or H. Some of the conceivable reduction products (notably  $\text{Na}_3\text{P}$ ,  $\text{Na}_2\text{S}$ ,  $\text{PH}_3$ ,  $\text{H}_2\text{S}$ , and  $\text{CO}$ ) are very toxic and could not responsibly be discharged into the environment. Additional treatment to destroy them would therefore be implied.

*Reactions with reducing agents used in organic synthesis.* In recent decades, many powerful or specific reducing agents have been found to be very useful

in organic synthesis. These include  $\text{LiAlH}_4$ ,  $\text{NaBH}_4$ ,  $(\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2)_3\text{SnH}$ ,  $\text{HPO}_2$  and tris(trimethylsilyl)silane (Ballestri et al., 1991). Plausibly, some or all of these can destroy GB, VX, and H, but to the committee's knowledge, this has not been demonstrated through research.

*Reactions with sodium in liquid ammonia.* Liquid ammonia ( $\text{NH}_3$ ) boils at  $-33^\circ\text{C}$ , far below the freezing point of water; special arrangements to contain it are necessary. It is widely used in the United States, mostly as fertilizer but also as a solvent in the chemical industry, which is experienced in its handling.

Sodium metal (Na) is soluble in liquid ammonia, and is a very strong reducing agent, easily cleaving carbon-halogen and carbon-sulfur bonds in molecules, as well as many other chemical bonds. Although the committee is unaware of studies of the action of Na in liquid  $\text{NH}_3$  on the chemical warfare agents in the U.S. stockpile, it believes that all the agents would be cleaved by Na in  $\text{NH}_3$  to form products of low toxicity. Also, they might be detoxified by reaction with  $\text{NH}_3$ . Before plans to use this methodology to destroy agents were made, these expectations would need to be confirmed by laboratory studies. If either expectation is fulfilled, pilot plant work could then be able to move rapidly forward, making use of well-known industrial equipment and techniques.

*Other methods involving use of sodium metal* Methods to dechlorinate polychlorobiphenyls and oligochlorodibenzodioxins by means of sodium metal have been developed. Picardi et al. (1991) suggested that these methods would also be useful for destroying CW agents. No doubt they would destroy the agents, although confirming would be needed before any of these methods could be seriously considered for large-scale use. An additional consideration is that all these methods involve an organic solvent (e.g., naphthalene-containing oil, tetrahydrofuran, amines) that would be unsuitable as such to release into the environment. Furthermore, they would probably form toxic compounds with phosphorus or sulfur, as mentioned above.

### DETOXIFICATION WITH IONIZING RADIATION

The use of penetrating ionizing radiation, including X-rays,  $^{60}\text{Co}$  gamma radiation, and radiation from spent nuclear fuel elements, to rearrange chemical structure of compounds is being actively investigated (Matthews, 1992; see Appendices F and I). The current program for use of ionizing radiation is focused on chlorinated hydrocarbons. However, the approach could probably also be applied to weapons containing chemical warfare agents. This process could occur within loaded weapons, such as artillery

shells, land mines, and rocket warheads, that contain agent and therefore could potentially detoxify agent before removal from the weapon.

Treaty requirements for demilitarization will likely require a high level of detoxification and also disassembly and destruction of the weapon. It is unclear whether the technique described here offers advantages over the currently planned disassembly and detoxification sequence in which very large quantities of agent must be greatly detoxified. This alternative technique could, however, offer some potential for managing small numbers of found weapons when transportation to a central demilitarization facility is prohibited.

### LOW-TEMPERATURE AND LOW-PRESSURE OXIDATION PROCESSES

The preceding discussion of detoxification was limited to systems that accomplish this goal by breaking such specific chemical bonds as P—S and C—Cl, thus destroying the structure and consequently the extreme toxicity of chemical warfare agents. Although such processes destroy the military utility and major risks of agent release during continued storage, further conversion may be required to meet the irreversibility criterion of the Chemical Weapons Convention (see [Chapter 1](#)). Ideally, the remaining material should then be completely oxidized, with all carbon converted to CO<sub>2</sub>, carbonates, or other innocuous carbon forms for final disposal. This section discusses possible methods for achieving this step under low-temperature and low-pressure conditions. These methods are also generally capable of detoxifying agent (some have been mentioned in preceding sections).

All these methods rely on oxygen-containing compounds that have demonstrated significant oxidation ability at low temperatures (up to 100°C). For oxidation of the more refractory residues, most of these oxidizing agents require an additional source of energy to increase reactivity at such low temperatures. Relevant research on ultraviolet (UV) radiation used for the treatment of contaminated water is discussed below, as is research on active species electrochemically generated with molecular oxygen. Biochemical oxidation, which is of interest for the oxidation of detoxified organic mixtures, is discussed in a final section.

#### Chemical Oxidation

Some chemical oxidizing agents of interest include peroxydisulfate salts, organic peroxy compounds, chlorine dioxide, H<sub>2</sub>O<sub>2</sub>, and ozone. The ongoing battlefield decontamination studies mentioned earlier, and the very active

search for cleanup techniques for water contaminated with chlorinated hydrocarbons are both relevant to destruction of bulk agents and their detoxified by-products. Little work has actually been done on these applications, however.

Lawrence Livemore Laboratory has proposed the use of electrochemically generated peroxydisulfate salts for detoxification and for completion of the oxidation process (Cooper, 1992). These salts can be purchased commercially. At 100°C, 98 to 99 percent oxidation of surrogates for products of agent detoxification were oxidized (to CO<sub>2</sub>) in 3 minutes. This reaction is routinely used for elemental analysis; however, for some refractory materials, such as esters and carboxylates, a catalyst is used to ensure conversion. Catalysts include Co (III), Ag(II), and UV light. Use of peroxydisulfate salts as an oxygen source produces a very large waste stream of sulfate and sulfuric acid (about 30 times the weight of the original agent). Recycling the sulfate and sulfuric acid for electrolytic regeneration is proposed by the investigators of the process. Peroxydisulfate is manufactured by electrochemical oxidation; however, systems development for removal of undesired by-products containing phosphorus and halogens will be needed.

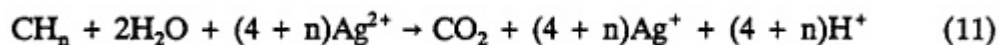
Because of its low cost, availability, and lack of troublesome residue, H<sub>2</sub>O<sub>2</sub> is an attractive candidate. However, it requires activation for this use. Fenton's reagents (H<sub>2</sub>O<sub>2</sub> catalyzed by iron or cobalt) are standard laboratory reagents for oxidation and are of considerable current interest for possible use in contaminated water and soil cleanup (Sun and Pignatello, 1993). For this application these compounds' strengths and limitations need to be established. Interference by halogen and phosphorous compounds and the ability to oxidize refractory organics are important considerations. Cooper (1992) suggested that use of Fenton's reagents followed by peroxydisulfate oxidation could be an optimal combination.

### Electrochemical Oxidation

Electrochemical oxidation of organic waste compounds is being studied for application to wastes from isotope separation and to sites where groundwater contamination has occurred (see [Appendix J](#) for a more detailed discussion). Although chemical intermediates are synthesized commercially through direct oxidation, the mediated electrochemical oxidation (MEO) process appears to be that most applicable to oxidation of chemical warfare agents and their organic by-products. The potential for completion of oxidation is of interest; however, a combination of detoxification and complete oxidation is probably also feasible.

The MEO process generates reactive ions such as Ag<sup>2+</sup>, Co<sup>3+</sup>, or Fe<sup>3+</sup>, which can react with an organic compound and water to produce CO<sub>2</sub>.

Equation 11 is an idealized equation, neglecting possible by-products and losses at the anode.

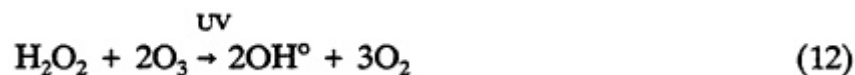


The hydrogen ions form hydrogen gas at the cathode. The oxidation can take place in bulk solutions either in a separate chamber or in the cathode chamber. The three metals identified above have been of greatest interest. Silver is the most active but will form insoluble AgCl if mustard is treated and may precipitate out. The solubilities of the phosphates, fluoride, and sulfate salts formed appear to be sufficient so as to cause few if any problems. Cobalt and iron salts are believed to be sufficiently soluble and would be used to avoid salt precipitation when treating mustard. The oxidized solution leaving the cell contains the mediating metal, which, for silver and cobalt, would require separation and recycling. Iron is not believed to present a special disposal problem and is relatively inexpensive, so that recycling may not be required.

Iron and cobalt, however, are relatively inactive for oxidation of the more refractory compounds such as organic compounds containing carbonyl groups. It appears that a substantial R&D and systems design program would be required to establish the performance of this technique with the three agents and their products of chemical detoxification.

### Oxidizing Agents Plus UV Light

UV radiation is capable of decomposing ozone ( $\text{O}_3$ ) or  $\text{H}_2\text{O}_2$  to hydroxyl radicals ( $\text{OH}^\circ$ ) that are capable of oxidizing most organic compounds. For a mixture of 2:1  $\text{O}_3:\text{H}_2\text{O}_2$  the stoichiometry is shown below:



In a high-pH solution in the presence of UV light, ozone will also react with  $\text{OH}^-$  to form the reactive radical  $\text{OH}^\circ$  (EPA, 1990).

Oxidation potentials provide a measure of oxidizing power, as indicated by [Table 6-1](#). The hydroxyl radical is seen to be exceeded only by fluorine.

Several processes have been developed by Ultrox, Halliburton NUS, Perox-Pure, Illinois Institute of Technology Research Institute, and others (Picardi, 1991; EPA, 1991) to treat water contaminated with a variety of organic compounds, including phenol and chlorinated solvents. Water flow rates have ranged from 10,000 to 1.3 million gallons per day. The contaminants have generally been found in concentrations of a few parts per



million or less. Electrical energy has been used to generate the ozone and UV light.

TABLE 6-1 Oxidation Potential of Different Chemical Species

Oxidation Species	Potential <sup>a</sup>
Fluorine	3.06
Hydroxyl radical	2.80
Atomic oxygen	2.42
Ozone	2.07
Peroxydisulfate	2.06
Chlorine dioxide	1.96
Ag <sup>2+</sup>	1.98
Peroxymonosulfate	1.98
Hydrogen peroxide	1.77
Perhydroxyl radicals	1.70
Hypochlorous acid	1.49
Chlorine	1.36
Ferric ion	0.77

<sup>a</sup> At 1M hydrogen ion concentration. The potentials change with pH.

The committee found no information on the treatment of concentrated organic wastes or chemical warfare agents. The best application of this technology would appear to be for final treatment of dilute solutions after bulk destruction and oxidation have been accomplished by other means.

**BIOLOGICAL PROCESSES**

**Introduction and Overview**

The use of biological processes to destroy chemical warfare agents is at an early stage of development (Ward, 1991; Harvey and DeFrank, 1992; Landis and DeFrank, 1991). Biological processing may be useful in detoxifying neat organophosphorus nerve agents and in destroying the reaction products from initial chemical detoxification of agents. In general, biological systems

are most appropriate for processing dilute aqueous solutions.<sup>2</sup> One of the most important issues about the applicability of available systems to chemical demilitarization is whether biological processes or biochemical reactions can be developed into functional engineering processes.

The most promising potential applications of biological processes to chemical demilitarization appear to be the following:

- direct detoxification of stockpiled organophosphate nerve agents using cellular or enzyme-based reactions (potentially applicable to GB and VX but not to sulfur mustard agents);
- biodegradation and mineralization of reaction products from chemical destruction of the nerve agents GB and VX;
- biodegradation of thiodiglycol or other products from hydrolysis or chemical oxidation of mustard (H); and
- biodegradation used as a final polishing process for aqueous effluents from other detoxifying processes, such as chemical or thermal oxidation.

The first two applications use biological processes in the primary detoxification stream or in secondary processing streams. They would entail the modification and integration of large-scale fermentation and waste treatment technologies developed for other applications, but not for agent demilitarization (Irvine and Ketchum, 1989). If biological processes are used for initial detoxification of agents, the control and management of agent toxicity during fermentations or enzyme-catalyzed reactions would be of critical concern. For example, residual toxicity from the partitioning or sorption of agents onto microbial cell mass or immobilized enzyme support matrices must be considered. In addition, the capability of enzyme or cellular-based processes to completely degrade the agents (e.g., to greater than 99.99 percent destruction efficiency) has not been demonstrated in a practical reactor system. A final consideration is the characterization of gaseous, soluble, and solid by-products of the biological processes. These include waste cell mass (sludge), products of incomplete biological mineralization, and agent or reaction products potentially volatilized during process aeration.

---

<sup>2</sup> Dilution to 5 to 10 percent aqueous solutions is an initial estimate of the maximum concentration of dissolved organic substrates (reaction products from initial detoxification of chemical agents) in solution that would be biodegradable. This is based on previous work in biological treatment of high strength industrial waste waters (Enzminger et al., 1987; Lepore et al., 1989; 1990a,b; 1991). Initial biological treatment studies would need to define this upper concentration limit for the particular reaction products to be treated. This would be accomplished through toxicity inhibition by using a climated cultures.

Biologically based technologies used as alternatives to incineration in destroying the current agent stockpiles are assessed below. The discussion is limited to the potential for destroying purified chemical agent stored in bulk containers or collected through the disassembly of chemical weapons.

### Direct Destruction of GB and VX

*Technology description.* Enzyme-based systems that can directly degrade GB have been identified from numerous systems (Table 6-2). The initial, enzyme-catalyzed hydrolysis of GB would result in the production of hydrogen fluoride (HF) and mono-isopropyl methylphosphonate. Several microbial strains capable of hydrolyzing VX have reportedly been isolated, but none has been characterized to date (Harvey and DeFrank, 1992). Several enzyme and cellular systems have been identified that are capable of cleaving the P-C bond and degrading the methylphosphonate products of agent hydrolysis. Microbial cultures capable of degrading the relatively nontoxic phosphonic acids are described in the section below on the biodegradation of the reaction products from chemical processing of GB and VX.

The main issues for enzyme- or microbial-based hydrolysis of the chemical nerve agents are not the intrinsic capability of biological systems to detoxify the agents, but rather system integration questions:

- What is the greatest degree of destruction that can practically be achieved, and what is the associated system efficiency?
- What are the impacts of impurities and stabilizing agents in the chemical warfare agent stockpiles?
- How much aqueous dilution will be necessary if biological processing requires solubilization with a solvent or another biological product?
- What volume of biomass and neutralization salts will be produced by biological destruction, and what are the characteristics of and management considerations for these components?
- What, if any, metabolic products result from biological treatment of materials containing significant amounts of trace compounds? (See the section on chemical processes for trace by-products.)
- Do the various physical states and chemical impurities of the stockpile materials interfere with the biological processes?
- Are the kinetics of the biological processes adequate for practical scaleup of degradation?
- What types of analytical and process control systems must be developed to monitor the processing streams.?

TABLE 6-2 Enzymes Capable of Degrading Organophosphorus Neurotoxins

Source (protein)	Substrate		P-X	Genetics	Reference
	P-O	P-F			
Human serum A	P,C	GD>GB	pac	cloned	Hasset et al. (1991); Furlong et al. (1991); Gan et al. (1991); Smolen et al. (1991)
Human serum B	P,C	GB>GD	pac	cloned	Hasset et al. (1991); Furlong et al. (1991); Gan et al. (1991); Smolen et al. (1991)
Rabbit serum	P	GB>GD	pac	cloned	Furlong et al (1991); Zimmerman and Brown (1986)
Rat serum	-	GD>GB>DFP	GA	-	de Jong et al. (1989)
Rat liver	P	GB>GD>DFP	GA	-	Little et al. (1989)
Hog kidney	-	GD>DFP>GB	GA	-	Mazur (1946); Hoskin (1990)
Sheep serum	P	DFP	-	-	Main (1960); Mackness and Walker (1981)
Pig liver	P	GB>GD>DFP	GA	-	Whitehouse and Ecobichon (1975)
Squid nerve	-	DFP>GD>GB	-	cloned	Hoskin (1990); Ward (1991)
Squid muscle	-	GD>DFP	-	-	Hoskin (1990)
Clam foot	-	DFP>GD	-	-	Landis (1991); Anderson et al. (1988)
<u>T. thermophila</u>	-	DFP>GD	-	-	Landis and DeFrank (1991); Landis et al. (1987)
<u>B. sterothermophilus</u>	NPEPP	GD>GB	-	-	DeFrank and Cheng (1991); DeFrank (1991)
<u>Ps. diminuta</u>	P,C+	GB>DFP>GD	VX	cloned	Dumas et al. (1989a,b); McDaniel et al. (1988); Lewis et al. (1988); Serdar et al. (1989)
<u>E. coli</u>	-	GD>GB>DFP	-	-	Zech and Wigand (1975)
Thermophilic bacteria	-	GD	-	-	Chettur et al. (1988)
Halophilic bacteria	-	GD>GB	GA	cloned	DeFrank and Cheng (1991)

Substrates: P—O bond: P, paraoxon; C, coumaphos; NPEPP, 7-nitrophenyl ethyl (phenyl) phosphinate; +, others. P—F bond: GB, Sarin; GD, Soman; DFP, diisopropyl fluorophosphate; M, mipafox. P—X bonds: GA, Tabun (P-CN bond); pac, phenylacetate (P-C bond); VX (P-S bond). The > sign indicates which agent is used more effectively by the substrates. Source: Based on Dave et al. (1993).

The following sections address the scientific principles of primary detoxification, availability of appropriate biological systems, and systems issues.

*Biological systems.* Numerous biological systems have defined enzyme-based capabilities for detoxification of nerve agents (Table 6-2). Several degradative gene systems have been cloned and subjected to genetic manipulation (*Pseudomonas*, halophilic bacteria, mammalian serum enzymes, and squid nerve enzyme). Several degradative enzymes (from squid nerve, soil bacteria, halophilic bacteria, and mammalian serum paroxonases) have been purified and to various degrees their interactions with G agents (GA, GB, and GD) characterized. The diversity and substrate preferences of agents treatable by enzyme-based systems are indicated in Table 6-2. In addition, numerous other biological systems have been shown to possess degradative capabilities, although the genes and enzymes have not been extensively detailed with multiple substrates and their specificity for GB and VX has not been determined (Mounter et al., 1955; Attaway et al., 1987; Mulbry and Karns, 1989a,b).

Bulk liquid GB has been directly hydrolyzed at laboratory scale by defined enzyme-based systems. Several biological systems that have been used to degrade GB are also applicable to other G agents.

Only a few of the enzymatic reactions identified in these various biological systems (*Pseudomonas*, the halophilic bacterium *Altermonas*, and squid nerve ganglion) have been well characterized with G agents; most of the others represent preliminary whole cell identification of biochemical capabilities. The direct use of biochemical degradation for G agents was first suggested for the squid enzyme in 1982 (Hoskin and Roush, 1982). The enzymes from *Pseudomonas* and squid have been purified and immobilized in active form on various matrices (Hoskin and Roush, 1982; Caldwell and Raushel, 1991), suggesting a potential for their use in bioreactor development. The organophosphate hydrolyzing systems of soil bacteria (the *opd* gene) have been successfully used in field studies to detoxify the insecticide coumaphos, a neurotoxic surrogate for the G agents (Kearney et al., 1988). Although the enzyme involved is also capable of GB hydrolysis (Dumas et al., 1990), the coumaphos studies address neither the actual substrate concentrations that could feasibly be used in direct treatment of agents nor the effect of stockpile contaminants on the activity and stability of these enzymes. These biological systems need further R&D before being used in biodegradation technologies (see Engineering Prospects).

## **BIODEGRADATION OF REACTION PRODUCTS FROM THE CHEMICAL PROCESSING OF GB AND VX**

An alternative to the direct biological or biochemical treatment of GB or VX would be to couple initial chemical processing of the agent with biological degradation of the reaction product, especially for the complete destruction of the products of well-defined chemical reactions (see the earlier sections in this chapter on chemical processes). Biological systems offer much promise to manage bulk materials of lower toxicity. The potential hazards of the longer reaction times and storage of these systems, and associated fermentation safety concerns would all be greatly reduced because of the lower toxicity of the chemical process streams. For this application, there are several major issues that require consideration:

- What are the reaction products of chemical processing of the primary agent and of the contaminants present with the agent?
- Are there efficient biological systems that have been adequately characterized for each specific purpose?
- What is the impact of carrier materials in the streams? For example, how much dilution of the products from chemical processing of GB and VX is necessary to provide concentrations of organic compounds appropriate for biological processing?
- What are the management considerations for the volume and characteristics of the resulting biomass and neutralization salts?

Each chemical process discussed earlier in this chapter results in reaction products that could be further treated by biodegradation (see earlier section on chemical detoxification processes). As an example, the biodegradation of the reaction products of H will be discussed in the next section.

When organic solvents are used for the chemical degradation of GB and VX, subsequent biodegradation must contend with the reaction solvent, reaction products, and impurities or their products. For example, reaction with potassium hydroxide in methanol would require degradation of the methanol carrier solvent as well as the reaction products; the aqueous reaction of GB and VX with ethanolamine would require degradation of ethanolamine as well as the reaction products. Biodegradation of the solvents is readily achievable; however, biodegradation of many of the reaction products has not been directly investigated. The most likely biodegradation pathways include the following:

- cleavage of the phosphonate ester linkage followed by oxidation of the resulting alcohol;

- cleavage of the amide linkage followed by reduction of the resulting cleavage products; and
- cleavage of the methylphosphorus bond of the phosphonate to produce methane (Harkness, 1986; Schowanek and Verstraete, 1990a,b) or biodegradation of the alcohols (the hazards associated with the methane, the main constituent of natural gas, would need to be addressed).

### **Chemical Hydrolysis and Bioremediation of Mustard**

The direct biodegradation of mustard agents containing sulfur is not promising because there are no corresponding microbial or enzyme-based systems. Unlike the G agents and VX, mustard compounds are toxic to most biological systems. For this reason, initial chemical processing, possibly to form thiodiglycol, might be used followed by biological degradation to eliminate possible regeneration of agent by reaction with HCl. Mustard has reportedly been hydrolyzed by  $\text{Ca}(\text{OH})_2$ , yielding thiodiglycol as the primary product. The thiodiglycol can be degraded by two different strains of recently isolated bacteria (*Pseudomonas* sp. and *Alcaligenes xylosoxidans*) that are able to use thiodiglycol as their sole source of carbon and sulfur. Mustard from 1-ton containers at Aberdeen Proving Ground was used to demonstrate that chemical hydrolysis by NaOH with  $\text{NH}_3$ , followed by biodegradation, was directly applicable to chemical agent stockpiles. The resulting culture medium was determined by bacterial toxicity studies to be nontoxic (Harvey and DeFrank, 1992).

### **Bioremediation of Explosives and Energetics**

Bioremediation of explosive and energetic materials has been demonstrated for dilute, purified materials (Kaplan, 1993). However, applications to the explosive and energetic materials in the stockpile do not seem expeditious because of the burnable characteristics of these materials and the ease by which they can be destroyed through combustion.

### **Engineering Prospects**

Numerous steps are required to assess the progression from scaling up of biological concepts to the practical engineering systems for chemical demilitarization.

*Direct destruction of GB and VX.* Further evaluations of the efficacy of enzymes and cellular-based systems for direct destruction of GB and VX should focus on several areas:

- identifying appropriate enzymes and cellular systems capable of detoxifying VX;
- defining the maximum extent of reaction (percent agent destruction) achievable for selected representatives of each potential system;
- defining the maximum aqueous concentration of chemical agent that each selected system can treat; and
- determining the usable life of each enzyme or cellular system and the quantities required for practical application.

If the results of these investigations encourage further studies, subsequent research should also focus on the following areas:

- defining a suitable reactor configuration, including reaction and reactor kinetics, to determine reactor size and processing time requirements for bioprocessing;
- determining the production requirements of the enzymes or cellular systems in quantities sufficient for scaleup; and
- defining the quantities and characteristics of process effluents, including exhausted enzymes or cells, and nonbiodegradable organic species and salts.

Biochemical processing would most likely involve either enzymes or whole cells dispersed in dilute chemical agent or immobilized as a catalyst bed through which the chemical agent would flow. The whole cells method would most likely require production of smaller quantities of enzymes or cells. In either case, considerable effort may be required to produce large quantities of purified enzymes.

Application of enzyme deactivation for the treatment of nerve agent using whole cells may be a viable option. Specific concerns over use of whole cells in this application would be (1) the sorption of non-deactivated agent to cellular material (biomass) resulting in residual toxicity problems; (2) potentially more rapid deactivation of enzymes; and (3) greater limitations on operating conditions (temperature, pH, agent concentration, etc.) for whole cell systems rather than isolated enzymes. Whether to use purified enzymes or whole cell systems should be based on the ease of enzyme purification and the relative activities of the two systems. Use of the agent (non-deactivated) as the carbon and phosphorus source for microbial growth would most likely be unattractive because of the relatively slow growth rates (compared to deactivation rates of either purified enzymes or those present in whole cells)



and the attendant requirement that the cell growth reactor be configured to contain active agent. Incineration of the resulting whole suspension is unattractive because of the large quantities of water that would have to be incinerated.

*Biodegradation of chemical degradation products.* Future investigations for biodegradation of chemical detoxification processes should initially focus on identifying organisms or mixed microbial populations with broad degradation capabilities for the defined categories of reaction products of selected processes. Success of this secondary degradation will be determined by the development of suitable microbial consortia capable of carrying out the sequence of biodegradation steps necessary for treatment of the mixed-reaction products.

Scaleup of potential biodegradation processes could be accomplished by using well-established fermentation and biodegradation technology. The most likely approach would use a series of sequencing batch reactors, as is common in the biodegradation waste treatment industry, or batch fermentation, as practiced in the biotechnology industry (Irvine and Ketchum, 1989). In either case, a series of batch reactors would need to be operated in parallel to permit the greatest process efficiency (this allows a reactor to start operation at a high substrate concentration and continue until the lowest residual concentrations are achieved). These engineering goals must be balanced with complete process control; all reactor contents should be tested before transport or final disposal.

The design of a biodegradation reactor will depend primarily on whether the initial chemical reaction is carried out in aqueous or organic solution. Preliminary process design estimates for aqueous chemical reactions suggest that a typical batch bioreactor size would be 10,000 gallons and that two reactors operating in tandem would be required for the biodegradation of residual products from the chemical processing of 1 ton of agent per day. The biodegradation of reaction products from chemical reactions carried out in organic solvents (methanol or ethanolamine) would require approximately a 10-fold increase in reactor size to accommodate biodegradation of the carrier solvent. (To facilitate biodegradation the carrier solvent most likely would have to be diluted with water to less than 10 percent by weight.)

*Waste streams.* Biodegradation of chemical reaction products would result in the following process waste streams:

- process waste water, including nondegradable process reaction or biodegradation products and neutralization salts;
- sludge from produced microbial cell mass; and
- gaseous bioreactor effluents.

Process waste water could most likely be treated through reverse osmosis or evaporation to remove the salts accumulated from pH neutralization and halogen ion released through agent degradation. Recovered water could be recycled into the chemical reaction process or biodegradation process steps. The resulting dry salt stream could be disposed of by conventional waste-disposal practices after the absence of residual toxicity is confirmed.

Sludge from microbial cell mass could be disposed of by using conventional commercial facilities for disposal of waste water treatment sludge disposal. Approximately 600 pounds (dry weight) of sludge could be expected for each ton of organic solute degraded.

Gaseous bioreactor emissions ( $\text{CO}_2$ ,  $\text{O}_2$ ,  $\text{N}_2$ , and methane [ $\text{CH}_4$ ]) would result from aeration of the bioreactors and the  $\text{CO}_2$  produced by organic solute mineralization. Emissions can be minimized by using either oxygen enrichment or pure oxygen instead of air to supply oxygen to the reactor, depending on microbial sensitivity to oxygen concentration and reactor design. Initial estimates are that between 20,000 and 40,000 cubic feet of oxygen (at standard temperature and pressure) would be required for each ton of organic solute biodegraded. This quantity is small enough to permit complete capture and testing of gaseous emissions before release. Effluent  $\text{CO}_2$  could be captured in alkaline solution to eliminate gaseous discharge. Effluent  $\text{CH}_4$  would need to be managed by the industrial processes commonly used for potentially flammable gaseous emissions.

*Developmental status.* Limited investigation has been carried out to date on the potential for biodegradation of chemical reaction products. The following steps would be required for process development and scaleup:

- identifying microorganisms capable of biodegrading specific chemical reaction products;
- determining the maximum initial concentration of reaction products that can be degraded without adverse effects on the microbial community;
- determining the maximum extent of biodegradation achievable;
- determining biodegradation stoichiometry and rates; and
- developing process-control strategies.

Some DOD agencies have established University Research Initiative programs involving several research centers for biodegradation to address the basic science and engineering of biodegradation of environmental contaminants. This joint work, which is being performed at the Army Research Office/Texas A&M University, Office of Naval Research/University of Washington (Seattle) and Advanced Research Projects Agency/Rutgers University, may help address some of the questions above.

### **Summary of the Potential Application of Biological Processes**

Some of the major observations in the preceding discussion lead to the following generalizations about potential applications of biological processes to demilitarization of the U.S. Stockpile:

- Processes where microbial consortia oxidize products from detoxification and partial oxidation can probably be developed.
- The nerve agent GB, and probably VX, can be directly detoxified by enzyme reactions; mustard probably cannot be directly detoxified.
- The application of biological processes to propellant and explosives does not appear useful at this time.
- Biological processes are not applicable to dunnage.

## 7

## Processes at Medium and High Temperatures

Processes beyond those previously discussed might be applied to the destruction of the chemical weapons stockpile.<sup>1</sup> In contrast to the liquid-phase processes reviewed in [Chapter 6](#) that operate at low temperatures and atmospheric pressure, most of the technologies reviewed in this chapter operate under much more severe conditions. Many of these technologies, even the oxidative ones, produce gaseous waste streams that would require further oxidation in some form of afterburner. The technologies examined here can be grouped in the following categories:

- Moderate-temperature, high-pressure processes: Wet air and supercritical water oxidation are processes that occur in water at moderate temperatures and high pressures.
- High-temperature, low-pressure pyrolysis: Some technologies involve agent vaporization and decomposition upon heating. The gaseous products resulting from this pyrolysis will generally need to be oxidized further to destroy organic by-products of agent breakdown. Molten metal and plasma arc (electric arc) are such technologies and will be discussed below. Gasification and steam reforming are also in this category.
- High-temperature, low-pressure oxidation: One class of technologies, including catalytic fluidized-bed systems, molten salt, and catalytic oxidation, entails agent reaction with oxygen to produce carbon dioxide, water, gases, and other inorganic substances.
- Other processes: A hydrogenation process might be used to destroy agent or a sulfur process might be used to create a polymer while destroying agent.

Reduction and pyrolytic processes will result in products that are themselves toxic, such as  $\text{PH}_3$  or  $\text{H}_2\text{S}$ . These will require safe handling as well as final destruction to create stable products.

---

<sup>1</sup> Much of the information presented in this chapter is based on presentations made at the committee's workshop ([Appendix F](#)).

### MODERATE-TEMPERATURE, HIGH-PRESSURE PROCESSES

Organic materials may be oxidized in the presence of water at moderate temperature and high pressure. Temperatures used are in the range 200 to 650°C, which is low compared with the usual combustion temperatures of about 1500°C (2732°F). The pressures used in this method are high, from 360 to 4,000 psi (25 to 275 bars). Processes have been developed at the low and high ends of both the pressure and temperature ranges. Wet air oxidation (WAO) is carried out in the liquid water phase, with pressures exceeding saturation pressure. Supercritical water oxidation is carried out at much higher temperatures and pressures, exceeding the critical temperature and pressure of water, that is, 374°C (705°F) and 3,205 psi (221 bars), respectively. The fluid properties under these conditions are very different from those of the liquid water used in WAO. For example, organic substances are completely soluble in water whereas salts are almost insoluble. In practice, the suggested operating pressures sometimes overlap; temperatures, however, differ by 200°C or more.

In many respects these processes are an alternative to incineration: they are broadly applicable to any oxidizable organic compound and could be used to treat chemical warfare agents, propellants, and explosives (solid materials would require comminution and would be fed as a slurry). These processes could also be used to oxidize the products of agent pretreatment, such as the products of hydrolysis.

Both of these oxidation processes offer some major advantages. Objectionable pollutants such as nitrogen oxides, dioxins, and particulates do not form at the relatively low temperatures used. Some nitrogen may show up as N<sub>2</sub>O or NH<sub>3</sub>, depending on its form in the feed material and the severity of the oxidation. Product volumes can be controlled to be small enough that dosed systems are practical, allowing products to be analyzed and their safety confirmed before release to the atmosphere.

WAO is reviewed below and is followed by a review of supercritical water oxidation (SCWO).

#### Wet Air Oxidation

*Technology description.* In WAO, oxidizable materials, usually organic materials, are oxidized in a dilute, aqueous, liquid matrix at temperatures of 200 to 300°C (392 to 572°F); the corresponding pressures required to maintain a liquid phase are in the range 230 to 1,250 psi (16 to 186 bars). The process is applicable to material in solution or to suspended solids in water (Copa and Lehmann 1992; Copa and Gitchel, 1989; Zimmerman, 1958).

In this process, air (or air enriched with oxygen) and an aqueous feed mixture are compressed to the required pressure (Figure 7-1). Heat is added as needed, and the mixture flows to a reactor. Oxidation of material in the feed releases heat and raises the reactor temperature further; some of this reaction heat may be recovered in a heat exchanger as shown. The amount of heat added and the amount of reaction heat used will depend on the concentration of organics in the water. Higher concentrations of organic matter will release more heat and lead to a greater temperature rise in the reactor. Most applications have been to wastewater with low concentrations of organic matter, about 1 percent (by weight) or less. Experience is limited to reactor temperatures of less than 350°C (660°F) with the organic content of the feed usually less than 5 percent, generally 1 to 2 percent. Feeds with higher concentrations could be processed, but there is little experience with such conditions and their greater temperature increases.

*Status and database* Approximately 200 WAO plants are operating worldwide. A variety of waste streams have been treated with this technology, including spent caustics, sludges in municipal and industrial wastewater treatment, wastewater from chemical production processes, pulp and paper wastes, and military wastes (Copa and Lehmann, 1992). In all these applications, organic and inorganic compounds are converted to simple products.<sup>2</sup> The process has been applied to pesticides with chemical structures similar to those of nerve agents, achieving greater than 99 percent destruction of malathion, parathion, and glyphosate.<sup>3</sup>

*Application to chemical weapons destruction.* Experience with pesticides and such materials as chlorinated compounds indicates that WAO could

<sup>2</sup> Organic compounds with carbon, hydrogen, and oxygen are converted to (–) carbon dioxide (CO<sub>2</sub>), water, and low-molecular-weight compounds such as acetic acid; sulfur – sulfate ion (SO<sub>4</sub><sup>2–</sup>); phosphorus – phosphate ion (PO<sub>4</sub><sup>3–</sup>); chlorine – chloride ion (Cl<sup>–</sup>); and nitrogen – ammonium (NH<sub>4</sub><sup>+</sup>), N<sub>2</sub>, nitrate ion (NO<sub>3</sub><sup>–</sup>), and nitrous oxide (N<sub>2</sub>O). For inorganic substances, sulfides – sulfate (SO<sub>4</sub><sup>2–</sup>) and cyanides – CO<sub>2</sub> and NH<sub>4</sub><sup>+</sup>. The particular nitrogen end products depend on the organic nitrogen compound converted.

<sup>3</sup> Reported destruction efficiencies for pesticides are: malathion, 99+ percent at 200°C; dyfonate, 99 + percent at 260°C; parathion, 99+ percent at 260°C; glyphosate, 99+ percent at 260 to 280°C; complete destruction of pesticides at 280°C. Glyphosate contains a phosphorus atom double-bonded to one oxygen and single-bonded to two oxygens; parathion has a phosphorus atom double-bonded to sulfur and single-bonded to three oxygens; and parathion and dyfonate have a phosphorus atom double-bonded to a sulfur and single-bonded to a sulfur and two oxygen atoms (Copa and Lehman, 1992).

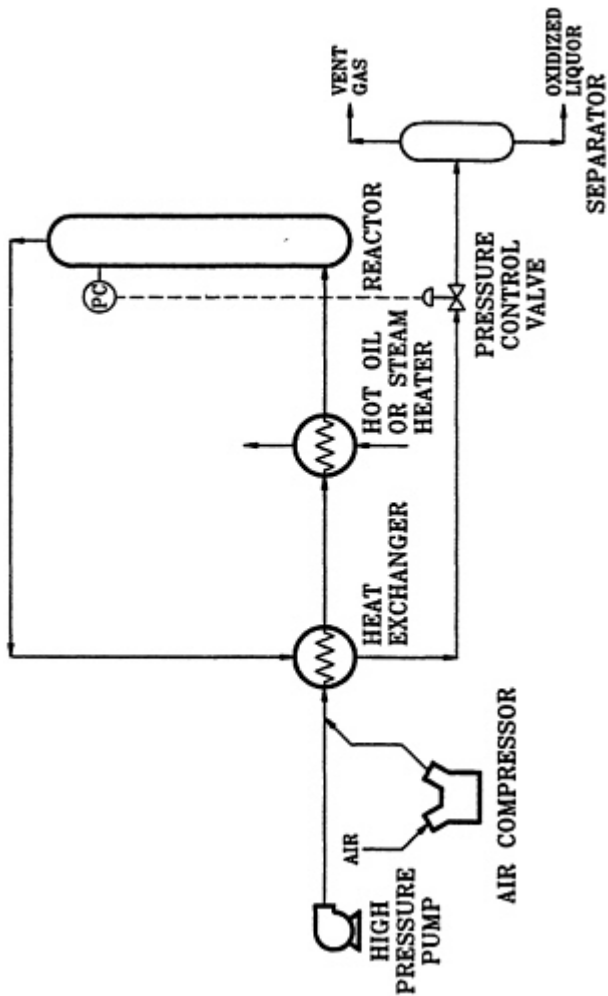


FIGURE 7-1 WAO flow diagram.  
Source: Adapted from Copa and Gitchel (1989).

destroy chemical agents. It could also be used to oxidize the products from a pretreatment of the agent, such as hydrolysis.

*Reaction rate.* Kinetic data on the rate of oxidation of large organic molecules in WAO processes are not available, although there have been tests on destroying compounds containing phosphorus. In WAO such molecules break down rapidly but yield a substantial amount of low-molecular-weight material that then oxidizes much more slowly. Some small organic molecules remain for further treatment. The rate of oxidation and the weight percent of organic compounds remaining as small, partially oxidized materials (e.g., acetic acid) depends on temperature and pressure. In typical applications, the weight percent remaining would be 25 percent of the weight of the original material. The P-C bond (GB or VX) is believed to react slowly.

Table 7-1 summarizes recommended operating temperatures and saturation pressures (pressures at the boiling point) for chemical warfare agent destruction by WAO. In actual operation in previous applications, however, the pressure is maintained substantially higher than the pressures shown, as much as twice as high. From experience (Copa and Lehman, 1992), agent destruction of 98 to 99 percent should be expected in a single reactor with a residence time of 1 to 2 hours.

WAO has been applied to some propellants and to wastewaters containing nitro-compounds from the manufacture of propellants and explosives. Solid propellants and high explosives would have to be fed to the reactor as a slurry in water.

*Special considerations.* High destruction efficiency will require the reactor to operate much like a plug flow,<sup>4</sup> which is difficult to achieve in a reactor with a long residence time and a very slow flow rate. Reactors have been built with internal baffles to suppress longitudinal mixing and they have also been built as separate vessels in series (three reactors in series). For the very high destruction efficiency required for chemical warfare agents, it appears that several reactors in series would be preferred. In such an arrangement—for example, hydrolysis followed by two WAO units, with each achieving 98 to 99 percent conversion—a very high overall destruction efficiency can be achieved. (Three reactors in series, each achieving 99 percent destruction, would attain an overall destruction of 99.9999 percent.)

The products from a chemical treatment of agent (hydrolysis) could be effectively mineralized by a WAO process; they are in a dilute aqueous

---

<sup>4</sup> Plug flow in a tube assumes that properties of the reacting mixture are uniform at any cross section of the tube and change in the longitudinal direction.

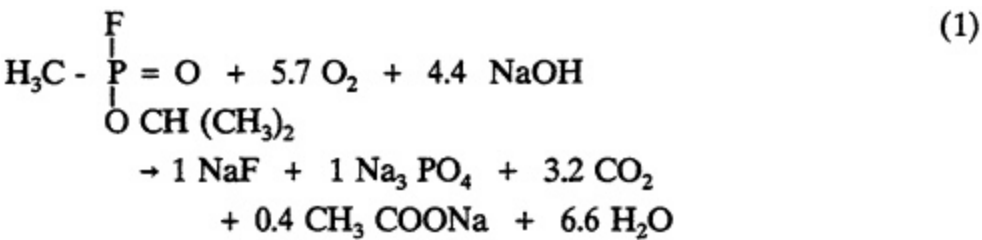


TABLE 7-1 Recommended WAO Operating Temperatures and Saturation Pressures for Destruction of Chemical Warfare Agents and Propellants

Agent/Component	Temperature (°C)	Saturation Pressure (bars)
Sarin	260	47
VX	260	47
Mustard	200-240	15-34
Propellants	260-280	47-64

Source: Copa and Lehman (1992).

solution with excess caustic, which is needed for pH control in a WAO unit. The stoichiometry for hydrolysis of GB followed by WAO might then appear approximately as shown in Equation 1.<sup>5</sup>



Corrosion is a concern with WAO conditions, particularly for materials containing chlorine, fluorine, sulfur, and phosphorus, which all form adds in solution on agent oxidation. In the example shown above, excess caustic is limited; more may be needed to neutralize such adds and reduce corrosion.

If hydrolysis and WAO are used sequentially, a large excess of caustic would be used to ensure complete hydrolysis (see [Chapter 6](#)), and this caustic would provide the pH control needed in the WAO process. In such an arrangement, caustic would certainly be added to react with the strong adds to form, for example, sodium fluoride and sodium phosphate as in the above equation. Addition of caustic beyond that required by the stoichiometry would

<sup>5</sup> The partially oxidized organic compound shown here is the sodium salt of acetic acid. Other materials would show up in actual practice. More NaOH than that shown might be used for corrosion control. Material balance for GB destruction is shown in [Appendix K](#).

need to be evaluated. With limited addition of caustic, an acidic solution is formed by the oxidation process. If more caustic is needed for corrosion control, the additional caustic would react with  $\text{CO}_2$  to form sodium bicarbonate or sodium carbonate, adding greatly (up to threefold) to the solid salts that must be handled in the process but reducing the quantity of waste gas volume.

The fluoride ion is particularly corrosive. A current limitation for WAO processing is 200 ppm of fluoride. Because fluorine is 14 percent of GB by weight, this corrosion limitation implies a GB feed concentration of only 1,500 ppm (i.e., 0.15 percent).

Insoluble deposits also appear to aggravate corrosion; the environment under a solid deposit may differ significantly from that of the bulk liquid. Scaling of heat exchangers may also pose a problem, caused, for example, by the hardness of water containing calcium, silicon, or iron salts. Such scaling is usually handled by acid washing (for example, to remove  $\text{CaSO}_4$  scale).

Even though a basic compound would be added to control WAO pH, the reaction conditions would still be very aggressive. Components sensitive to corrosion include the reactor, heat exchangers, piping, valves, and tanks, which would require materials resistant to corrosion.<sup>6</sup> For example, high-chromium materials, such as Hastelloy C-276, could be expected to stand up very well in the WAO environment. Titanium has been used in experimental work, but it cannot be used in a pure oxygen environment because of its flammability.

Like combustion, WAO is highly exothermic, and its reaction rates are sensitive to temperature. WAO temperature excursions are limited, however, by the presence of a large amount of water. Most of the industrial wastes treated with WAO have had organic contents of less than 1 or 2 percent. Larger throughputs with higher concentrations are possible but would result in larger heat releases and the possibility of larger temperature excursions. In practice, the organic concentration in the feed water should preferably be limited to 5 percent or less. If temperature and pressure excursions occur outside of the normal operating regime, an alarm system is triggered and the system shuts down.

The use of pure oxygen rather than air as the oxidizing agent would reduce gas production by 85 percent or more and make it easier to operate the process as a closed system in which the gaseous emissions would be stored and analyzed before release to the environment. Some fixed gas is considered desirable, however, for stable operation (Copa, 1992). Any variations in

---

<sup>6</sup> Applicable materials include 304L and 316L stainless; Carpenter 20CB-3; Incoloy 800 and 825; Inconel 600 and 625; Hastelloy C-276, G-3, and C-22; and titanium grades 1, 2, 3, 7, 11, and 12.

oxidation will go to changing reactor temperature and to evaporation (or condensation) of water. The latter is important for system stability and will depend on the presence of a fixed gas. Thus, although pure oxygen has been used in WAO, enriched air (e.g., 50 percent oxygen) is preferred.

*By-products and waste streams* Gas leaving a WAO unit is said to be free of most of the objectionable pollutants associated with combustion gases, such as the usual oxides of nitrogen, dioxins, furans, and particulate matter in the gas phase. For a WAO process using air, typical effluent gas composition is shown in [Table 7-2](#). This has been estimated for oxidation of GB; estimates for excess O<sub>2</sub> and for carbon monoxide (CO) and hydrocarbons are based on experience with other materials. Gas composition and volume will differ if the gas used is air enriched with oxygen.

Some final gas cleanup may be required. Small concentrations of CO and some trace hydrocarbons can be eliminated by a thermal or catalytic oxidizer (described later in this chapter). An activated-carbon-bed adsorber would also ensure against discharging chemical agent or polar organics to the atmosphere.

A substantial fraction (by weight) of organics in the feedstock will remain in the water as small oxygenated species; typically, 70 percent by weight is oxidized to CO<sub>2</sub> and water and 30 percent remains as acetic acid and other organic compounds. The feed to a subsequent treatment unit (for biological or chemical oxidation) would have requirements of 5 to 10 g/L of biological oxygen demand (BOD) and 10 to 20 g/L of chemical oxygen demand (COD).

For a biological treatment process, water is usually removed from solids and the solids are then sent to a landfill. For WAO some additional treatment may be needed because of the solubility of the large quantity of inorganic salt that remains.

*Advantages and disadvantages.* There are several major advantages of WAO compared with the baseline technology of incineration:

- The gas effluent is free of SO<sub>2</sub>, dioxins, and particulate matter, and the only N oxide reported is N<sub>2</sub>O.
- The large water dilution could be a significant advantage in treating energetic materials (propellants and explosives). Explosion or detonation should not occur if there is adequate mixing, although this would require demonstration.
- WAO is particularly well-suited for treatment of dilute wastewater. It has not been used commercially for feedstocks containing concentrated organic compounds that require dilution.

TABLE 7-2 Estimated Effluent Gas Composition for Two-Step Destruction of GB, Hydrolysis Followed by WAO (Using Air)

Component	Typical Gas Composition (by volume)
Oxygen (O <sub>2</sub> )	3-6 percent
Nitrogen (N <sub>2</sub> )	78-82 percent
Carbon Dioxide (CO <sub>2</sub> )	8-12 percent
Carbon Monoxide (CO)	10-1,000 ppm
Hydrocarbons	100-1,000 ppm
Solids	0

WAO also has several major disadvantages:

- It operates at high pressures (e.g., at 1,450 psi, or 100 bars). This pressure is well within common industrial practice. Nevertheless, there might be some concern about operating with agent under high pressure; thus, it might be preferable to use WAO to oxidize products from pretreatment of agent, such as the products of hydrolysis.
- WAO does not oxidize all of the material completely. A posttreatment, usually biodegradation, is required to meet Resource Conservation and Recovery Act (RCRA) standards and Clean Air Act National Emission Standards for Hazardous Waste Pollutants (NESHAP).

*Development needs.* Several steps would be needed for WAO to be used in chemical weapons destruction:

- Corrosion testing on possible construction materials would be required because of the fluoride, chloride, sulfate, and phosphate ions present in solution.
- Pilot plant work could be done on related compounds to establish the reaction conditions and the treatment process for the liquid product. Process conditions must be set on the basis of experimental work, ultimately with the materials of actual interest. The amount of caustic agent required,

reactor temperature and pressure, reactor flow rates, reactor configurations, and other variables would all have to be set.

- Bench scale and pilot plant testing and demonstrations with chemical agents would be conducted at military sites.
- Tests on intermediate products, such as material from the hydrolysis of agents, would also be conducted at a military site; simulants could be tested elsewhere.
- Energetic materials, propellants, and explosives have been treated with WAO. A demonstration program would be needed for the slurry mixture, concentration levels, and other requirements of the process as applied to chemical weapons.

The development work required would take at least 1 year, after which construction could begin on a full-scale demonstration unit.

### Supercritical Water Oxidation

*Technology description.* In SCWO, organic materials, including materials containing heteroatoms such as chlorine, can be effectively oxidized by O<sub>2</sub> in an aqueous medium above the critical point of pure water, that is, at 374°C (705°F) and 3,205 psi (221 bars). At temperatures above 500°C (930°F), high conversions are possible with short reactor-residence times. Hydrocarbons can be converted completely to CO<sub>2</sub> and water. Supercritical water is an attractive medium for the oxidation reactions because it offers high solubility for both organic compounds and oxygen; the usual transport and mixing problems associated with reaction of two or more phases reacting are absent.

There are many research groups worldwide actively pursuing aspects of SCWO. This report was current at the time it was written.

The properties of supercritical water, which are quite different from those of liquid water at ambient conditions, resemble more closely those of steam. The dielectric constant for supercritical water is about 2 at 450°C (840°F) and 250 bars, and the ionic dissociation constant falls from its usual value of 10<sup>-14</sup> to a value of about 10<sup>-23</sup>. As a result, supercritical water acts as a nonpolar fluid. Its solvation properties resemble those of a low-polarity organic fluid; hydrocarbons are highly soluble, whereas inorganic salts are almost totally insoluble.

The SCWO flow sheet (Figure 7-2) resembles that of WAO, but operation is at higher temperatures and pressures, resulting in different products. Air or oxygen and the feed mixture are compressed to the required pressure. Heat is added as needed, and the mixture flows to a reactor. The reaction raises the temperature to the final level desired. Oxidation occurs

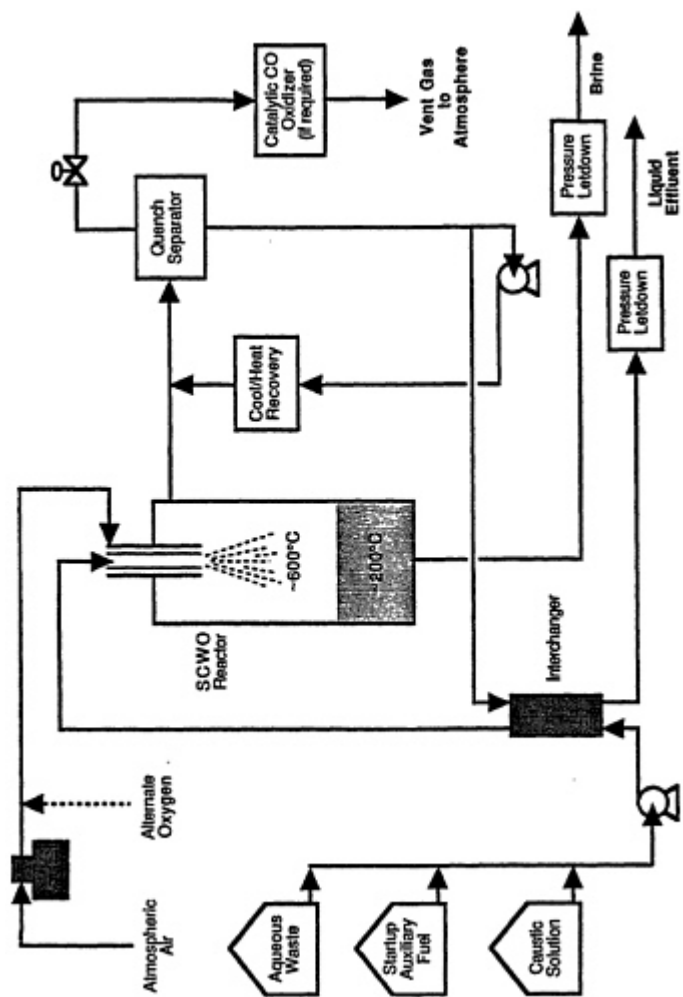


FIGURE 7-2 SCWO flow sheet (MODAR type).  
Source: Adapted from Barner et al. (1991).

spontaneously. Heat transfer equipment is included to recover some of the process heat and to cool products before release.

The feed to the reactor may include a caustic solution if the organics contain heteroatoms such as the Cl, F, P, and S contained in chemical warfare agents. The products of their oxidation are then solid salts, which are almost completely insoluble. The formation of solids with plugging of the reactor has been a major problem in developing SCWO, but reactor designs are now available that may handle this problem.

Like WAO, SCWO can be considered an alternative to incineration, because it is broadly applicable to any oxidizable organic compound. It could be used to destroy chemical warfare agents or to oxidize the products from a pretreatment process for the agent, such as hydrolysis. It could also handle slurries of propellant or explosive. The process has been operated to produce very little waste gas by substituting pure oxygen for air.

*Status and database.* The SCWO process has been under active development for more than 10 years (Modell, 1989). The largest pilot plant has a capacity of about 1500 gallons per day. Laboratory and pilot plant units have been operated for treating hazardous wastes. Exploratory work has been done with surrogate compounds similar to chemical warfare agents and propellants. Commercial application appears imminent. There is a substantial research program on supercritical phenomena, and particularly on oxidation reactions, supported significantly by such federal agencies as the Army Research Office, Department of Energy, National Science Foundation, National Aeronautics and Space Administration, and, more recently, Advanced Research Projects Agency.

The phase behavior of mixtures of water with many other materials under near-critical conditions has been reported for: benzene; C<sub>2</sub>-C<sub>7</sub> alkanes; naphthalene; 1,3,5-trimethyl benzene; and permanent gases such as nitrogen, oxygen, hydrogen, CO<sub>2</sub>, and CH<sub>4</sub>. All compounds studied to date are completely miscible with water above 400°C (750°F) and 250 bars. However, inorganic salts have very low solubilities, even including such salts as NaCl that are very soluble in liquid water.

Some kinetic data on oxidations have been reported. In general, complex organic molecules break up rapidly to smaller oxygenated species. Further oxidation of these fragmentation products is slower, and eventually the oxidation of simple compounds such as CO and NH<sub>3</sub> becomes rate limiting. Global kinetic data have been gathered for a number of small molecules, such as ammonia and methane (see [Figure K-1](#)). Destruction efficiencies for bench-scale and pilot-plant systems have been reported for a large number of substances including species containing chlorine, phosphorus, sulfur, and nitrogen (see [Appendix K](#); Helling, 1986; Helling and Tester, 1987, 1988;

Holgate and Tester, 1991; MODAR, 1992; Modell, 1989; Tester et al., 1991; Tester, 1992; Thomason et al., 1990).

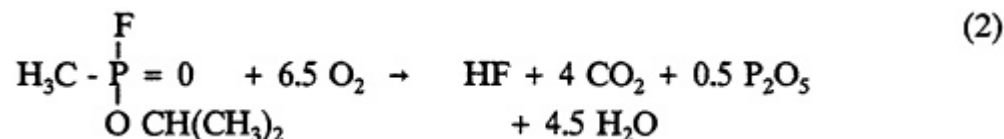
The solvation characteristics of supercritical water affect chemical reactions. Reaction rates can be rapid and oxidation reactions can proceed to completion in contrast to the WAO process. Hydrocarbons are converted to  $\text{CO}_2$  and water. Heteroatoms are converted to inorganic compounds in high oxidation states that can be precipitated as salts with the addition of some base. SCWO has not been applied to compounds containing fluorine. Sulfur goes to sulfate, phosphorus to phosphate, chlorine to chloride, and nitrogen primarily to  $\text{N}_2$ , with some  $\text{N}_2\text{O}$ . To reduce oxides of nitrogen in SCWO may require some after treatment.

The process is operated with a concentration of organics in water of 10 to 20 percent (by weight), which is much higher than in WAO. The larger organic content is needed to maintain the higher reaction temperature. The amount of water present is large enough to stabilize operation, probably with little opportunity for temperature excursions, although this will need verification.

*Application to chemical weapons destruction.* SCWO should be effective in destroying chemical warfare agents or their products from pretreatment. It could probably also handle propellant and explosives; they would have to be ground to a fine particle size and fed as a slurry. The process could also decontaminate metal parts, but this would require intermittent operation, an inconvenience for such a high-pressure process.

*Special considerations.* Two significant and interrelated problems for SCWO have received much attention: corrosion and solid salt precipitation from the reacting medium.

Chemical agents, propellants, and explosives could be oxidized in an SCWO reactor with no formation of solids. The products formed, however, would be acidic and likely very corrosive. Oxidation of GB, for example, would produce HF and  $\text{P}_2\text{O}_5$ :



This process would be carried out as shown in the flow sheet of [Figure 7-2](#). The GB-water mixture fed to the reactor would contain about 10 percent GB. GB content would be chosen to raise the temperature of the feed entering the reactor by approximately  $400^\circ\text{C}$  ( $750^\circ\text{F}$ ), to the final reactor temperature. The strong acid gases leaving the reactor would dissolve in the liquid water after

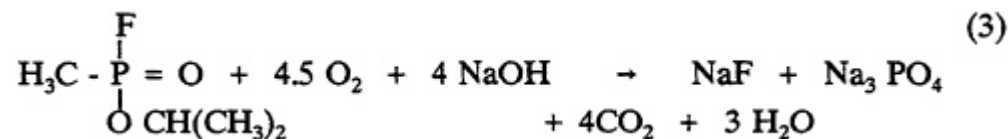


cooling and pressure decline (letdown); the gas would consist primarily of unused oxygen, nitrogen (if air was used as the oxidant), and  $\text{CO}_2$ .

The process described would appear applicable to propellants and explosives (fed as slurries). However, the strong acids formed from chemical agents may require the addition of caustic for corrosion control; the salts formed would be insoluble solids under SCWO conditions.

Alternatively, the preferred feed may be a hydrolyzed agent that would also result in insoluble solids in the SCWO reactor. Reactor design to eliminate the plugging associated with solids is still under development.

The overall reaction with GB (hydrolysis followed by oxidation) would be



The caustic used to neutralize the strong acids formed in the oxidation is twice the amount required for hydrolysis alone. More caustic could be used to increase pH but would react with  $\text{CO}_2$  to form solid sodium carbonate ( $\text{Na}_2\text{CO}_3$ ), greatly increasing the solids burden in the final discharge. The final solution is usually slightly acidic to avoid  $\text{Na}_2\text{CO}_3$  formation. The precise mode of operation to best control corrosion and solids plugging will need to be developed.

Solids formation in the reaction affects both the reactor design and the flow sheet. Reactor design, for example, may include two temperature levels; a lower temperature will result in a subcritical condition with liquid water present to dissolve the solid salts. Flow sheets have been modified to avoid solid precipitation in the inlet lines, that is, by maintaining subcritical conditions. Various reactor discharge and cooling arrangements have been suggested for separating or redissolving the solids.

Very high destruction efficiencies will require reactor designs that provide no opportunity for bypassing or short-circuiting through the reactor. That is, reactors will need to operate as plug-flow reactors or will require staging. One preferred reactor when solids are present is a larger vessel, which would not operate as a plug-flow reactor. A second reactor in series, possibly a tubular design, would probably be necessary for very high conversion (99.9999 percent) of the organic feed content.

Corrosion is expected to be a severe problem for SCWO, with fluoride and chloride ions being particularly aggressive. No data appear to have been reported on fluorine compounds. Reactor construction materials and much of the upstream and downstream equipment must be corrosion resistant as well as high in strength. High-nickel alloys (Inconel, Hastelloy C276) have been

used. Ceramic materials may be used in some locations but no details have been disclosed. It has been suggested that corrosion may be a less serious problem at supercritical conditions than at lower temperatures because of the special physical properties of the supercritical fluid, that is, its lower dielectric constant and a lower electrolytic corrosion. However, no quantitative information has been disclosed. Subcritical conditions will exist in the outlet lines, and electrolytic corrosion should be expected there.

Experience with WAO revealed an additional problem with solids deposits: corrosion (pitting) was increased underneath the deposits. This may also be a factor in SCWO.

Methods are needed for pressure letdown and to remove brines or slurries from the reactor and salt separator. Such methods have been achieved satisfactorily in existing pilot plant equipment. Chemical agents will have a much larger yield of solid products than most materials tested to date.

*By-products and waste streams.* The usual gaseous effluent of SCWO treatment of chemical warfare agents consists of the oxidation products  $\text{CO}_2$ ,  $\text{N}_2$ , and some  $\text{N}_2\text{O}$  and residual  $\text{O}_2$  and  $\text{N}_2$  (from the air). If acid gases are not neutralized by added caustic, then the gas effluent might also contain HF, HCL,  $\text{SO}_2$ , or  $\text{P}_2\text{O}_5$ , depending on the feed.

The aqueous liquid product will contain the acidic components or corresponding salts. Excess caustic will react with  $\text{CO}_2$  to form solid  $\text{Na}_2\text{CO}_3$ . As noted previously, usual operation runs very slightly acidic with the  $\text{CO}_2$  as gas. Excess caustic may be needed if corrosion proves to be too severe, although it would have a pronounced effect on the product. The  $\text{Na}_2\text{CO}_3$  formed would greatly increase the solids to be handled while reducing the gas discharge.

*Advantages and disadvantages.* Major advantages of SCWO include the following:

- The gas effluent is claimed to be free of the usual troublesome components found in typical incineration processes, such as  $\text{NO}_x$ , dioxin, and particulate matter. Some final gas treatment may be provided as a precaution against undesirable gaseous effluents resulting from system upsets.
- The system could be treated as a dosed system, with no discharge of products until analyses are complete. The use of oxygen instead of air reduces gas discharge volume; in conjunction with  $\text{CO}_2$  removal as carbonate, the gases discharged could be reduced (theoretically) almost to zero.
- Dilute aqueous wastes with up to 20 percent organic content are particularly well suited to SCWO. The process is thus well adapted to handling products from a prior aqueous treatment.

- The high reaction rate in SCWO is its major advantage over WAO. Reactor residence times are much lower-1 minute rather than 1 hour-and the oxidation reaction goes to completion. The process also has most of WAO's advantages. Major disadvantages of SCWO are the following:

Major disadvantages of SCWO are the following:

- Pressures are very high.
- Corrosion will be severe, although it can probably be handled with suitable construction materials. The fluoride ion (resulting from GB) is a major concern, being highly corrosive.
- Salts will precipitate and may cause plugging problems in the high-pressure vessels and the pressure letdown system.

*Development needs.* SCWO oxidation of slurries of propellants and explosives requires demonstration. (In principle, these materials need very little additional oxygen to complete their oxidation.) The behavior of such materials under SCWO conditions needs evaluation. For example, will the oxidizer in the solids themselves (nitro groups) be reactive? Will reaction rates be extremely fast, possibly explosive? The products of oxidation of these materials should be relatively easy to handle.

The chemical warfare agents present problems of corrosion and solids handling because of the heteroatoms they contain. One question is whether suitable materials are available to withstand attack by F and Cl ions under either mildly acidic conditions or strongly alkaline conditions.

The formation and precipitation of solid salts caused plugging problems in early SCWO experimental work. Proposals for handling the problem included a dual-temperature reactor with supercritical and subcritical conditions in separate parts of the reactor. Thus, a solution to the problems of solids precipitation may be available but demonstration is needed.

The choice of feed concentration, reactor and process conditions, and reactor design will need study and ultimately some test work with actual agents. Experimental work on agents is underway.

## **HIGH-TEMPERATURE, LOW-PRESSURE PYROLYSIS**

### **Molten Metal Pyrolysis**

*Technology description.* In the proposed molten metal processes, metals, such as copper, iron, or cobalt, are used at 1650°C (3000°F) to decompose organic compounds thermally and dissolve inorganic materials to form a slag. The process vessel is a steel converter as developed by Molten Metal

Technology (MMT) and Elkem Technology (Nagel, 1992; Aune, 1991; see Figures 7-3 and 7-4). The metal bath is heated by passing a current between electrodes in the bath. The material to be destroyed (gas, liquid, sludge, or solid) is pumped into the bottom of the vessel containing the molten metal. The waste material dissociates into small molecules or atoms and is distributed throughout the bath. The gases formed are emitted to an air pollution control system in which oxidation is completed and solids are removed. A molten inorganic slag insoluble in the liquid metal rises to the top and is skimmed off. The final gaseous products are the same as those of incineration.

*Development status.* The Elkem Multipurpose Furnace and the MMT catalytic extraction process are essentially developed technologies. They are very similar to those used in steel production. However, the use of these technologies in the destruction of chemical agents, munitions, or propellants has not been tested or evaluated.

*Application to chemical weapons destruction.* The Elkem furnace has been used for recovery of zinc and lead from electric arc furnace dust. MMT technology has been applied experimentally to many organic materials, such as alkanes (methane to pentane), aromatics (benzene to anthracene), alcohols (methyl and ethyl), olefins (ethylene to pentane), and mixtures (No. 2 fuel oil, polychlorinated biphenyls [PCBs], and others). No detailed analytical work has been presented. The Elkem furnace accepts only solids in the form of briquettes. The MMT process accepts feeds in any form. Both are potentially capable of destroying chemical agents, propellants, and explosives. They can melt metal parts while destroying any agent residues on them.

*Special considerations.* The specific products from agent destruction are unknown and questions of operability have yet to be answered. Some polymeric material and soot will probably require subsequent processing. Products from the heteroatoms F, Cl, S, and P are not known. They may cause problems with refractory linings.

Liquid feeds, particularly aqueous solutions, increase the possibility of superheated vapor explosions.

*By-products and waste streams.* The pyrolysis products from agent destruction would be oxidized in an afterburner. Product gases would contain the usual acidic components, such as HF, which would have to be scrubbed and converted to their salts. Very high gas temperature and accompanying high NO<sub>x</sub> formation can result when air is added to the hot gases leaving the molten metal bed. Control of gas phase temperature and time will be important.

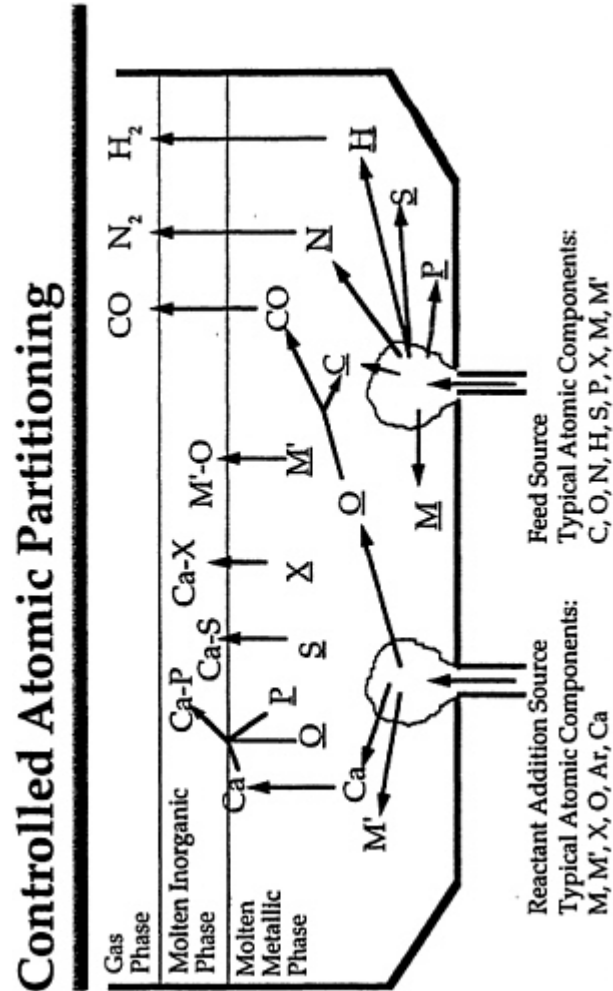


FIGURE 7-3 The Molten Metal Technology.  
Source: Nagel (1992).



An inorganic slag would be produced that might contain some soluble salts requiring landfill disposal. Metal parts fed to the unit would be drawn off with the liquid metal of the furnace.

*Advantages and disadvantages.* The process is broadly applicable to a variety of materials, including agents, metal parts, propellants, and explosives. The molten metal furnace could combine the functions of the three incinerators of the baseline technology.

The metal furnace does not eliminate the need for a combustion process; the product gases would be oxidized in a separate unit. These gases would likely be very dirty, containing soot from the metal pyrolysis and possibly some slag particulate matter. Gas cleanup will be required before the gas is released.

*Development needs.* To the extent that this technology is similar to that of steel production, it is well developed. However, it has not been applied to destruction of highly dangerous substances like agent. Whether there is much experience with remote operation of molten metal reactors is unclear. The exact gas and solid products that would be produced and their properties would need to be determined. Pilot plant work would probably need to precede construction of a demonstration unit.

### Plasma Arc Processes

*Technology description.* Plasma arc torches generate ionized plasmas at temperatures of 3000 to 12,000 K<sup>7</sup>. At such high temperatures, waste materials can be completely pyrolyzed. Organic compounds in the presence of a small amount of oxygen are oxidized to a product gas consisting principally of hydrogen, CO, some CO<sub>2</sub>, and small hydrocarbons such as methane, ethylene, and acetylene. The source of oxygen may be steam or air used for the plasma. Some torches use nonoxidizing plasmas such as nitrogen or argon. Heteroatoms from the organic feed will eventually be bound in gaseous products such as HCL, HF, phosphorous oxides, H<sub>2</sub>S, or SO<sub>2</sub>, depending on temperature and oxygen availability. Salts or metallic elements will be melted or vaporized; such materials are usually recovered as slags and sometimes as molten metal. The gaseous product is a fuel with a low heating value, which would be burned with added air. Heteroatoms in the gas would be scrubbed out by aqueous alkaline scrubbers to form salts. Phosphorus or metal components in the vapor can be quenched rapidly to give a metallic

---

<sup>7</sup> A number of plasma arc technology designs were presented at the committee's workshop (see [Appendix F](#); Keairns et al., 1992; Schlienger, 1992; Titus, 1992).

powder (particles less than 1  $\mu\text{m}$ ) or, under oxidizing conditions, metallic and phosphorous oxides.

Figures 7-5 and 7-6 portray some possible plasma arc furnace designs. Most furnaces use gases other than air for the plasma, for example,  $\text{N}_2$  or steam. An oxygen source is needed to prevent formation of carbon soot particles; steam is frequently chosen as the oxygen source, although power consumption increases because energy is required to dissociate the water.

*Development status.* Plasma arc furnaces have been developed and used for recovery of waste metal in foundries. Both nontransferred arcs (two independent electrodes) and transferred arcs (molten metal product forming one of the electrodes) have been used. Large furnaces with very large melting capacity (about 45 tons/hour) have been reported, with power inputs of 9 MW. More recently, the technology has been applied to mixed solid wastes and liquid wastes, such as PCBs. Destruction efficiencies of 99.9999 percent were reported for PCBs and  $\text{CCL}_4$  (Lee, 1989).

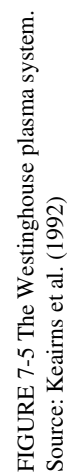
*Application to chemical weapons destruction.* The plasma arc process could be used on chemical warfare agents for detoxification and destruction. It could also be used to destroy the products from a prior treatment, such as hydrolysis. Plasma arc furnaces can handle large solid-metal objects, such as rocket cases, but most of the energetic contents would need to be removed first to avoid possible destructive events in the furnace. Propellants and explosives could be destroyed but would obviously require careful control of feed rate to avoid destructive explosions or detonations.

Air supply would represent only a small part of the stoichiometric requirement for liquid agent. The gas produced would consist predominantly of  $\text{H}_2$  and  $\text{CO}$ , with smaller amounts of  $\text{CH}_4$ , acetylene, and other materials (e.g.,  $\text{HCL}$ ,  $\text{H}_2\text{S}$ , or  $\text{HF}$ ), depending on the composition of the liquid agent. The gas product is at a lower temperature than the plasma because of the endothermic heat of reaction and would be oxidized in a second burner. Combustion products would require treatment to remove acidic components such as  $\text{HCL}$ .

*By-products and waste streams.* The waste streams from plasma arc destruction of agent would be essentially the same as those from incineration. The two-step operation of the plasma arc followed by a burner or catalytic oxidizer is itself a safeguard against transient breakthrough of agent. The following waste streams would be formed by plasma arc destruction of chemical agents:

- gases: carbon dioxide, nitrogen, oxygen, and steam;
- liquids: alkaline scrubbing liquid containing salts (e.g.,  $\text{NaF}$ ); and





Source: Keairns et al. (1992)

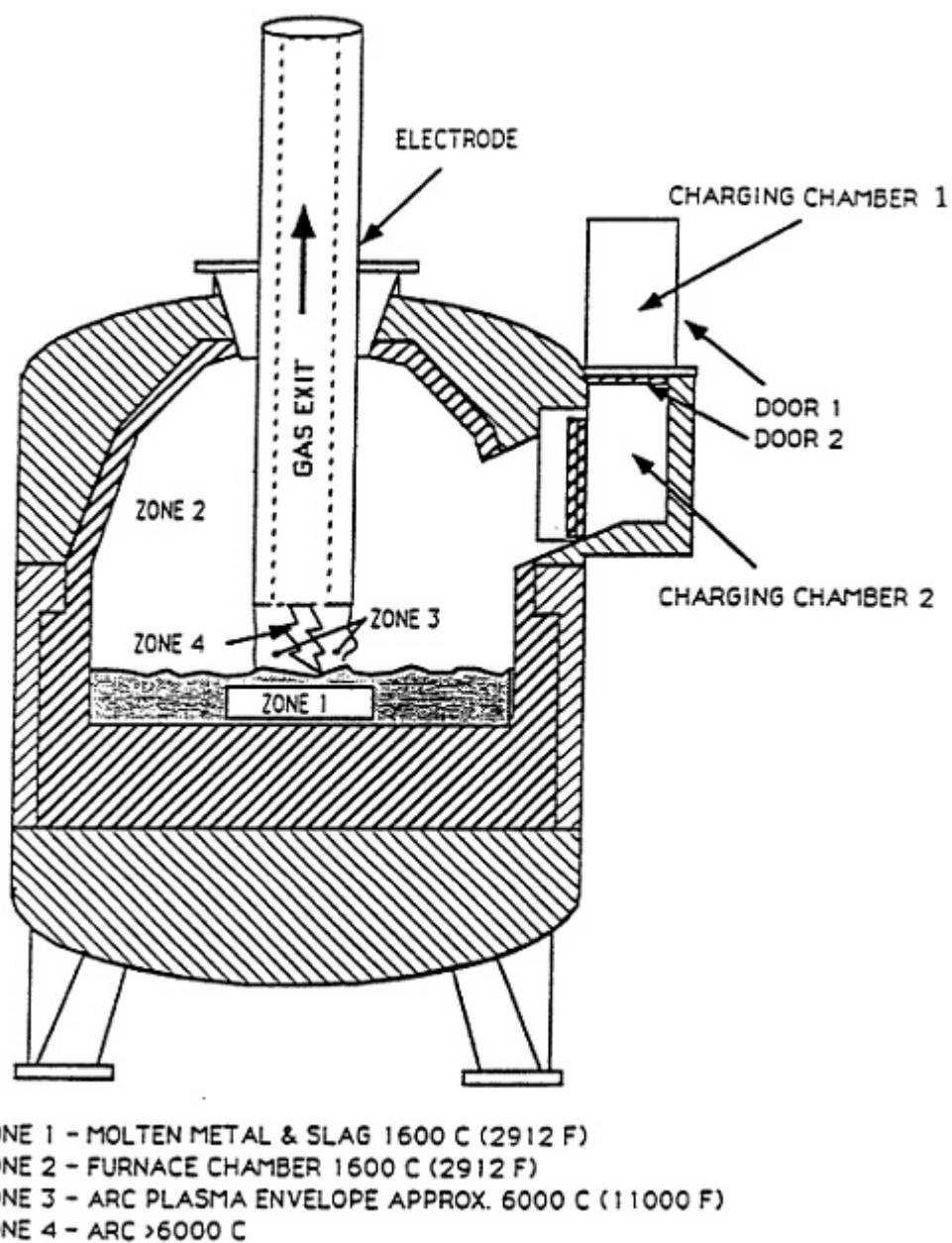


FIGURE 7-6 The Electro-Pyrolysis, Inc. (EPI) furnace design.  
Source: Titus (1992).

- solids: possibly small (less than 1  $\mu\text{m}$ ) metals and oxides from the feed material; metal parts fed to the furnace would be withdrawn as liquid.

*Advantages and disadvantages.* One advantage of the plasma arc furnace is that it acts as a two-stage system: a first detoxification reactor (the plasma arc) and a second destruction reactor (such as a burner or catalytic oxidizer). Arc furnaces have very short startup and shutdown times (e.g., startup of about 5 minutes to stable operation).

Disadvantages of these furnaces include their complexity and their significant labor requirements for operation (e.g., electrodes require frequent replacement, either weekly or monthly). The heat of combustion to be dissipated is the same as for incineration, but in addition, the energy drawn by the arc must be dissipated.

*Development needs.* Although plasma technologies have been available since the late 1940s, only one chemical process has been commercialized, a duPont process for producing acetylene from methane. Only metallurgical processes have been commercialized; there is at present a large steel remelting capacity. No other technology application is fully developed. Adapting the technology to the demilitarization program would require substantial design, development, and demonstration.

### Gasification Processes

*Technology description.* Several devices have been developed that partially oxidize pulverized coal with steam and either air or oxygen to produce a fuel gas. The use of air produces a gas with a low heating value (5.60 MJ/m<sup>3</sup>, or 150 Btu/ft<sup>3</sup>), whereas oxygen produces a gas with an intermediate heating value gas (11.2 MJ/m<sup>3</sup>, or 300 Btu/ft<sup>3</sup>; Shaw and Magee, 1974a,b). Pressures are usually above atmospheric, up to 400 psi (27 bar). Adding a methanizer can convert CO and hydrogen to CH<sub>4</sub> or synthetic natural gas (SNG).

Some developers of these coal gasifiers have proposed using them to destroy chemical warfare agents completely under the partial-oxidation operating conditions. Gasifiers that could be considered for this use are listed in [Table 7-3](#). [Figure 7-7](#) illustrates one design of a gasifier.

*Development status.* The technologies as applied to coal gasification are either commercial or have been tested on a very large pilot scale. Their use to date has been limited by economics, namely, the low price of natural gas. None has been tested with agent or energetics.

TABLE 7-3 Some Characteristics of Gasifiers

Process	Operating Conditions		Status	References
	Temperature (°F)	Pressure (atm)		
Koppers-Totzek	350	1	Commercial	Magee et al., 1974
Lurgi	2200	30	Commercial	Shaw and Magee, 1974a
Texaco	2500	20	Commercial	Shaw and Magee, 1974b
Toriplex	3000	30	Pilot Scale	Schulz, 1992

Gasifiers for use at demilitarization sites would require design and testing of equipment of the appropriate scale. If energetics are to be included in the feed, additional pilot studies may be needed.

*Application to chemical weapons destruction.* On the basis of available experience, agent would be broken down to such small molecules as PH<sub>3</sub>, NH<sub>3</sub>, H<sub>2</sub>S, HF, HCL, H<sub>2</sub>, and CO. Acidic molecules would then be removed by aqueous scrubbing. The agent typically represents a small fraction of the hydrocarbon fed to an industrial gasifier. The product gas would then be used for producing power in a conventional facility.

The size of the gasification plant precludes its double containment. It would be feasible, however, to contain the gasifier and scrubber.

*Special considerations.* Commercial gasifiers can accept gases or entrained liquids with air or oxygen. Solids would need to be fed with the coal. Under gasification conditions, it is reasonably certain that the agent would be destroyed if it enters the gasifier. As noted above, some gasifiers operate under considerable pressure. Some of the gases formed (e.g., PH<sub>3</sub> and HF) may attack refractory linings.

*By-products and waste streams.* The final products from destruction of agent or energetics would be similar to those of the baseline incineration technology: combustion products and such salts as NaF.

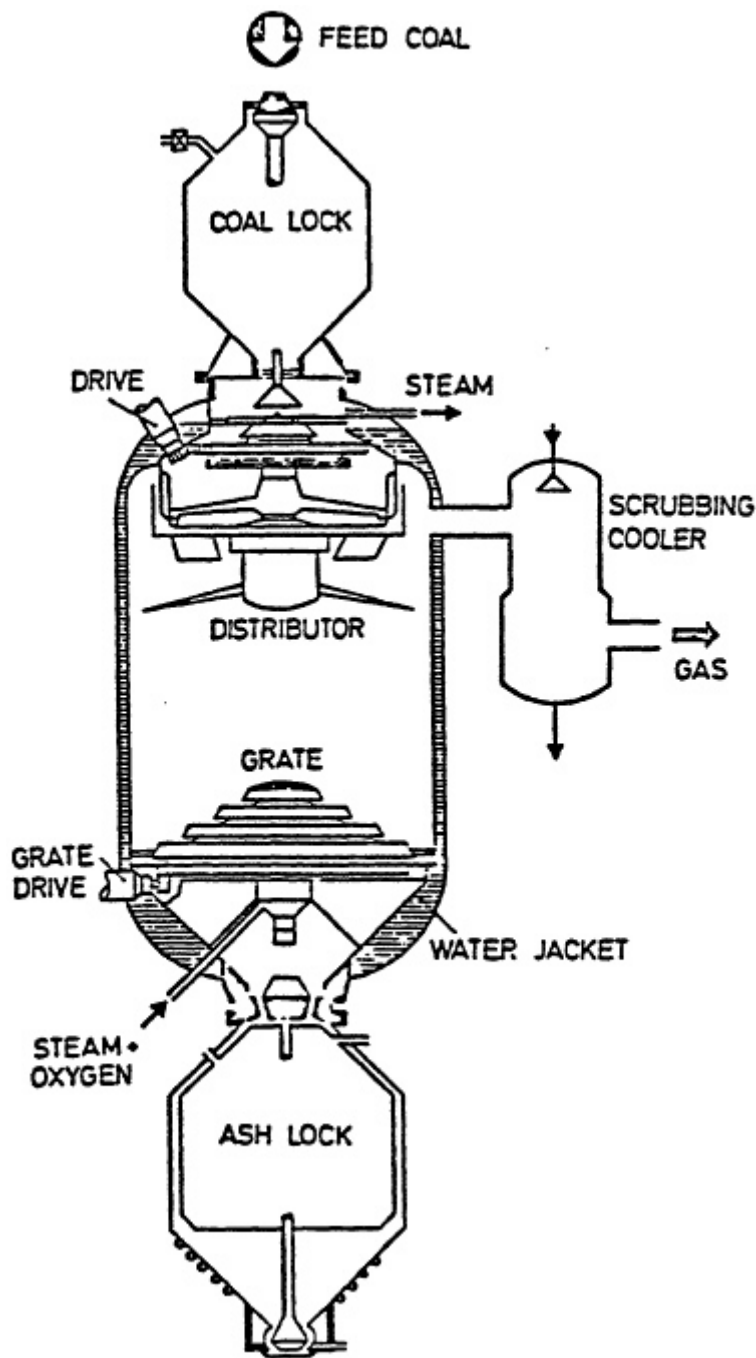


FIGURE 7-7 Lurgi gasifier.  
Source: Shaw and Magee (1974a).

*Advantages and disadvantages.* The destruction process for agent in this case is a two-step process: an initial steam reforming at high temperature followed by combustion. The possibility of agent breakthrough is therefore remote.

Gasifiers are very high throughput devices, and the treatment of agent would have little effect on the operation. They are easily controlled and quite stable. The inventory of agent would be small because of the very high processing rate possible.

The disadvantages of this process are inherent in the primary purpose of the equipment, which is to gasify coal. It would be difficult to combine agent destruction with any ongoing industrial process, considering the lethal nature of chemical agents. Furthermore, industrial designs would need to be revised and scaled down for application to chemical weapons destruction.

*Development needs.* Gasification is commercial technology. Safe feed mechanisms to bring the agent or the energetics into the gasifier need to be developed. Operation of gasifiers with the materials containing the heteroatoms of chemical agents would need to be demonstrated. Such problems as attack on refractory lining and metal corrosion could be expected. The process would also need to be integrated with the subsequent combustion and gas cleanup system. Consequently, substantial design and development would be required.

### Synthetica Detoxifier

*Technology description.* Distinct from many of the other proposed unit operations, the Synthetica Steam Detoxifier consists of a series of processes integrated into an overall equipment package, complete with controls, monitoring equipment, and other features (Figure 7-8). The same figure is repeated in Appendix K and shows an estimated heat and material balance. Agent destruction takes place by high-temperature pyrolysis followed by low-pressure gasification. This series of processes treats organic materials as follows:

- Evaporation and treatment of the feed material: The feed material is evaporated into high-temperature steam, and pyrolysis and some reaction with steam occurs. Alternative evaporators might be used. A promising evaporator for applications to chemical warfare agents is the moving bed evaporator (MBE), which consists of a descending bed of uniform-size solid balls about 3/8 in. in diameter. Evaporator capacity is specified as up to 3 drums per day by the developer, Synthetica Technologies, Inc., Richmond, Calif. Hot gas enters the bottom at about 700°C (1290°F). Feed, such as

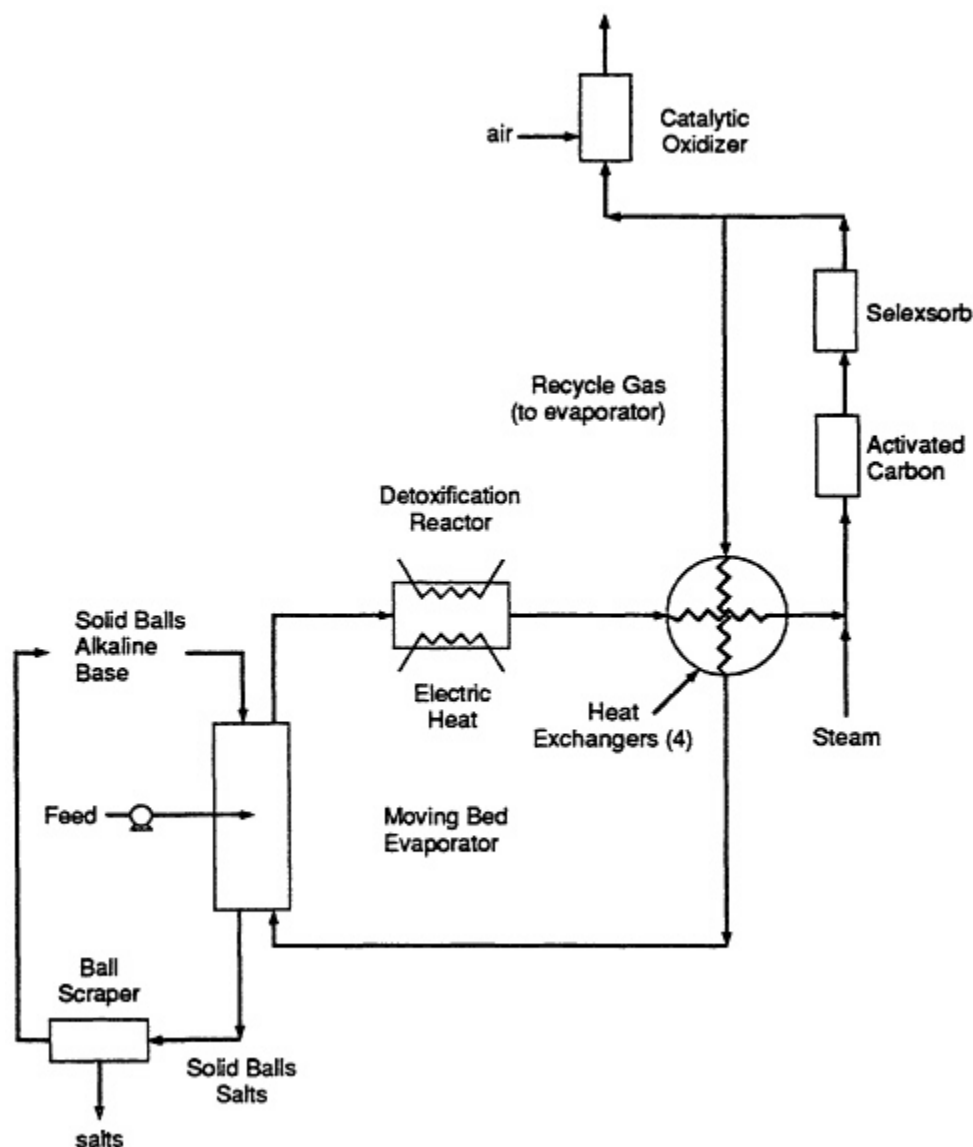


FIGURE 7-8 Schematic flow sheet for the Synthetica Steam Detoxifier.

Source: Synthetica Technologies, Inc.

evaporator (MBE), which consists of a descending bed of uniform-size solid balls about 3/8 in. in diameter. Evaporator capacity is specified as up to 3 drums per day by the developer, Synthetica Technologies, Inc., Richmond, Calif. Hot gas enters the bottom at about 700°C (1290°F). Feed, such as chemical warfare agent, is injected at about the midpoint. The solids contain a reactive alkaline material.

temperature of about 425°C (795°F). The gas consists primarily of C-H-O species.

Yet another form of evaporator for this type of system is simply a drum of the feed material bathed in an atmosphere of hot gas, that is, steam and reaction products, at a temperature as high as 650°C (1200°F). This approach might be preferred for handling solid propellant or high explosives. Development work would be needed to establish desirable operating conditions in this case, because these materials are reactive and potentially explosive.

- Further destruction in the detoxification reactor: The vapor leaving the evaporator, consisting of remaining organics, steam, and products of the steam-reforming process, passes to a detoxification reactor. In this reactor the material is heated electrically to a higher temperature, typically about 1300°C (2370°F). Reaction rates at such high temperatures are rapid and the product is believed to closely approximate thermodynamic equilibrium. A small excess of steam drives the products predominantly to CO and H<sub>2</sub>, with negligible residues of larger molecules, such as compounds with benzene rings. Chemical warfare agents should be completely destroyed at this point.
- Gas stream cleanup: The gas is given a final "polishing" by beds of activated carbon and of Selexsorb, a patented zeolite adsorption bed that adsorbs and neutralizes acid gases. These treatments require the gases to be cooled from the temperature in the detoxification reactor of 1250°C (2280°F) to about 175°C (350°F). The cooling is accomplished by a series of heat exchangers: a ceramic exchanger and a series of stainless steel exchangers, followed by addition of 100°C steam. Although not shown on the flow diagram, a heat balance indicates that external cooling will also be needed. The exchangers also permit the cooled gases at 175°C (350°F) to be reheated to 700°C (1290°F) for use in the first unit, the MBE.

The actual product gas is a small slip stream removed from the treated gas before the gas is recycled at about 175°C (350°F). It consists primarily of CO, H<sub>2</sub>, and steam, with trace quantities of light hydrocarbons such as CH<sub>4</sub>. It could possibly be diluted and oxidized at a lower temperature in a catalytic oxidizer.

- Gas recycle: The recycle gas stream carrying heat to the evaporator is a relatively large stream. As a result of the recycling, most of the gas goes through the detoxification reactor and subsequent cleanup beds several times before being released to the catalytic oxidizer and the atmosphere. The unit operates at a slight negative pressure; any gas leak would be from ambient air into the equipment.

*Status and database.* A series of full-size detoxifier tests was conducted under a California state grant program. The feed used was generally a mixture of materials, such as 66 percent acetone, 32 percent xylene, 1 percent



trichloroethane, and 1 percent dichlorobenzene (Galloway, 1989). High levels of destruction were demonstrated at 1150°C (2100°F), well below the maximum temperature claimed for the detoxification reactor (about 1500°C, or 2730°F; see [Appendix K](#); flow rates can also be found in Galloway, 1989).

Two commercial units have been installed and tested at customer sites. Reaction rates are high at the very high temperature used. It is assumed that the gas composition from the detoxification reactor approaches equilibrium. The effects of changing feed composition, the ratio of steam to organics materials, and temperature have been demonstrated by calculation of equilibrium compositions. These calculations also show that high temperatures and excess steam limit the formation of aromatics such as benzene to very low amounts. At moderate temperatures—those less than about 1250°C (2280°F)—CH<sub>4</sub> is a significant equilibrium product. It represents a few percent depending on the steam content.

The MBE, with its bed of uniformly sized balls containing alkaline agent, is a fairly new development. It is reported to be in operation but no details of its operability, extent of reaction, solids handling problems, and other features are known. Proprietary information has been held until suitable patent protection has been obtained.

*Application to chemical weapons destruction.* Chemical warfare agents are expected to be as reactive as materials that have already been tested. High levels of destruction are anticipated at the higher temperatures (greater than 1500°C) that the equipment is designed to meet. There is no direct experience with organics containing F, P, or S, although there has been some test work on pesticides containing P (Galloway, 1992, personal communication). Equilibrium calculations for the high temperatures used suggest these atoms should all go primarily to acid products (HF, H<sub>2</sub>S, and P<sub>4</sub>O<sub>6</sub>), which can be adsorbed. Materials tested to date have had a much lower content of heteroatoms than do neat chemical agents.

Propellants and explosives would probably be reacted first in the drum feed evaporator (a simple drum). Their behavior would need to be evaluated. Presumably they will react (oxidize) spontaneously at some high temperature. The amount of these materials fed into the unit at any one time might be critical. If the materials reached a spontaneous ignition temperature they would burn up very quickly, liberating a large quantity of heat and a very large burst of gas. Detonation would be possible if a critical amount of these materials were exceeded. Because of the minor amounts of metallic compounds they contain, a small quantity of solid residue should be expected from both propellants and explosives.

Metal parts can be treated in the drum feed evaporator and should reach the 3X level of decontamination. Dunnage could possibly be handled similarly.

*Special considerations.* Corrosion in the system has been controlled by suitable construction materials. Most components of the feed system, such as piping, are 316-L stainless steel; ceramics are used in the highest temperature zones. The system has been run hot, above the condensation point of water and acid gas (about 180° C, or 360°F). Thus, electrolytic corrosion has been avoided. Data have been reported with feeds containing chlorine but not the other heteroatoms (in particular, fluorine) found in chemical agents. The corrosiveness of their products needs to be explored.

Propellant and explosive would presumably be fed to the unit intermittently. They would need to be removed from their containers and fed in small increments. Detonation is possible if a critical size of batch feed is exceeded (very small in the case of explosive). The potential for sudden gas generation and detonation will need to be addressed in the evaporator design and may preclude the use of the equipment for energetic materials.

*By-products and waste streams.* Product gas has passed through an extensive cleanup system, adsorbent beds, and catalytic oxidation. Organic matter should thus be largely eliminated, to a destruction level of 99.9999 percent or more. The spent solid adsorbents (carbon and Selexsorb) will have to be managed appropriately.

Other waste streams will include any solid residue remaining from the high-temperature evaporation and spent caustic slurry with salts of the acid gases that have been absorbed. These will show up separately or as a mixture, depending on the front-end evaporation process.

The solid waste from treating chemical agents would be relatively large primarily because of the salts formed, amounting to more than double the weight of the original agent. This waste will require further stabilization (oxidation) before disposal because of the presence of phosphite or sulfide salts. The solid waste from disposing of propellant or explosive should be very small.

Upsets in the operation (e.g., a power failure) are possible. Provision could be made for all waste streams to be retained until analytical work has shown that they can be released appropriately. Estimates of the stream sizes and heat requirements for GB destruction are given in [Appendix K](#).

*Advantages and disadvantages.* The advantage of steam reforming lies in the product distribution obtained. The reaction with steam leads to different products than reaction with oxygen. Equilibrium calculations indicate that troublesome products such as NO<sub>x</sub>, SO<sub>x</sub>, and solid particulates are not formed at the very high reforming temperatures used. Trace amounts of some stable aromatics, such as benzene, toluene, styrene, naphthalene, or dichlorobenzene, could be formed. However, the amounts formed can be controlled by the

mount of excess steam supplied and by temperature. In any case, final gas cleanup is provided.

The process operates essentially at atmospheric pressure. The reactions in steam reforming are endothermic, with the required heat supplied electrically. Reactions would likely proceed with no large temperature transients as a consequence. The system is totally integrated and could be operated as an enclosed system, with no discharge of product before analysis and verification. A major structural problem resulting in a significant air leak could lead to fires. However, the control system has instrumentation and shutdown features to handle usual problems such as air leaks.

Some solid residue should be anticipated in the evaporator. Chemical agents contain poorly characterized impurities, including some metallic compounds, which can have high boiling points; they will probably decompose on heating to form solid carbonaceous residue. These solids will presumably be left in the evaporator; they will be mixed with acid salts in the MBE. The residues may be considered toxic because of their metal and fluoride content.

The process is very energy intensive. Electric power consumption for destruction of 1 ton of agent per day is estimated to be 335 kW (with 24-hour operation). Because all of the materials will ultimately be oxidized to final stable products, the overall process is exothermic. All of the exothermic heat of reaction, as well as the energy of electric power consumption, must be removed by suitable cooling.

Phosphorus and sulfur in agents are recovered as solid phosphite and sulfide salts. These are not stable materials and will require further oxidation.

*Development needs.* The Synthetica process consists of several steps in series, with no intermediate storage. Process integration will have to be demonstrated. Some of the technology is novel or unusual:

- The moving bed evaporator is being developed; a prototype is operating.
- The detoxification reactor operates at extremely high temperatures (1200°C). The gas being heated and reacted will contain small amounts of very corrosive chemicals, such as HF or HCl, which might cause operational difficulties.
- The heat exchangers operate at very high temperatures and with some very large temperature differences. Industrial experience has shown thermal stress to result in cracking and leakage under these conditions.

Thus, further work in several areas would be needed to use the Synthetica process for chemical demilitarization. Surrogate materials with appropriate concentrations of heteroatoms (F, P, and S) would need to be tested to validate equilibrium product calculations and to evaluate corrosion,

operation of the MBE and the slurried alkali treater, and other operational features. Sodium phosphite formed in the MBE is probably not stable and is possibly accompanied by phosphine formation. It would have to be oxidized further. Similarly, the sulfide formed from destruction of mustard gas would require further oxidation for stability.

Propellants and explosives would present special problems because of their reactivity. Related test work would be needed. In addition, heat and material balance information would be helpful.

## HIGH-TEMPERATURE, LOW-PRESSURE OXIDATION

### Catalytic Fluidized-Bed Oxidation

*Technology description.* Catalytic fluidized-bed oxidation uses a fluidized, granular solid as a heat transfer medium; for chemical agent destruction, the solids of choice would be aluminum oxide (alumina) or calcium oxide. The material is kept in suspension by the gas flow, which is primarily air. A wide range of gas velocities has been used. A velocity of 1.5 m/s will produce a dense-phase bubbling fluid bed (e.g., as in test work at Picatinny Arsenal; Liota and Santos, 1978); much higher velocities, of 10 m/s or higher, lead to highly loaded dilute phase beds (e.g., as in the Circulating Bed Combustor of Ogden Environmental Services). High gas velocity can also be used in a spouted bed, depending on the configuration and method of gas injection.

The beds act as well-mixed reactors with high thermal inertia. Fuel can be liquid, solid, and gaseous. Temperatures are kept relatively low, at roughly 800 to 1000°C (1470 to 1830°F), reducing potential emissions of NO<sub>x</sub>, dioxins, and CO. The exhaust from the reaction chamber is passed through a hot cyclone and the solids are circulated back to the reaction chamber. The gas would be treated further as necessary, possibly by a catalytic afterburner and a packed bed scrubber for removal of acid gases.

For the destruction of explosives, the formation of NO<sub>x</sub> could be minimized by operating the bed in a staged mode into which is fed 63 percent of the air theoretically needed to oxidize an aqueous slurry of 15 to 25 percent TNT. An additional 59 percent of the air theoretically needed is fed in a secondary stage in the zone immediately below the disengaging section from the fluidized solids. With the addition in the TNT slurry of nickel equivalent by weight to 6 percent of the total fluidized solid, emissions of NO<sub>x</sub> have been kept to about 60 ppm, unburned hydrocarbons to about 10 ppm, and CO to 4 ppm. The addition of nickel to the fluid bed solids would add a possible carcinogenic hazard; extra care would be needed to handle solids and to capture dust from the bed.

*Development status.* A catalytic fluidized bed incinerator was operated at Picatinny Arsenal for about 1 year. The unit was 2.44 m (8 ft) in diameter and 9.14 m (30 ft) high with a charge of 10,000 kg of alumina. Runs were made at 165 kg/h of 25 percent TNT slurry. Liota and Santos (1978) provided a very favorable evaluation of the technology. However, the technology was not adopted by the Army. Related technology has been demonstrated for the Environmental Protection Agency (e.g., the circulating bed combustor). Fluidized-bed applications are widely used in the petroleum industry, and fluidized-bed combustion is used in the utility industry and for waste disposal.

*Application to chemical weapons destruction.* Slurries of organic materials of up to 25 percent in water have been successfully destroyed in a commercial size unit. To achieve high levels of destruction with a fluidized bed, an afterburner will be needed to complete the destructive process. Fluidized-bed equipment can be used to treat both hydrolysis products and energetics. Solids up to approximately 1 inch diameter can be handled offering the potential for dealing with shredded dunnage and metal parts.

*By-products and waste streams.* A fluidized-bed oxidizer operating with a bed of alumina would yield products similar to those of baseline incineration. When the bed is lime or dolomite, a large fraction of the acidic components (HCl, HF, and SO<sub>2</sub>) are removed. This variation has not been tested by the Army.

*Advantages and disadvantages.* Fluidized-bed oxidizers have many similarities to conventional rotary kiln incinerators. They have the following major advantages:

- Operating temperature is low enough to avoid formation of some undesirable products, such as NO<sub>x</sub> or dioxins.
- High thermal inertia of the bed avoids the flame-out and bypass of agent.
- Mixing also avoids a major combustion puff.
- High water content and small particle size in a slurry mitigate the concern for an explosion when feeding propellants or explosives.
- With a preheated bed, the unit allows rapid startup and shutdown of the feed stream.

There are several disadvantages of fluidized-bed oxidation:

- Nickel on the fluidized-bed particles will lead to a disposal problem. The nickel will have to be recovered before solids disposal.

- Granular material of the bed can lead to problems. Finely divided dust can be difficult to capture or could end up in the acid scrubbing solutions or salts formed by reaction with bed materials, which could cause particle agglomeration with poor fluidization.
- The very high destruction desired for chemical agents (99.9999 percent) is difficult to achieve in a fluidized bed; staging would be needed.

*Development needs.* The technology must be demonstrated on the feed materials of interest. The presence of heteroatoms will affect the chemistry and possibly the operability of the process. A pilot plant and a demonstration plant would be required.

### Molten Salt Oxidation<sup>8</sup>

*Technology description.* Molten sodium carbonate at 900 to 1000°C (1650 to 1830°F) is used with air as a medium in which to oxidize mixtures of combustible solids, organic liquids, aqueous solutions, and/or slurries. Acidic products, such as HF, HCl, SO<sub>2</sub>, and P<sub>2</sub>O<sub>5</sub>, would react to form salts that would dissolve in the molten salt bath (Figure 7-9). The sodium salts of chlorine, fluorine, phosphorus, arsenic, sulfur, and silicon as well as iron oxide, silver, and copper all end up in the molten salt bath. The gaseous effluents need to be filtered to remove some of the fine particulates formed in the bath, and the process would probably require an afterburner. Spent salt is discarded or could be recycled. Alternatively, a molten salt countercurrent tower design could be used as an afterburner and for removal of acid gases in the waste gas streams from other processes.

*Status and database.* The Atomic Energy Commission began research and development on molten salt oxidation in the early 1950s. It funded Rockwell International in the early 1960s to further develop the process, and other work followed (Taylor, 1992). The U.S. Department of Energy (DOE) recently sponsored work on the application of the process to mixed waste

---

<sup>8</sup> Subsequent to the committee's data collection activities, a large R&D program on molten salt oxidation has been implemented.

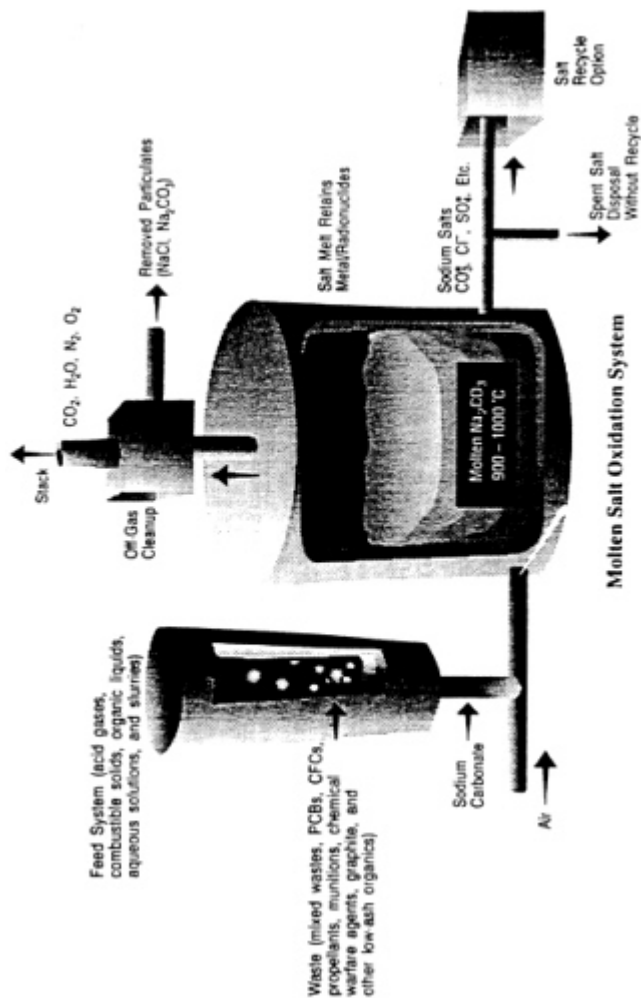


FIGURE 7-9 Molten salt oxidation system.  
Source: Taylor (1992).

treatment. It was also tested on chemical warfare agents (VX, GB, and mustard) at Edgewood Arsenal, Maryland, in 1976, achieving 99.9999 percent destruction of agent, and is was tested on a number of propellants and explosives.

Molten salt baths are used commercially for heating and pyrolysis operations. The current application would use the high heat capacity of the bath for two purposes: to carry out oxidation at relatively low temperatures (much lower than those used for incineration), which would minimize some undesirable combustion products ( $\text{NO}_x$  and dioxins), and to avoid large temperature changes that can occur in conventional incineration that can result from variations in feed rate or composition.

*Application to chemical weapons destruction.* Molten salt baths could be used to destroy agents, hydrolysis products, propellant, and highly explosive materials. Finely ground explosive and propellant solids would be fed at a low enough rate to avoid explosion. The small dimensions of these materials would also accelerate oxidation in the bath.

*Special considerations.* The suggested salt bath material would be  $\text{Na}_2\text{CO}_3$ , which has a melting point of  $851^\circ\text{C}$  ( $1564^\circ\text{F}$ ). It should react with acidic combustion products to form sodium salts and emit fixed gases free of undesirable components (after filtration for fine solids). The hazards of handling a molten carbonate bed are minimal. These beds have been considered for commercial applications in molten carbonate fuel cells (Kalfadelis, 1977).

Reactants and products rise through the hot molten salt as bubbles. As a result, some reactants may bypass the system. Very high conversion levels (99.9999 percent) may require staging or further product treatment, such as the use of an afterburner. Oxygen rather than air might be used as the oxidant to minimize the volume of gas effluents.

One hazard of the process is potential superheated-vapor explosions when liquid agent or hydrolysis products are introduced. The presence of propellants or explosives could also lead to explosions. If not well dispersed, energetic materials could cause explosions or puffs.

*Waste streams.* Very fine (possibly smaller than  $1\text{ }\mu\text{m}$ ) salt particles may be formed and carried with the gaseous discharge. Filters would be needed to prevent these salt particles from being emitted with the otherwise clean flue gas components. No liquid would be emitted. A certain fraction of the molten salt bath must be removed and fresh sodium carbonate added to maintain desirable salt composition. The total salt requiring disposal would be several times the weight of the chemical agent destroyed.



*Advantages and disadvantages.* The advantages for molten salt oxidation are as follows:

- The process allows gaseous oxidation to occur at relatively low temperatures, thus minimizing the formation of such emissions as  $\text{NO}_x$ .
- Most acid gases formed would be retained in the bed. Wet scrubbing would be minimized, possibly eliminated.
- This technology can be used for secondary oxidation after a primary agent detoxification process, such as hydrolysis or pyrolysis.
- It is a versatile technology, able to destroy agents, explosives, and propellants and to decontaminate metal parts. Energetic materials would have to be fed carefully (probably in slurry form) to avoid disastrous explosions.

Disadvantages of the process include the following:

- The means of disposing of the salt removed from the system (blow-down) is currently uncertain; the salt is soluble.
- A better fundamental understanding is needed to avoid the possibility of superheated-vapor explosions.

*Development needs.* This technology has been used on a small scale since 1950. Molten carbonate is a fairly well-known material, and there is some experience in using it for agent destruction on a laboratory scale. Specific development problems have not been identified, but a pilot plant and demonstration effort would be required.

### Catalytic Oxidation

*Technology description.* Catalytic oxidation uses an oxidation catalyst with natural gas to heat the catalyst to an operating temperature of about  $500^\circ\text{C}$  ( $930^\circ\text{F}$ ). (It is also possible to preheat the feed stream by using other direct or indirect methods.) This technology is normally applied only to very dilute gas streams for final cleanup. With some modification, possibly with electrical heating, it could be used to replace the baseline combustion-based afterburner. The required operating temperature would depend on catalyst activity.

For a temperature of  $500^\circ\text{C}$  and a space velocity of about 7,500 V/h/V, the catalyst can destroy volatile organic compounds containing halogens, sulfur, and phosphorus when they consist of about 0.1 percent of the gaseous feed. The catalysts are generally available on a cordierite monolith to avoid problems of drops in pressure and often contain noble metals on a gamma-alumina washcoat (Shaw et al., 1993; Wang et al., 1992; Yu et al.,

1992). The technology is very similar to that used in the automobile industry to reduce emissions of unburned hydrocarbons and CO.

*Development status.* Laboratory data available in the literature are adequate for commercial design (Shaw et al., 1993). Catalyst manufacturers such as Engelhard (Farrauto, 1992) and Allied (Lester, 1992) have announced the availability of commercial oxidation catalysts that are not degraded by elements such as chlorine, phosphorus and sulfur. However, few data are available in the technical literature to verify these claims. Proprietary catalysts (of unknown composition) were tested on chemical agents in air streams at high dilutions with successful results (Snow, 1992). A full-scale test for the destruction of trichloroethylene will be conducted in early 1993 under the U.S. EPA Site Program (Shaw et al., 1992).

*Application to chemical weapons destruction.* Laboratory results have demonstrated the destruction of trichloroethylene, methylene chloride, and hydrogen sulfide (to better than 99.9 percent) to the products hydrogen chloride, sulfur dioxide, and sulfur trioxide; little deactivation occurred after the initial drop in fresh catalyst activity of about 25 percent. This technology can be used to fully oxidize trace gases produced in well-mixed oxidizing systems that need an afterburner. A lab demonstration showed that oxidation can be promoted by using the support material (cordierite) without catalyst; the temperature required was much higher, 1000°C (1830°F) versus the 500°C (930°F) when using catalyst. The oxidation was not as complete as with catalysis; some chlorinated hydrocarbon species survived in the product.

For use of highly active catalysts, the best application appears to be for treatment of gases from low-or medium-temperature processes, such as chemical and biological oxidation and WAO or SCWO when the concentration of catalyst poisons can be within acceptable limits and where heat must be added to bring the gases to reactive temperature. For high-temperature agent oxidation the heteroatom content can limit catalyst activity; however, the available high temperature allows use of a rugged low-activity catalyst.

*Waste streams.* Liquid products of oxidation may need to be removed, possibly by using scrubbers or activated-carbon filters. Scrubber effluent liquids contain unreacted alkaline materials and salts of chlorine, fluorine, sulfur, and phosphorus. The spent sorbent will need conventional disposal. The solids will contain calcium chloride, fluoride, sulfate, and phosphate. Similarly, the spent catalyst will need to be discarded.

*Advantages and disadvantages.* Catalytic oxidation is used commercially for the oxidation of trace hydrocarbons, because of its several advantages over

conventional incineration: reducing the need for fuel or other heating media, avoiding the need for high-temperature materials of construction, and offering the possibility of overload with catalytic solids to achieve high destruction levels.

The disadvantages of catalytic oxidation are associated with the poisoning and deactivation of the active metals by the heteroatoms found in agent. Thus, system lifetime is highly uncertain. The technology is generally used for dilute gas streams. It would not be a reasonable technology for initial agent destruction.

*Development needs.* The scaleup of catalytic oxidation is generally accomplished from tests on very small reactors. Thus, the testing of a catalytic oxidizer with agent heteroatoms should take less than 1 year. To the extent that the catalyst is adequate, the next step would be a full-scale test. Some catalyst development and pilot plant work would be required.

## OTHER PROCESSES

### Hydrogenation Processes

*Technology description.* Catalytic hydrogenation is very widely practiced, particularly in the oil industry. It usually involves temperatures high enough to promote cracking and rearrangement reactions along with hydrogenation. The technology is now being pursued to convert hazardous wastes into useful materials.

Organic materials containing a high concentration of sulfur are commonly treated with hydrogen to eliminate the sulfur (as  $\text{H}_2\text{S}$ ). The hydrogenation process is now being developed to attack chlorine similarly (for removal as  $\text{HCl}$ ). Presumably other heteroatoms, such as P and F, would also be reactive with hydrogen under appropriate conditions; this remains to be demonstrated.

Usual operating conditions are a temperature of up to  $450^\circ\text{C}$  ( $840^\circ\text{F}$ ) and pressure in the range of 116 to 1,450 psi (8 to 100 bars) with a large excess of hydrogen gas, typically about 80 percent by volume. The hydrogen reacts with the heteroatom and also saturates the remaining hydrocarbon. Figure 7-10 is a block design for the UOP process, a by-product conversion process.<sup>9</sup> This process consists primarily of a reactor for removal of the chlorine in the material, followed by separation and recovery of the  $\text{HCl}$  and saturated hydrocarbon (Hedden, 1992).

<sup>9</sup> For example, trichloroethylene reacts with hydrogen to form ethane and hydrochloric acid:  
 $\text{ClCH} = \text{CCl}_2 + 4\text{H}_2 \rightarrow \text{C}_2\text{H}_6 + 3\text{HCl}.$

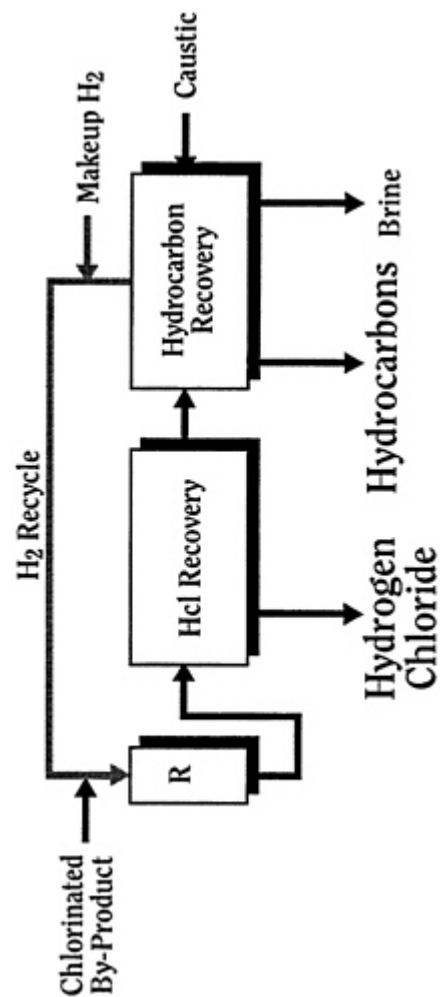


FIGURE 7-10 Block flow diagram of the UOP HyChlor conversion process.  
Source: Hedden (1992).

*Status and database* Laboratory and pilot plant equipment are in place and could be used to examine surrogate materials for chemical agents. Little if any work has been done on fluorine and phosphorus compounds. The central requirement for this process is a suitable catalyst, one that will bring about the reaction desired and is rugged enough to have a long useful life, typically 1 year or more. Desulfurization catalysts are well-known. Catalysts for chlorine removal have been developed but are probably optimized for particular feedstocks. Different catalysts may be needed depending on the heteroatom to be removed.

The UOP process has been used on several waste streams: PCBs, to form biphenyl and HCl; cresol, to form toluene and water; trichloroethylene, to form ethane and HCl; tetraethyl lead (treated with  $H_2S$ ), to form ethane and  $PbS$ ; and waste streams from the manufacture of epichlorohydrin and vinyl chloride.

*Application to chemical weapons destruction.* Hydrogenation is certainly capable of destroying chemical agents. The high conversion level needed is not typical, however, and would have to be demonstrated. The process is applicable to liquid feedstocks. Hydrotreating of propellants and explosives would not be useful.

*Special considerations.* Care must usually be taken to prevent loss of catalyst activity. Contaminants can be destructive; for example, small concentrations of metals or heavy ends that crack and form coke on the catalyst can destroy catalyst activity. Almost any new feedstock will require extended process runs to ensure catalyst life.

Hydrocracking is exothermic, but the large excess of hydrogen limits the temperature rise, allowing the hydrogenation processes to operate in a stable manner. Conversion amounts, for example, for sulfur removal, can be high. Test work would be needed to demonstrate the extremely high levels of destruction required for chemical agents.

*By-products and waste streams.* The exact nature of the waste streams would have to be determined by work on the agents. Gaseous waste streams of HCl, HF, and  $H_2S$  and possibly  $PH_3$  would be produced in a dilute mixture with hydrogen. They all may pose problems to catalyst performance. They could be separated from the hydrocarbon product by distillation and then would need to be treated appropriately. The hydrogen would be recycled. The gaseous products in this case represent safety and toxicity hazards.

Liquid product would probably be burned. Combustion products might require a water or caustic wash, resulting in a waste aqueous stream.

Agents might require distillation before being run over the catalyst. The residue from the distillation would be a waste stream that might, for example, be coked to a stable carbon residue. The composition of gas produced by coking is unknown; it might contain some of the agent heteroatoms and require further treatment. Ultimately, the catalyst would have to be removed and possibly reworked.

*Advantages and disadvantages.* There are several advantages of the process:

- It is a closed system; material can be recycled if the processing is incomplete.
- Useful products are recovered, and waste streams are minimized; the products would probably be used as fuel within the plant.
- The operating pressure and temperature for the kinds of materials in chemical agents would most likely be at the low end of the scale, perhaps 360 psi (25 bars) and 400°C (750°F); these are conditions within the range of common industrial experience.
- The product streams are small in volume compared with those of oxidation processes; they could be retained easily for certification before release.

The major disadvantages are as follows:

- The three chemical warfare agents would probably require the development of three catalysts; some of the heteroatoms would be expected to be poisons for normal hydrogenation catalysts, nitrogen and phosphorus in particular.
- Small system leaks would be hazardous and would require more than usual care. Substantial leakage in any enclosed space containing air could lead to an explosion; special mitigation measures will be needed.

*Development needs.* Hydrogenation process development would require catalyst developments and process definition, including operating conditions and recovery and treatment of products. Development based on surrogate chemical agents could be achieved in a few months. Work would be necessary with actual agents, however, because of the presence of impurities that could affect the catalysts and process.

### The Adams Process-Reaction with Sulfur

*Technology description.* The Adams process is a patented method that relies on the reactivity of elemental sulfur vapor to destroy organic materials at temperatures of 500 to 600°C (930 to 1100°F) (Berkey and Hendricks, 1992). Gaseous and solid products are formed. Gases such as CS<sub>2</sub>, COS, HCl, and H<sub>2</sub>S require recovery or further destruction. The solid formed is a high-molecular-weight carbon-sulfur material of uncertain composition, probably containing some of the heteroatoms (P, Cl, F, or O) of the original organic materials.

The process involves several steps (Figure 7-11). Liquid agent, possibly preheated, and sulfur vapor are fed to a reactor; an oxygen-free atmosphere is maintained by using nitrogen at a pressure slightly above atmospheric. The reactor suggested in a process patent is a "rotating screw-type oven heated by electric induction heating coils to maintain temperature..." (the ratio of sulfur vapor to organic has not been disclosed; there is presumably a range of compositions over which reaction is possible, analogous to upper and lower flammability limits in combustion with air) (Adams, 1990).

The solid product formed is further heated to drive off unreacted sulfur vapor. The result is a black glassy product, primarily carbon and sulfur in a highly cross-linked molecular structure. No residual reactant (e.g., PCB) has been detected. Experiments suggest that about 90 percent of the carbon in the feed is converted to this solid product.

The gas leaving the reactor contains nitrogen and unreacted sulfur vapor along with products of the reaction, such as CS<sub>2</sub>, H<sub>2</sub>S, COS, S<sub>2</sub>Cl<sub>2</sub>, CSCI<sub>2</sub>, and HCl. A series of gas-treating steps are envisioned:

- condensers to remove condensibles such as S, CS<sub>2</sub>, and S<sub>2</sub>Cl<sub>2</sub>;
- scrubbers to remove acid gases, such as HCl and H<sub>2</sub>S, which will require further disposal (the precise steps for separating all of the products do not appear to have been considered by the developers because they consider them to be existing technology); and
- recycle of fixed gases, primarily nitrogen.

*Status and history.* The process has been tested at the University of Pittsburgh and at Picatinny Arsenal. Bench-scale tests carried out by the Center for Hazardous Material Research (University of Pittsburgh) demonstrated the application of the process to a number of organic and chlorinated organic materials. A pilot-scale continuous unit was operated by the National Environmental Technology Applications Corporation (University

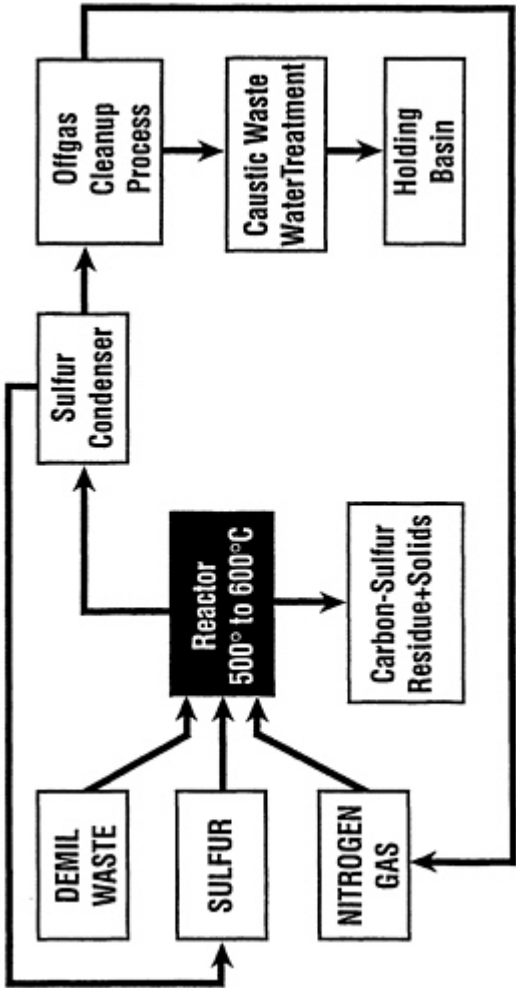
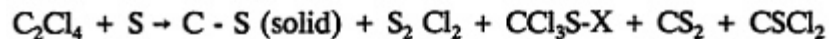
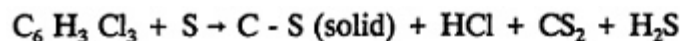


FIGURE 7-11 A process flow sheet for the Adams process as presented by CHEMLOOP, L.P.  
Source: Berkey and Hendricks (1992).



of Pittsburgh), where a number of chlorinated organic compounds were destroyed.<sup>10</sup>

According to the developers of the process, experimental work with chlorinated compounds has produced the following compounds:



where X = Cl, SCl, C Cl<sub>3</sub>, C Cl<sub>3</sub>S, or Cl<sub>3</sub>SS.

Reaction rates have not been measured but are believed to be high. Experimental work on chlorinated compounds has shown high destruction levels. Staging, with reactors in series, would ensure against the agent bypassing the system and ending up in the product.

The detailed chemistry of the process does not appear to have been addressed. The solid residue is reported to be stable and insoluble, but the effects of phosphorus, fluorine, nitrogen, or oxygen in the feed have not been studied.

The solid product is apparently produced in a range of particle sizes. Some buildup of deposits has been observed, and one plugging problem has been reported during continuous operation of the pilot unit.

*Application to chemical weapons destruction.* In principle, the process of reaction with sulfur is applicable to liquid agents, propellants, explosives, metal parts, and dunnage. Such a broad array of treated materials would require various furnace designs to accommodate the corresponding range of reactivity, heat release, and feed type (solids and liquids). Propellants and explosives would generate fixed gases, and their reaction might be very rapid or explosive. The chemistry of these materials with sulfur has not been investigated.

The process is probably not applicable to agent detoxified in a previous operation. Any large amount of water would have to be handled separately; the process would therefore not appear suitable as a process subsequent to chemical hydrolysis or bioprocessing.

<sup>10</sup> Information presented at the committee's workshop (see [Appendix F](#)).

The reaction appears to be stable. The possibility of hazardous reactions or explosions needs to be considered, however, including the possible explosion of hydrocarbon-sulfur vapor mixtures and rapid reaction with air leaked into the system.

*By-products and waste streams.* This process has waste streams that differ greatly from those of the other technologies. Many different carbon-sulfur-chlorine-hydrogen compounds have been observed in the produced gases. Other heteroatoms found in chemical weapons (F, P, and O) have not been studied. Conventional acid gas scrubbers such as Catacarb or other alkaline media could probably be used to remove most, if not all, gaseous components. Thus, the only gaseous emission would be N<sub>2</sub>.

No liquid products are withdrawn from the reactor. Some of the products appear large enough, however, to condense at moderate temperature.

A black polymer, which has not been characterized, is the only solid product. It appears to be very stable. Some of this product will appear as very fine dust dispersed in the gas. Intermediate or low-molecular-weight C-S polymers may be adsorbed on the solid, particularly on the fine dust dispersed in the sulfur vapor. Complete characterizations of these solids have not been reported. The adsorbed material may represent a disposal problem.

*Advantages and disadvantages.* The Adams process is considered innovative and appears to incorporate most of the hazardous material in a very stable solid believed to be a carbon-sulfur polymer. The other by-products are well known and treatable with conventional technology. Furthermore, the operation at atmospheric pressure and temperatures of 500 to 600°C (930 to 1100°F) are not very demanding in terms of construction materials or energy needs.

The major disadvantages of this process concerns the lack of knowledge of its chemistry. This omission makes it difficult to project scaleup problems and long-term stability of the solid products. Other problems include the need to process a gas containing fine solids in such conventional equipment as pipes and blowers. Solids produced by condensation from vapor are typically very fine dusts (e.g., 1  $\mu$ m). Problems involving plugging, adsorption of agent or other hazardous gases and liquids on the solid, and the effect of electrostatics on the solid have not been considered.

*Development needs.* An extensive development and scaleup program would be required to apply this process to the destruction of the chemical weapons stockpile and satisfy environmental standards. The development program would include pilot plant operations using agent surrogates followed by confirmation with some runs using agents. Ultimately, a full-scale

demonstration would be necessary. The process appears to present many uncertainties related to chemistry and solids handling; resolving these uncertainties would require a substantial research and development effort.

## 8

# Application of Alternative Technologies to the Destruction of the U.S. Chemical Weapons Stockpile

This final chapter discusses the use of alternative destruction and decontamination technologies to manage the components of the U.S. chemical weapons stockpile, namely, chemical agents, energetics, and contaminated metal parts and containers. Several major issues are addressed: possible improvements in the composition of the waste streams produced, principal destruction options for achieving demilitarization goals, and substitution of alternative processes for elements of the baseline process. The discussion draws on the preceding chapters, summarizing the characteristics of different technologies and providing perspective on their use in the Army Chemical Stockpile Disposal Program.

### DESTRUCTION TECHNOLOGIES

The destruction technologies investigated by the committee include those under development for disposal of other types of toxic wastes (especially chlorinated hydrocarbons) as well as those specifically for chemical warfare munitions destruction. Other alternative technologies, such as high-temperature ovens, are more widely available components that have been developed and used by private industry. Technologies are sorted here by unit processes. Unit process groups include all technologies that appear useful for accomplishing a distinct step in the destruction process. Major categories of these processes are the following:

- low-temperature, low-pressure, liquid-phase detoxification;
- low-temperature, low-pressure, liquid-phase oxidation (including biological oxidation);
- moderate-temperature, high-pressure oxidation;
- high-temperature, low-pressure pyrolysis;
- high-temperature, low-pressure oxidation; and
- other technologies.

The first two types of technologies are discussed in more detail in [Chapter 6](#), the remainder in [Chapter 7](#).

[Table 8-1](#) provides summary information on the applicability and status of all these destruction technologies. Comments on them follow.

### **Low-Temperature, Low-Pressure, Liquid-Phase Detoxification**

Reaction in high Ph (alkaline or basic) solution offers the potential to convert all three agents in the U.S. chemical stockpile to products of much lower toxicity, that is, such reactions can be used for detoxification:

- The agent GB has been detoxified by using sodium hydroxide (NaOH) in the United States and worldwide.
- Limited laboratory studies suggest that the agent VX can be detoxified if hydrogen peroxide ( $\text{H}_2\text{O}_2$ ) is added to the NaOH.
- Agent HD has been successfully detoxified by calcium hydroxide ( $\text{Ca}(\text{OH})_2$ ) at a higher temperature (90° to 100°C).
- When an alcohol or ethanolamine is used as solvent instead of water it is believed that all three agents will be detoxified.

Reactions in low pH (acidic) solutions make use of oxidizing agents ( $\text{Cl}_2$ , peracids, or hypochlorite). All three agents should be treatable in this manner, but little information was found except for VX. Application to HD was ineffective under the conditions used because of poor contact between reacting chemical species.

At ambient temperatures HD solubility is very low. Its high viscosity, when it contains thickeners, makes adequate contact with aqueous solutions difficult. Yet HD is quite reactive, and with an adequate extent of HD-aqueous phase interface, many of the reactions useful for GB are likely to be effective with HD. High interfacial surface area can be obtained by high-energy physical dispersion or use of emulsifying agents. The latter approach, for microemulsions, requires about equal quantities of agent and emulsifier, which will increase the amount of organic waste. Operations at 70° to 100°C may alleviate the phase interface problem, as illustrated by the success of the  $\text{Ca}(\text{OH})_2$  treatment discussed in [Chapter 6](#). Physical dispersion may still be required for the gelled HD found in the stockpile.

Although the above reactions convert agent to less toxic compounds, some of the reaction products could be converted back to the original agent. They would not, therefore, meet the treaty demilitarization requirements of irreversibility while stored. However, they would be more suitable as a feed

TABLE 8-1 Summary of Process Capabilities and Status

Process	Stream Treated		Metal and Energetics				Next Step	Comments
	Agent	Initial Agent Detox	Complete Organic Oxidization	Metal Need Gas Afterburner	Energetics	Metal		
Low-temperature, Low-pressure detoxification								
Base hydrolysis (NaOH)		GB	No	?	No	No	pp	Has been used in field; for HD, limited by contacting problems
NaOH + H <sub>2</sub> O <sub>2</sub> Ca(OH) <sub>2</sub> (at 100°C)	VX HD		No	Yes	No	No	Lab	New finding
			No	?	No	No	Lab/pp	Limited use in England
KOH + ethanol Hypochlorite ion	HD, GB, VX HD		No	?	No	No	Lab	Difficult
			No	Yes	No	No	Lab	contacting problem with HD
Organic base (ethanolamine)		GB, HD, possibly VX	No	?	No	No	Lab/pp	Limited use in Russia; increase in organic waste
Acidic systems								
HCl hydrolysis								
Peracid salts								
(OXONE, others)								
Chlorine								
Ionizing radiation		GB, perhaps VX, perhaps GB and HD	No	Yes	No	No	Lab/pp	Increased inorganic waste
			No	?	Yes?	Yes?	Lab	High conversion not yet established

Stream Treated		Metal and Energetics						
Process	Agent	Complete Organic Oxidation	Need Gas Afterburner	Energetics	Metal	Afterburner Needed	Next Step	Comments
	Initial Agent Detox							
Low-temperature, low-pressure oxidation Peroxydisulfate, ClO <sub>2</sub> , H <sub>2</sub> O <sub>2</sub> , O <sub>3</sub>	All	Yes	Yes	No	No	N.A.	Lab	Catalysts generally needed for complete conversion; spent peroxydisulfate can be electrochemically regenerated
	N.A.	Yes	Yes	No	No	N.A.	pp	Very large power requirement; applications have been for very dilute solutions
	All	Yes	Yes	No	No	N.A.	Lab	
Electrochemical oxidation Biological oxidation Moderate-temperature, high-pressure oxidation Wet air and supercritical water oxidation	N.A.	Yes	Yes	No	No	N.A.	Lab	
	All	Partially	Yes	Yes?	No	Yes	pp	Residual organic components can be low for supercritical; residual materials are believed suitable for biodegradation

Stream Treated		Metal and Energetics					
Process	Agent	Initial Agent		Complete Organic		Metal and Energetics	
		Detox		Oxidation		Need Gas Afterburner	
						Energetics	Afterburner Needed
High-temperature, low-pressure pyrolysis Kiln (external heat)	All		Partially		Yes	Yes	Yes
Molten metal	All		No		Yes	Yes?	Yes
Plasma arc	All		No		Yes	Yes?	Yes
Steam reforming	All		Yes		Yes	No?	Yes
High-temperature, low-pressure oxidation							
Catalytic, fixed bed	N.A.		N.A.		N.A.	No	No
Catalytic, fluidized bed	All		Yes		Yes	Yes	Yes
Molten salt	All		Yes		Yes	Yes?	Yes
Combustion	All		Yes		Yes	Yes	Yes
Other technologies							
Hydrogenation	All		No		Yes	No	No
Reactions with sulfur	All		Yes		Yes	No	No

NOTE: Question mark (?) indicates uncertainty about the noted application. N.A., not applicable; pp, pilot plant; demo, demonstration; lab, laboratory.

May need more than one unit to deal with all streams

pp  
Lab/pp  
Lab/pp

Useful for afterburner

Possible use for afterburner and acid gas removal

Baseline technology

—

Lab  
Lab



to subsequent processing steps that accomplish irreversible conversion by oxidation.

### **Low-Temperature, Low-Pressure, Liquid-Phase Oxidation**

Although demilitarization goals can be met by detoxification, oxidation of all carbon to carbon dioxide ( $\text{CO}_2$ ) is highly desirable for final disposal. There has been little investigation of the use of low-temperature oxidation processes for waste streams resulting from low-and medium-temperature detoxification processes. However, treatment of contaminated groundwater by low-temperature oxidation is an active field of investigation that provides some leads on treating wastes from agent detoxification.

At temperatures below the boiling point of water, very active oxidizing agents (with catalysis) are required for oxidation. Peroxydisulfate salts are capable of oxidizing most organic compounds to  $\text{CO}_2$  but would produce a very large solids waste stream. It has been proposed that to optimize the process, spent reagent be recycled to electrolytic regeneration and catalyzed  $\text{H}_2\text{O}_2$  be used to convert the more reactive components (Cooper, 1992).

Ultraviolet light can activate mixtures of ozone ( $\text{O}_3$ ) and  $\text{H}_2\text{O}_2$  and is an option in treating contaminated groundwater. However, the large electricity requirements of this process for treating large reaction product streams are disadvantageous compared with other options.

Biological oxidation is commonly applied for industrial and municipal waste streams. Although applications to the waste stream from demilitarization have not been developed, research on such processes might well prove successful.

### **Moderate-Temperature, High-Pressure Oxidation**

Both wet air oxidation (WAO) and supercritical water oxidation (SCWO) processes can detoxify and convert residual organic materials to  $\text{CO}_2$ . WAO is carried out at lower temperatures than SCWO, and requires residence times greater than 1 hour. Even then, more refractory organic compounds remain. However, these residuals are judged by the committee to be suitable for biological degradation.

SCWO, at higher temperatures and pressures, can achieve a greater conversion of all organics in about 10 minutes. Because pure oxygen is used in this process, waste gas is primarily  $\text{CO}_2$ , which can, if necessary, be removed as solid calcium carbonate ( $\text{CaCO}_3$ ) or limestone). Adaptation of WAO to use pure oxygen would require a pilot plant program.

Both these oxidation processes can treat all three agents. Both are expected to be capable of treating a slurry of finely divided energetics if care is exercised in the control of feed rates. Some mechanical addition to the disassembly process would be required to remove and make a slurry of the energetics. Their removal from containers is not expected to be complete, so some energetics residues would still need to be destroyed in a metal deactivation process as in the baseline system.

SCWO could also oxidize gaseous products from pyrolysis or other processes and is an alternative to the combustion variations discussed later. It has the disadvantage of requiring gas compression to 3,000 psi; however, it offers a high conversion efficiency.

Application of these processes to chemical agents would still require a problem-solving pilot plant stage. The high operating pressure will call for appropriate confinement, as in industrial operations. Current baseline facilities are remotely operated and designed for energetics explosions and capture of agent released inadvertently. The high-pressure oxidation process might call for some extension of these safeguards.

### **High-Temperature, Low-Pressure Pyrolysis**

As shown in [Table 8-1](#), many high-temperature pyrolysis and oxidation processes are capable of treating all major stockpile components (agent, energetics, and metal). High temperatures are required to decontaminate metal parts and ignite and destroy energetics (see [Chapter 5](#)). These temperatures should be sufficient to ignite energetics and to achieve the equivalent of the 5X criterion (treatment at 1000°F for 15 minutes) for metal decontamination.

Kilns with electrical heating can meet these requirements and avoid dependence on the internal firing now used. This approach has the advantage of reducing total flue gas volume. However, air (or oxygen) must be supplied to oxidize unburned pyrolysis products, a step that can be achieved within the kiln or in a secondary burner. An afterburner would be needed to ensure complete oxidation. Variations of this system can accept ton containers as well as energetics and small metal parts.

Plasma arc and molten metal processes use electrical heat and operate at higher temperatures under oxygen-deficient conditions. They generally introduce air to burn the products resulting from the initial pyrolysis but still require an afterburner. In principle both can handle chemical warfare agents, fragmented energetics, and metal parts. The molten metal system would be expected to handle a larger range of material sizes than do the plasma arc systems.

In steam-reforming processes, steam is reacted with carbon-containing feed at high temperatures to produce a gas containing the combustible components hydrogen, carbon monoxide, soot, and low-molecular-weight hydrocarbons. Other elements (S, P, F, and Cl) require oxidation and removal. The gas formed, after purification, can be a generally useful fuel; however, destroying it may be more practical, as is proposed for the products from pyrolysis. Steam reforming is more limited than pyrolysis because it does not appear directly useful for metal decontamination. However, combined pyrolysis and steam gasification is under private development for possible use in hazardous waste destruction.

### **High-Temperature, Low-Pressure Oxidation**

High-temperature, low-pressure oxidation is the current workhorse for destroying toxic waste materials. There are several variations of interest. Molten salt and fluidized-bed oxidation, because of the large heat capacity of the molten salt and the pulverized-solids bed, are less likely to suffer flame-out than are the fast-response gaseous system of conventional combustion. These alternative methods also provide good contact between air and fuel. There would be some tendency for bubble formation to result in bypassing of agent through the combustion zone; thus, afterburners are still needed. These systems can also retain much of the oxidized halogens, sulfur, and phosphorus if appropriate basic acceptors are part of the salt or solids system. They can also manage energetics of small-particle size, although their ability to handle metal parts seems limited. Both molten salt and fluidized-bed systems are used for toxic waste disposal, and it would probably be possible to proceed directly to design and construction of a demonstration unit for demilitarization applications. Molten salt designs might also be used as afterburners and for acid gas removal from gaseous waste streams.

The catalytic fixed bed is of special interest for use as an afterburner for the final oxidation of any unoxidized material in gas effluents from an agent destruction process. The familiar automobile catalytic converter is an example of this application. The presence of halogens, phosphorus, and sulfur in the agent and the presence of products from energetics destruction will probably preclude the use of very active catalysts. However, operation at higher temperatures could allow use of rugged catalysts or even common ceramics. For many situations, external heat (electrical) will minimize the need for internal firing to generate heat in the catalytic oxidation unit, thus reducing the production of waste gas.

An important variation on all these high-temperature oxidation systems is their operation with pure oxygen instead of air. As discussed below, the volume of waste gas can be greatly reduced (or almost eliminated for some

processes) by substituting oxygen for air. Although technology is available to shift from air to oxygen, demonstration of operation with oxygen would be required.

Combinations of the unit processes in [Table 8-1](#) into systems for use in the stockpile disposal program are considered later.

## WASTE STREAM HANDLING PROCESSES

The waste streams of conversion processes for agent, energetics, and metal parts will require additional processing to meet standards for release to the environment. In all cases, monitoring via chemical analysis is an integral step. Ideally, each waste stream should be stored until chemical analysis is completed and the waste stream can be certified for compliance with the required standards for environmental release (i.e., the process can be operated as a closed system). Discussion of solid, gas, and liquid waste streams follows.

### Solid Waste

*Waste metal.* In the baseline process, all metal is heat-treated to qualify for the 5X decontamination rating (1000°F for 15 minutes) and can be released to the public and recycled for other uses. The metal parts (traveling-grate) furnace is designed to perform this function for drained ton containers and artillery shells. 5X heat treatment is believed to make monitoring by chemical analysis unnecessary. Treatment to a decontamination level of 3X, to allow transport and disposal as toxic waste, would permit eliminating the traveling grate-kiln, but monitoring would then be necessary.

*Waste salts.* Salts of  $\text{H}_2\text{CO}_3$ , HF, HCl,  $\text{H}_3\text{PO}_4$ , and  $\text{H}_2\text{SO}_4$  are formed by neutralization of these acidic products of agent and by energetics oxidation and are a major waste stream. They can be formed directly in the destruction process (as in NaOH hydrolysis) or in the gas pollution abatement system. If  $\text{CO}_2$  is discarded as a gas, oxidation of GB forms 2.3 pounds of calcium salts for each pound of GB destroyed; if the  $\text{CO}_2$  from oxidation is discarded as  $\text{CaCO}_3$ , an additional 2.8 pounds of salts per pound of GB must be discarded. Excess base, as used in the baseline pollution abatement system, will increase this amount to a total of about 10 pounds of dry salts per pound of GB. If agent destruction involves additional organic solvents or reagents or if flue gas from fuel combustion is treated, additional  $\text{CO}_2$  will be generated.

Although methods for chemical analysis are available, the inherent problem of obtaining a representative sample of a heterogeneous solid for

analysis and the need to establish the absence of even very small amounts of residual agent and other toxic organic materials may still require that the waste salts be heated to the 5X criterion. Equipment for drying and heating waste salts would be required. Even so, the presence of fluoride and small amounts of heavy metals will generally result in this waste stream being classified as hazardous.

### Gas Waste Streams

Because of their relatively large volumes, gas waste streams from common industrial oxidation processes are generally not stored before release. Instead, reliance is generally placed, as in the baseline technology, on chemical analysis of the leaving gas stream and on process control to verify that it meets all health-related requirements.

However, the high toxicity of chemical warfare agents calls for special care in avoiding small transient emissions (puffs). Even with the careful design and operation of destruction processes, off-design conditions can occur. The current baseline system uses an afterburner to guard against agent puffs that might emerge from the primary combustion system. An additional precaution that could be used by the baseline system is the capture of gas emissions resulting from off-design operation until chemical analyses have been completed and needed corrective measures taken. There are three major options for managing such potential off-design agent emissions in chemical demilitarization:

- capture of transient puffs by activated-carbon adsorption;
- gas storage for time sufficient to allow chemical analysis and certification before release (gas of unsatisfactory purity would be recycled to an afterburner); and
- drastic reduction of waste gas stream volume by using oxygen and capturing CO<sub>2</sub> with lime to form CaCO<sub>3</sub> (a small amount of nitrogen from air leakage into the system and from the nitrogen in energetics and in VX will require treatment and discharge to the atmosphere). Any remaining waste gas stream could be stored and tested or purified by activated-carbon adsorption.

*Activated-carbon adsorption.* Activated-carbon (charcoal) adsorption can remove extremely low concentrations of organic compounds. Activated carbon is the adsorbent used in gas masks. Because the organic compounds are stored on the charcoal, a series of charcoal beds is used and performance is monitored by analysis of the gas between beds. When the first bed is saturated, unadsorbed organic materials break through and are captured on the next bed. The saturated activated carbon must be removed and discarded

or detoxified (probably in the facilities used for metal detoxification), and discarded. This approach is best used for removing very small mounts of organic compounds, as for protection from transient puffs. Carbon adsorption beds are part of current Army designs to treat potentially contaminated ventilation air.

In May 1992, the NRC sponsored a workshop that led to a recommendation that the Army consider using activated-carbon adsorption for chemical disposal facilities located in populated areas (NRC, 1993). Its use in treating waste gas from agent destruction is currently under study by the Army as is the use of the gas storage facilities discussed below.

*Gas storage and certification.* For large-scale combustion operations, storage of waste gas before analysis and release generally requires a storage volume too large for gas holders to be economically viable. However, the smaller scale of chemical stockpile disposal facilities makes the gas holder a potentially practical option for ensuring that the waste gas meets environmental and health-related standards.

A system of four gas holders could be used to store the gaseous effluents of any disposal process, including the current baseline technology. As one gas holder is filled, a second could be analyzed, a third could be emptied, and a fourth could be linked in as a spare at any juncture.

Required gas holder volume varies over a wide range depending on cycle time and gas flow rate. The example presented in [Chapter 5](#) estimates needed gas holder volume at 92,000 cubic feet for 8 hours storage, using air for internal firing, for oxidation of 100 pounds of GB per hour. The diameter of such a gas holder would be about 35 feet. Industrial atmospheric pressure gas holders that have been used for many years have storage volumes of several million cubic feet. Use of oxygen instead of air for oxidation would reduce needed storage volume to one-seventh the volume required for air. Capture of CO<sub>2</sub> as solid carbonate could further reduce waste gas volume to that of air leakage and unused oxygen. Flue gas from fuel combustion (for internal firing) would increase gas volume.

Either a gas storage system or a system of charcoal scrubbers can be designed to capture and hold pulses of agent that might be released by an accident or malfunction during disassembly of a munition or destruction of agent. Either approach can also handle lower amounts of contamination that might result from off-design operation. Facilities for storage, chemical analysis, and certification of the quality of the waste gas stream can convert all technologies for treating agent and weapon parts to a closed-loop system so that gases are not released to the environment until chemical analysis has demonstrated their satisfactory composition.

*Mineralization of gas streams.* Waste gas streams from the destruction process could be greatly reduced by use of pure oxygen and capture of CO<sub>2</sub> and other acidic gases (such as HCl, HF, and SO<sub>2</sub>) by reaction with lime. All gas, except for excess oxygen and nitrogen from energetics and air leakage, would be converted to waste solids. The relatively small amount of remaining gas could be stored and tested, or purified by activated-carbon adsorption. Use of pure oxygen in combustion would require the redesign of fuel and oxidant injection and mixing components to avoid unduly high temperatures. These designs are available but have not been extensively used.<sup>1</sup> Their demonstration will be required, which could add to the time before system installation and use.

### **Liquid Wastes**

Water is formed by agent oxidation and is used in the pollution abatement system, in decontamination fluid, and as a solvent in some alternative agent destruction processes. Design for zero liquid water discharge is increasingly being adopted for industrial plants that work with hazardous chemicals. It is the current practice for the baseline technology, where water discharge as vapor in the flue gas makes liquid water recycling unnecessary. Storage of waste gas streams would reduce the water vapor content of the waste gas, so that some reuse of water within the plant may be necessary. If this water enters the normal wastewater system, the wastewater will need to be processed to meet water quality standards.

## **GOALS, STRATEGIES, AND SYSTEMS FOR CHEMICAL DEMILITARIZATION**

### **Program Goals**

In the committee's view, the following goals must be met by any system used for the demilitarization of the U.S. chemical weapons stockpile:

- satisfy congressionally mandated and international treaty demilitarization and timing requirements;

---

<sup>1</sup> Some of the processes reviewed in this report are designed for use with pure oxygen. The supercritical water oxidation process, for example, is designed to use pure oxygen, but it is still in the development stage.

- minimize risks of agent release to nearby communities, risks both associated with continued storage of agent and with the demilitarization operation itself;
- ensure the reduction of toxic materials from air in gaseous wastes to acceptable levels; and
- minimize final disposal problems for solid and liquid wastes by oxidizing all organic material in solid wastes and minimizing water discharge.

The current program schedule has some flexibility, with completion of demilitarization set as late as December 31, 2004, under the international treaty on disarmament. Even so, this outside date will be difficult to meet at sites where construction and operations are delayed. (Treaty requirements for demilitarization are briefly reviewed in [Chapter 1](#).) The risk of catastrophic agent release from continued storage provides an additional incentive for prompt and acceptable choices of technology.

### Strategies for Disposal

At U.S. chemical stockpile disposal facilities, chemical munitions and bulk agents must be removed from storage and transported to the treatment site, where they will be unpacked and disassembled before disposal. Two major demilitarization strategies can be identified:

*Strategy 1. On-site disassembly and agent detoxification to meet demilitarization requirements and permit transportation to another site or continued local storage of residues.*

Strategy 1 allows treaty demilitarization requirements to be met with liquid-phase processes that do not produce a significant quantity of gas emissions. Final oxidation of all organic residues, energetics destruction, and decontamination of metals can be deferred by continued local storage or conducted at another site to which materials can be transported for final treatment.

This strategy is illustrated in [Figure 8-1](#). Drained agent is destroyed by conversion to less toxic compounds, as through chemical hydrolysis, or completely oxidized and converted to CO<sub>2</sub>, water, and salts, as through low-pressure, liquid-phase oxidation or high-pressure, wet air or supercritical water oxidation. Energetics and contaminated metal parts and containers would be treated with decontamination fluid to reduce toxicity to level 3X before transportation to another site.

Strategy 1 has the advantages of nearly eliminating local discharge of flue gas, meeting the requirements for demilitarization, and eliminating the



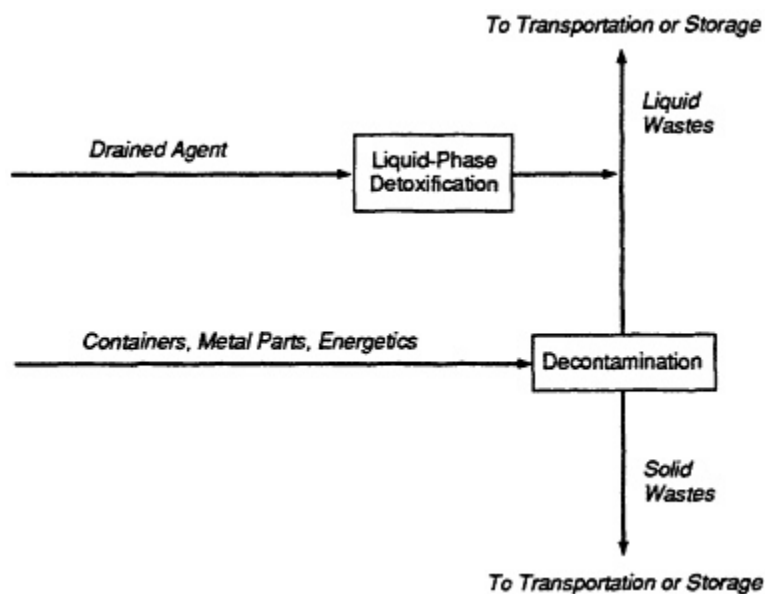


FIGURE 8-1 Unit processes in demilitarization Strategy 1: disassembly and agent detoxification, with storage or transportation of residue.

risk of agent release from continued storage. It has the disadvantage of requiring additional time (5 to 12 years) for the research, development, and demonstration of new technologies. It would also delay final disposal of energetics and contaminated metal.

It is assumed here that the small amounts of waste gas could be treated along with ventilation air by the activated-carbon adsorption beds that are part of the baseline design.

*Strategy 2. Conversion of agent and disassembled weapons to salts, CO<sub>2</sub> water, and decontaminated metal (mineralization).*

In Strategy 2, mineralization is completed without long-term storage of agent, energetics, or metal parts and containers. This strategy meets all stated goals by oxidation and heat treatment to produce the waste streams noted. Strategy 2 is illustrated in [Figure 8-2](#).

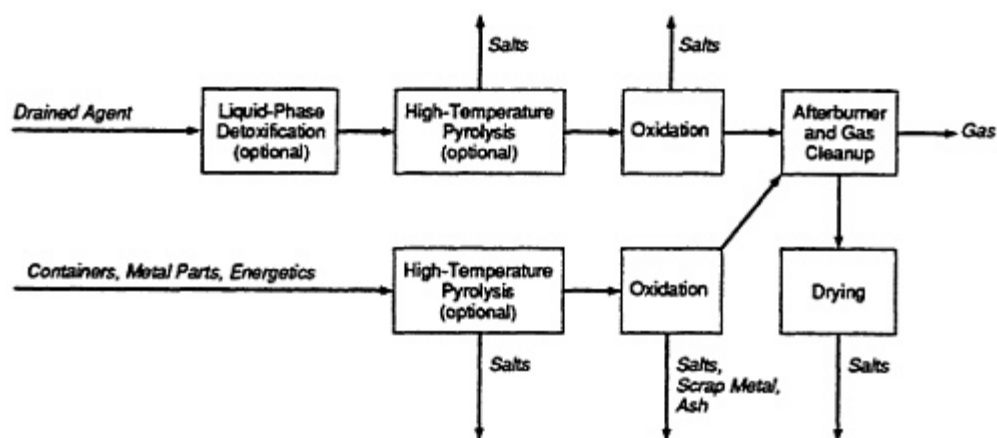


FIGURE 8-2 Unit processes for demilitarization Strategy 2: mineralization.

For agent, detoxification (as in Strategy 1) can precede the final mineralization processes, or agent can be directly mineralized, as in the baseline technology. The two-step procedure of detoxification by hydrolysis followed by incineration to complete oxidation has been used in the United States and worldwide. It is apparently of some continuing interest for the Russian stockpile disposal program. In this approach, primary oxidation products are treated with an afterburner to destroy any remaining trace organic components, and acid gases (HF, HCl,  $P_2O_5$ , and  $SO_2$ ) are neutralized and removed in the gas cleanup system.<sup>2</sup>

<sup>2</sup> The mineralized oxidation products from halogens, phosphorus, and sulfur are all acidic and readily removed from gas streams by alkaline scrubbers, leaving  $CO_2$  and water vapor as the principal gaseous wastes. However, the gas scrubber effluents must be monitored and disposed of as hazardous wastes. All of these can be reacted with lime at high temperatures to avoid liquid wastes.

Energetics, as well as metal parts and containers, are heated to a high temperature. The vapors from the decomposition and vaporization of these materials are then oxidized and cleaned before release. Metals are detoxified to the 5X level to allow recycling, and salts are rendered suitable for landfill disposal. All waste streams are tested to ensure their suitability for release.

### System Considerations

As Figures 8-1 and 8-2 show, unit processes and technologies must be combined to form a system that meets all demilitarization requirements. The two demilitarization strategies provide a framework for examining the potential roles of alternative technologies. Strategy 1, which delays or avoids local disposal, is discussed first.

*Alternative processes for Strategy 1 (disassembly and agent detoxification).* The only major agent conversion process required for Strategy 1 is detoxification (Figure 8-1). However, decontamination of the disassembled weapon parts and containers will probably be necessary as well for achieving agent demilitarization and acceptable agent emissions during storage or transportation.

Table 8-2 shows the alternative processes that might be used in this strategy. Because high-temperature processes to mineralize agent are similar in effect to the baseline incineration technology, these processes are considered as part of Strategy 2 (mineralization).

The low-temperature, liquid-phase chemical detoxification processes are particularly suited for Strategy 1. It is assumed that the same process equipment can be used for all three agents and, taken as a whole, this approach is at the laboratory data-gathering stage of development. Because each agent may require different reagents, three separate laboratory and pilot plant programs would be required. Although each of these programs might normally require 12 years to progress through demonstration, they could be run in parallel and use common equipment. One of the processes (NaOH hydrolysis of GB) could form the basis for early demonstration. With skilled management and adequate talent and resources, the time to application of these processes probably could be significantly shortened.

An attractive feature of the low-pressure, liquid-phase detoxification processes is their production of little or no gas. The high-pressure oxidation processes, however, produce a waste gas stream, which could be largely eliminated by capture of CO<sub>2</sub> by lime. There would probably be few significant differences in the equipment requirements for the three agents for these high-pressure processes, apart from those related to corrosivity.

TABLE 8-2 Low-and Moderate-Temperature Agent Detoxification Processes

Process	Special Gas Treatment Needed	Number of New Processes (Development Status)
Low-temperature, liquid-phase detoxification	No	3 (laboratory)
Wet air or supercritical water oxidation	Yes	1 (pilot plant)
Removal of agent from metal parts and containers, and agent detoxification with decontamination fluid	No	1 (pilot plant)

The drainage of agent from weapons and containers is never complete. The amount of agent remaining might normally be between 1 and 5 percent. Thickened or degraded mustards, however, can leave larger residues. In all cases these residues must be removed and detoxified to meet demilitarization requirements and to be suitable for storage or transportation. The baseline technology does not require this step because the residual agent is immediately destroyed in the high-temperature kilns. Using this alternative strategy, additional facilities to clean out the residual agent would need to be added to the current disassembly procedure. Agent removal by water jets, solvent, or decontamination fluids should produce a stream that can be processed in the detoxification step. Such residual agent removal processes could be developed and demonstrated in parallel with development of the detoxification processes.

*Alternative processes for Strategy 2 (mineralization).* As shown in Figures 8-1 and 8-2, drained agent is generally treated separately from the energetics, metals, and other solids resulting from weapons disassembly. Table 8-3 indicates the processes that might be used for agent mineralization and their development status.

TABLE 8-3 Agent Mineralization Processes

Case/Process	Number of New Processes (Development Status)	
	Using Air	Using Oxygen
1. Baseline incineration	0 (operational)	1 (demonstration)
2. Baseline incineration plus gas storage and certification	0 (operational)	1 (demonstration)
3. Fluidized bed or molten salt combustion	1 (demonstration)	1 (pilot plant)
4. Molten metal or plasma arc plus burner	1 (pilot plant)	1 (pilot plant)
5. Steam gasification plus burner	1 (pilot plant)	1 (pilot plant)
6. Supercritical water oxidation or wet air oxidation	1 (pilot plant)	1 (pilot plant)
	1 (pilot plant)	1 (pilot plant)
7. Low-temperature, low-pressure oxidation	1 (laboratory)	1 (laboratory)
8. Biological oxidation	1 (laboratory)	1 (laboratory)

For agent treatment, the liquid-phase detoxification processes mentioned under Strategy 1 could be followed by incineration (such as the baseline incineration technology) or by some combination of the pyrolysis and oxidation alternatives to complete the oxidation process. If supercritical water or wet air oxidation is chosen for detoxification, these follow-on processes might be unnecessary; however, some treatment of unoxidized organics might be necessary for wet air oxidation.

Cases 1 and 2 in [Table 8-3](#) incorporate the baseline technology, which uses air and additional fuel in a two-step burner and afterburner system. This process is operational at Johnston Island without storage and certification of the flue gas stream. It is believed that addition of the storage and certification feature (Case 2) would not require demonstration beyond the normal startup and testing programs for a new installation.

About an 85 percent reduction in flue gas volume can be achieved by substituting oxygen for air. Removal of CO<sub>2</sub> by reaction with lime would give a large additional reduction in flue gas volume. Such systems could be designed and built based on current experience but would require demonstration.

If the current incineration process is not chosen, a number of alternatives could be developed. For these technologies, development could be based on the use of oxygen without adding appreciably to technological risk or development time. In all these cases, at the least a pilot plant program would be needed, and in some cases additional laboratory data would be needed as well.

Cases 3 to 5 in [Table 8-3](#) are high-temperature, atmospheric pressure oxidation systems that, combined with appropriate afterburners, may be capable of mineralizing agent. Case 6, high-pressure, supercritical water or wet air oxidation, has the potential, with additional pilot plant work, to oxidize agent at relatively low temperatures. The water streams from both processes may require additional oxidation for complete mineralization. Cases 7 and 8 are low-temperature, liquid-phase oxidation processes that could potentially be used to complete the oxidation of agent detoxification products. Both are in a very early laboratory stage. However, they are similar enough to oxidation processes used for other waste streams for the committee to be optimistic about their chances of success. Gas treatment would be necessary for these processes and, with biological oxidation, a waste sludge stream would be produced.

For final disposal of energetics and metal parts and containers, destruction of energetics and heat treatment of metal parts and containers is required to eliminate any residual agent. The alternatives for carrying out these operations, in contrast to those for agent destruction, all require high temperatures. [Table 8-4](#) lists these processes.

The baseline system (Case 1 in [Table 8-4](#)) makes use of an internally fired rotary kiln to destroy energetics and small metal parts. An internally fired traveling-grate kiln is used for the larger metal parts, such as drained ton containers and drained 155-mm artillery shells. The mixture of pyrolyzed organic compounds and combustion flue gas from these kilns then enters a secondary burner for completion of combustion. As in the agent incinerator, the volume of gas in this system could be reduced by using pure oxygen rather than air. This modification again would require demonstration. Case 2 ([Table 8-4](#))

TABLE 8-4 Processes for Treatment of Energetics and Metal Parts and Containers

Case/process	Number of New Processes (Development Status)	
	Using Air	Using Oxygen
1. Baseline kilns	0 (operational)	2 (demonstration)
2. Baseline kilns plus gas storage and certification	0 (operational)	2 (demonstration)
3. Electrically heated kilns	2 (demonstration)	2 (demonstration)
4. Molten metal furnace	1-2 (pilot plant)	1-2 (pilot plant)

indicates a modification to the baseline that allows certification of gas emissions before release to the environment.

The volume of gas can be further reduced by replacing internal firing with electrical heat (Case 3 in Table 8-4). Use of electrical heating and oxygen for oxidation would, after CO<sub>2</sub> removal, almost eliminate flue gas. Any air leakage into the system would be discharged after cleanup and analysis.

In Case 4 (in Table 8-4), a molten metal furnace could destroy energetics and all metal pieces (ton containers might need to be cut into smaller pieces). Combining the function of the baseline rotary kiln and the traveling-grate furnace could be a useful simplification.

Energetics could probably be destroyed in other alternative processes (supercritical water oxidation, molten salt, fluidized-bed combustion, and plasma arc processes) if separated from their metal containers and broken into small particles. Complete removal of energetics from metal containers is expected to be difficult, and high-temperature treatment of metals would still be required. No large advantage is seen for these variations.

All the high-temperature systems shown in Table 8-4 require afterburners and similar gas cleanup and handling technologies. The main difference between these systems and the baseline technology is substitution of electrical heating for internal firing. All of these processes also have the potential to destroy bulk agent. Treatment of all streams in one device, as in

the proposed cryofracture process, offers equipment simplification but with some loss of process control because the several streams are processed together. This approach could lead to uncontrolled production of undesirable gas pollutants, for example.

Afterburners are needed to ensure complete oxidation for all systems with waste gas production. The baseline practice is to use internal firing if additional heat is needed. Substituting oxygen for air and external heat for internal firing would minimize waste gas, but the former substitution would require demonstration. Catalytic oxidation could reduce the temperatures required, but the use of highly active catalysts is made difficult by the deactivation potential of the P, F, Cl, and S content of the agents. Molten salt systems might also be used as afterburners and for acid gas removal. Another variation would be to complete gas oxidation by supercritical water oxidation. In this case, it would be necessary to compress the gas to 3,000 psi.

With use of afterburners, gas streams from any of the processes can be brought to specified levels of agent and organics destruction, which can be confirmed by storage and certification. Thus, waste gas purity can be ensured independently of the process used.

### GENERAL OBSERVATIONS

- 1. The risk of toxic air emissions can be virtually eliminated for all technologies through waste gas storage and certification or treatment by activated-carbon adsorption. Either of these options can be combined with methods to reduce the volume of gas emissions.**

Agent releases from accidents in the destruction facility and releases to the atmosphere of residual unreacted agent or toxic products from equipment malfunction can all be avoided for any alternative technology by applying a dosed system concept to all gas streams leaving the facilities. That is, gas streams can be stored until chemical analysis has demonstrated their compliance with regulatory standards. The storage volume needed to handle gaseous oxidation products can be made adequate to store any accidental release of vaporized agent from the destruction facility. Large activated-carbon (charcoal) adsorbers can perform much the same function. In this case, agent and products of incomplete combustion are captured and retained on the charcoal.

The amount of gas released can be greatly reduced by the use of pure oxygen in destruction processes instead of ordinary nitrogen diluted air. Waste gas can be further reduced by capturing the carbon dioxide it contains with lime, as well as capturing HCl, HF, SO<sub>2</sub>, and P<sub>2</sub>O<sub>5</sub>, at the cost of increasing



the amount of solid waste produced. These techniques can be applied to all technologies.

**2. There are many possible destruction processes.**

A wide variety of processes have been proposed to replace or augment components of the current baseline destruction system. The scope of possible modifications ranges from simply replacing one component, such as the agent combustion process, to replacing all current combustion-based processes. New components would likely require 5 to 12 years for research and demonstration, the lower figure representing the time required for construction and testing of demonstration facilities, the higher figure including research and pilot plant work as well.

**3. Initial weapons disassembly and agent detoxification and partial oxidation could meet international treaty demilitarization requirements and eliminate the risk of catastrophic agent releases during continued storage.**

The strategy of disassembling weapons and applying liquid-phase processes to destroy agent can meet treaty demilitarization requirements. By destroying the stored agent, the risk of catastrophic agent release during storage is avoided. Final disposal of the wastes generated would be delayed until complete oxidation processes are developed.

**4. There are a number of promising chemical processes for agent detoxification or oxidation.**

Chemical techniques could allow agent detoxification in low-temperature, aqueous systems. The reaction products could be confined and tested to determine whether further processing is needed to meet demilitarization requirements and also for suitability for release to a disposal facility or to local storage. The best results with such processes have been seen in GB destruction. Although there are laboratory leads for similar VX and mustard treatments, this work is at the early laboratory stage.

The combined use of peroxysulfates and hydrogen peroxide shows promise for detoxification of agent and also for complete oxidation of its organic components. Biological and electrochemical processes might be used to further oxidize liquid wastes from detoxification processes, but they are in an early stage of research.

**5. Processes used in combination with an afterburner can be used to oxidize agent.**

Processes proposed for oxidation of agent or of products from its chemical detoxification include wet air and supercritical water oxidation, molten salt oxidation, fluidized-bed combustion, steam gasification, plasma arc (electric arc) furnaces, and molten metal baths. All require an afterburner to complete oxidation, and all are promising but would require development and demonstration.

**6. There are technologies to replace the baseline metal parts furnace.**

Alternative technologies to destroy energetics and reliably detoxify metal parts and containers involve heating to high temperatures. Using electrically heated ovens in place of the baseline internally fired kilns would reduce the amount of flue gas produced. Molten metal or salt baths could also treat these stockpile materials. Like the combustion-fired kilns, all these approaches require the use of afterburners to ensure complete oxidation.

**7. Afterburner technologies might be used to control waste gas purity.**

Alternative afterburner options include external heating, catalytic combustion, molten salt, or supercritical water oxidation. Afterburners can be designed to meet requirements for contaminant oxidation for both baseline and alternative processes and are essential in control of waste gas purity.



A

Statement of Task

The Committee on Alternative Chemical Demilitarization Technologies, established at the request of the Assistant Secretary of the Army (Installations, Logistics and Environment), will carry out a study of alternatives to the baseline technology for chemical munitions demilitarization. The committee will operate under the auspices of the Board on Army Science and Technology of the Commission on Engineering and Technical Systems, which provides independent technical advice to the Army.

The committee will meet approximately four times and will conduct a workshop at which interested parties will have the opportunity to present their analyses of proposed alternative technologies. If necessary, the committee will make field trips to examine relevant processes. The committee will:

- develop a comprehensive list of alternative technologies to the baseline technology for destruction of chemical agents and munitions;
- develop screening criteria for alternative technologies;
- test alternative technologies against the criteria to select those that merit full evaluation;
- establish evaluation parameters to fully assess and characterize selected alternative technologies; and
- hold a workshop to:
  - describe each alternative technology;
  - present and discuss technical aspects, strengths and weaknesses;
  - assess advantages and disadvantages;
  - focus on plausible, developmental tasks to implement each alternative technology; and
  - assess the time period for implementation.

After reviewing and evaluating this information, the committee will prepare a report of its findings. The committee will not select or recommend any specific alternative technology.

## **B**

### **Letter from James R. Ambrose, Dated October 21, 1987**

This appendix contains a briefing letter from James R. Ambrose, Under Secretary of the Army, on the subject of Ocean Transport of the Aberdeen Proving Ground Stockpile.

Source: PEIS (1988).



S-3

DEPARTMENT OF THE ARMY  
OFFICE OF THE UNDER SECRETARY  
WASHINGTON, D C. 20310-0102

October 21, 1987

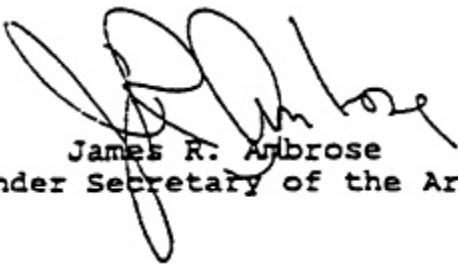
MEMORANDUM FOR PROGRAM MANAGER FOR CHEMICAL DEMILITARIZATION  
SUBJECT: Ocean Transport of Aberdeen Proving Ground Stockpile—INFORMATION MEMORANDUM

I have decided that, for the purpose of making a final determination of the programmatic alternative for the national disposal of obsolete chemical munitions, further consideration of the alternative to transport ton containers of bulk mustard chemical agents by ocean barge from Aberdeen Proving Ground, Maryland, is not reasonable. The reasons for this decision are as follows:

- Given our Congressional mandate to destroy the stockpile by 1994, and the public interest in destroying the already leaking munitions as quickly as possible, the overall programmatic decision, which has already been delayed by a year, should not be further delayed for an indefinite period by necessary studies of a complex transportation scheme coupled with a multiplicity of different environmental areas. The word "areas, as used in this paragraph, refers only to the waterway systems and contiguous land areas which lie within the jurisdiction of the continental United States.
- Rail transportation as an alternative to on-site disposal provides adequate consideration of transportation for the purposes of a national programmatic EIS. Analysis of this method of transportation will be accomplished in sufficient detail to provide reasonable comparison of the alternatives of removal from site versus disposal on site.

S-4

- Adequate consideration of the range of possible environmental impacts on the ecology of complex water systems such as the Chesapeake Bay and its tributaries would entail, in all likelihood, lengthy and extensive studies.
- A national programmatic decision does not foreclose subsequent consideration of site-specific alternatives at a later date.



James R. Ambrose  
Under Secretary of the Army

cc:

Assistant Secretary of the Army (Installations and Logistics)  
The General Counsel  
Chief of Legislative Liaison  
Chief of Public Affairs (SAPA-PP)  
Deputy Chief of Staff for Operations and Plans (DAMO-SW)  
Commanding General, U. S. Army Materiel Command (AMCCN)  
Chairman, Council on Environmental Quality

## C

### **Letter from Charles Baronian, Dated August 7, 1992**

This appendix contains a letter dated August 7, 1992 from Charles Baronian, Program Manager for Chemical Demilitarization, Aberdeen Proving Ground, Aberdeen, Maryland and provides the following information to the committee:

- A paper (enclosure 1) providing estimates for the times and testing required for development and implementation of an alternate technology.
- An information paper (enclosure 2) that discusses chemical agent monitoring limits.
- An information paper (enclosure 3) that summarizes the criteria and costs for disposition of hazardous waste from Johnston Atoll Chemical Agent Disposal System (to include material designated as "3X").





DEPARTMENT OF THE ARMY  
PROGRAM MANAGER FOR CHEMICAL DEMILITARIZATION (PROVISIONAL)  
ABERDEEN PROVING GROUND, MARYLAND 21010-5401

-7 AUG 1992.



REPLY TO  
ATTENTION OF

Office of the Program Manager  
for Chemical Demilitarization

Dr. John P. Longwell  
Professor, Chemical Engineering  
Massachusetts Institute of Technology  
77 Massachusetts Avenue, Room 66-456  
Cambridge, Massachusetts 02139

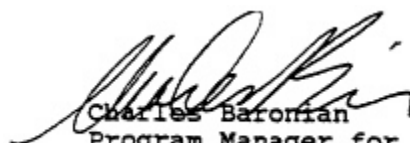
Dear Dr. Longwell:

Enclosed are material requested by the Alternatives Chemical Demilitarization Technologies Committee. Specifically, the following information is included:

- a. A paper (enclosure 1) providing estimates for the times and testing required for development and implementation of an alternate technology. Time estimates are provided for taking a technology from lab scale to full scale and for a more mature technology (one which has been demonstrated at the pilot plant scale).
- b. An information paper discussing chemical agent monitoring limits is included at enclosure 2.
- c. An information paper summarizing the criteria and costs for disposition of hazardous waste from Johnston Atoll Chemical Agent Disposal System (to include material designated as "3X") is included at enclosure 3.

Please let me know if you request additional information on any of these topics.

Sincerely,

  
Charles Baronian  
Program Manager for  
Chemical Demilitarization

Enclosures

Copies Furnished:

Mr. Donald Siebenaler, Board on Army Science and Technology, 2101 Constitution Avenue NW MH294,  
Washington, DC 20418

## ALTERNATIVE TECHNOLOGY DEVELOPMENTAL COST AND SCHEDULE ESTIMATES

### 1. Purpose.

This paper addresses the impacts on the program in the event the McMillen amendment is adopted by Congress. Basically, the amendment mandates stoppage of all work at the Aberdeen Proving Ground (APG), Newport Army Ammunition Plant (NAAP), and Lexington-Blue Grass Army Depot (LBAD) sites until a Congressionally-established commission reviews alternative technologies and provides a report to Congress and the Secretary of Defense. The Secretary of Defense then would have to submit to Congress a program plan implementing the alternative technology into a demilitarization program based on his determinations. The commission study is required to be available 1 January 1994, and the Department of Defense plan six months later, or 1 July 1994.

### 2. Discussion.

- a. Two results can ensue from the commission. The first is that they recommend an alternative technology (probable). The second is that they conclude there is no alternative technology (relatively improbable). In the event of no new technology the increase in the costs would be limited to the delay caused by deferring all work on the three sites including design and environmental documentation until January 1994 when the report is received and design is restarted. In the event of new technology recommendation, however, the delay would be much more severe as a developmental program must be created to confirm the technology in a laboratory as well as a pilot plant facility. It would be irresponsible of the Army to not confirm the commercially available data base by running actual agent and energetic operations in these two steps.
- b. In order to project a schedule and costs with any degree of validity one should know the technology, the maturity of the technology, and the data base associated with the particular technology. Obviously, there is no technology selection at this time. Therefore, one can only conceptualize generic schedule and cost estimates that are somewhat independent of the technology. Thus the schedules and costs must be considered rough order of magnitude projections which cannot be utilized for any purpose other than conceptual cost and schedule impacts.
- c. Currently there is on-going activity at all three of the affected sites in terms of design, Environmental Impact Statements (EIS), and Resource Conservation and Recovery Act

(RCRA) permitting work. Based on the McMillen amendment, if enacted, all this work would stop immediately.

- d. To further complicate this exercise, it is known that the alternate technology is specific to the purpose of eliminating incinerators. Yet the baseline incorporates four types of incinerators each with a separate and distinct requirement: (1) to destroy agent; (2) to destroy energetics; (3) to provide 5X decontamination; and (4) to process dunnage. Obviously, a developmental program that addresses one or two of these incinerators would take less time than a program addressing all four. Alternate technologies which have been postulated do not appear to address the 5X or dunnage requirements. This paper limits the new technology program to the first two incinerator processes, agent and energetic destruction, and is consistent with the current National Research Council (NRC) review of alternative technology. If indeed a developmental program for all incinerators becomes a requirement, then it is possible that a significant increase in time and costs may have to be added to this proposed program. At this time, however, there is no valid basis to include these costs.
- e. In summary, the following depicts generic costs and schedules based on a set of assumptions. The actual program costs and schedules could be significantly less or greater, depending on the selected technology and the scope of the effort.

### **3. Assumptions.**

- a. Complete commercial laboratory data are available and laboratory equipment for use by the Government is available from the technology developer.
- b. The laboratory program will be accomplished in a Government laboratory which has been approved for agent operations.
- c. The laboratory program will address all three agents and energetics.
- d. Complete commercial data are available, and this data base coupled with the laboratory program is sufficient to design and procure a pilot plant capability with minimum actual agent and energetic laboratory data.
- e. No pilot plant capability exists in industry which can operate with agent.

- f. The process is applicable to agent and energetic destruction but not to current 5X decontamination and dunnage processing.
- g. The equipment utilized in the process has no unusual characteristics, i.e., exotic metals, special patents, etc.
- h. Funding will be available.
- i. Permitting and other environmental requirements will not present unusual obstacles.
- j. The process is capable of being operated remotely and can be maintained by a normal chemical process maintenance workforce.
- k. Pilot operations will be required but no significant new construction for a pilot facility is required.
- l. Modification of the Chemical Agent Munitions Disposal System (CAMDS) facility can be implemented for the required pilot plant operations.
- m. The three applicable plants will be built simultaneously. The schedule does not include operational testing of the first new technology plant prior to construction of the last two.
- n. No new special procedures are required to access the explosives or agent.
- o. The chemical materials utilized in the new technology are compatible with current Demilitarization Protective Ensemble, monitoring, and safety procedures.
- p. It is assumed that only one alternative technology will be pursued in both the laboratory and pilot phases.

#### **4. Schedule.**

a. Case 1: Based upon the assumptions cited above, the following activities are required for a developmental program in the event that an alternate technology is recommended by the commission and accepted the Secretary of Defense.

##### **(1) LABORATORY VERIFICATION WITH AGENTS AND EXPLOSIVES.**

##### Schedule Assumptions:

- (a) Existing surety laboratory is available.

(b) Laboratory-scale equipment is available.

(2) PILOT-SCALE PROGRAM.

Schedule Assumptions:

- (a) CAMDS will be modified for new process; no significant new construction.
- (b) Normal equipment leadtimes (1 year).
- (c) RCRA permit can be obtained in 24 months.
- (d) Sufficient laboratory data is available for design of pilot plant.
- (e) National Environmental Policy Act (NEPA) processing will not cause unusual delays.
- (f) Pilot test program will not result in a "smoking gun" process problem.

(3) FULL-SCALE PROGRAM.

Schedule Assumptions: (The schedules for each of the activities are detailed in Enclosure 1. In essence the schedules depict APG agent operations being completed in March 2007; NAAP being completed in January 2007; and LBAD in July 2008.)

- (a) Sufficient design information is available from pilot program.
- (b) RCRA permit can be obtained in 24 months.
- (c) Normal equipment leadtime (1 year).
- (d) NEPA processing will not cause unusual delays.
- (e) Systemization or testing program will not cause unusual delays.

b. Case 2: In this particular alternative, it is assumed that the commission cannot recommend an alternative technology. Thus the work on the three involved sites begins in January 1994. This primarily consists of design, EIS, and RCRA restarts. The delay attributed to this scenario and the revised schedules are depicted in Enclosure 2. In essence the delay causes completion of APG agent operations from June 1999 to July 2000; NAAP from April 1999 to May 2000; and LBAD from February 2000 to November 2001. Enclosure 2 provides a detailed schedule.

5. Cost Discussion.

a. Case 1. Again, the viability of cost projections on an unspecified technology mandates that at best the costs represent rough order of magnitude estimates which cannot be utilized meaningfully for any purpose but rough approximations.

(1) Laboratory Phase: Assumption is that the work will be done in a Government laboratory and by Government personnel, i.e., Chemical Research, Development and Engineering Center where agent-approved laboratory capability exists. The work to be done incorporates laboratory studies on both agent and explosives materials. Approximately four months could be reduced if the work was limited to agent studies.

Basis of Estimate:

Duration: 1 Year	
Labor Costs: 4 people @ \$100,000 per man-year	\$400,000
Equipment, Supplies, Material	100,000
Consultant Services	100,000
Total	\$600,000

(2) Pilot Phase: It is postulated that the pilot studies will be performed at CAMDS, located at Tooele Army Depot, Utah. Current plans call for the CAMDS pilot facility to be closed and decontaminated by September 1995. However, the Army would have to retain this capability. This results in a limited core staff to maintain the facility in a ready condition for 36 months. The labor costs for the operations and environmental activities can be reasonably estimated. However, the design and capital costs for an undefined technology represent gross approximations with no major Military Construction, Army (MCA) costs in the estimate. However, the process may require MCA construction to safely house a supercritical water oxidation process which operates at or above 3,000 psi. This would not only represent a major cost, but obviously would also affect schedules. Conversely, the modifications could be less than what is estimated based on availability of equipment from the commercial developers of the process.

Activity	Duration	Cost Estimate (\$000)
Design	12 mos	2,000
Environmental	24 mos	1,000
Modifications & Equipment Procurement/Installation	15 mos	15,000
Core Staffing	36 mos	35,000
(75 people -24 mos)		
(115 people -12 mos)		
Operations	24 mos	42,000
(150 people)		
Closure	12 mos	12,000
(75 people)		
Consultation Services	N/A	1,000
	Total	108,000

(3) Full-Scale Production Phase: Estimating the full-scale phase of a new undefined technology is considered to be an exercise in futility. Therefore, this study assumes that the current baseline technology costs for facilitization, systemization, and operations are valid for the alternative technology plan. This makes even more sense as the incinerators, which the new technology would replace, account for less than 10% of the capital costs. A substantial increase in design costs, however, is included as the current program bases its design costs on cloning of presently completed baseline designs, while the new or alternative technology designs must be developed from "scratch." The same applies to the environmental work. Therefore, the information presented below for facilitization, systemization, operations, and closure costs represent merely the inflation factors of moving the program into downstream years to incorporate the alternative technology.

Site	Current Costs (\$000)	Revised Costs (\$000)
<u>ABERDEEN PROVING GROUND</u>		
Design	8,000	10,000*
Environmental	800	1,000
Facilitization	248,000	311,000
Systemization	37,000	46,000
Operations	111,200	140,000
Consultants	N/A	1,000
Closure	33,000	41,000
Total	438,000	550,000
<u>NEWPORT ARMY AMMUNITION PLANT</u>		
Design	12,000	15,000*
Environmental	800	1,000
Facilitization	230,000	287,000
Systemization	37,000	46,000
Operations	88,200	112,000
Consultants	N/A	1,000
Closure	28,000	35,000
Total	396,000	497,000

\* Includes Title II Services

\* Includes Title II Services; Provides Inforamtion to APG Design



Site	Current Costs(\$000)	Revised Costs (\$000)
<u>LEXINGTON-BLUE GRASS ARMY DEPOT</u>		
Design	9,000	18,000*
Environmental	800	1,000
Facilitization	374,000	476,000
Systemization	65,000	82,000
Operations	164,200	210,000
Consultants	N/A	1,000
Closure	44,000	55,000
Total	657,000	843,000

\* Includes Title II Services

**5. Program Costs.**

- a. In addition to the above, additional program costs can be expected. These costs are calculated on a 7.8 year program extension for APG and NAAP, and 8.4 years for the LBAD site.

Activity	Estimated Costs (\$000)
Internal Operating Budget	80,000
Support Contracts	40,000
Emergency Response	125,000
Continued Storage	125,000

- b. For Case 2, the costs reflect inflation from stopping work when the amendment is passed (October 1992) and restarting in January 1994 as well as the associated inefficiencies involved with stoppage and restart of work. In essence, therefore, the costs of delaying the three sites by 13 months for both APG and NAAP, and 21 months for LBAD, are reflected for this case.

5. Summary.

CASE 1.

(1) Schedule:

Site	Current Schedule	Revised Schedule	Change
APG	Jun 1999	Mar 2007	93 mos
NAAP	Apr 1999	Jan 2007	93 mos
LBAD	Feb 2000	Jul 2008	101 mos

(2) Costs:

Site	Current Costs (\$000)	Revised Costs (\$000)	Change
APG	438,000	550,000	112,000
NAAP	396,000	497,000	101,000
LBAD	657,000	843,000	186,000

(3) Programmatic Costs Addition:

Activity	Costs (\$000)
Internal Operating Budget	80,000
Support Contracts	40,000
Emergency Response	125,000
Continued Storage	125,000

CASE 2

(1) Schedule:

Site	Current Schedule	Revised Schedule	Change
APG	Jun 1999	Jul 2000	13 mos
NAAP	Apr 1999	May 2000	13 mos
LBAD	Feb 2000	Nov 2001	21 mos

(2) Costs:

Site	Current Costs (\$000)	Revised Costs (\$000)	Change
APG	438,000	456,000	18,000
NAAP	396,000	412,000	16,000
LBAD	657,000	696,000	39,000

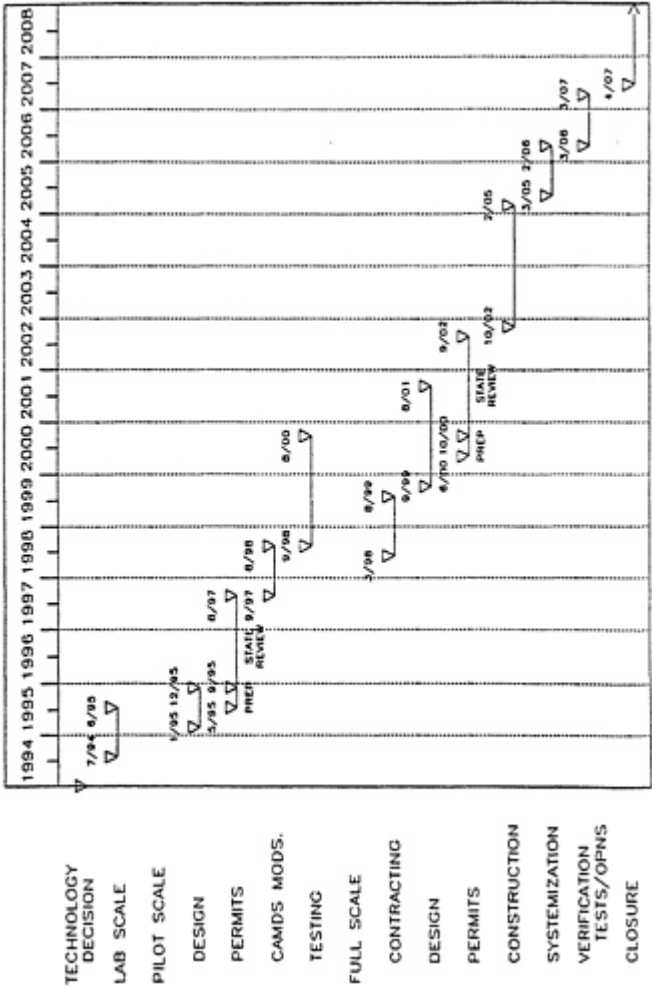
(3) Programmatic Costs Addition:

Activity	Costs (\$000)
Internal Operating Budget	12,000
Support Contracts	5,000
Emergency Response	20,000
Continued Storage	20,000

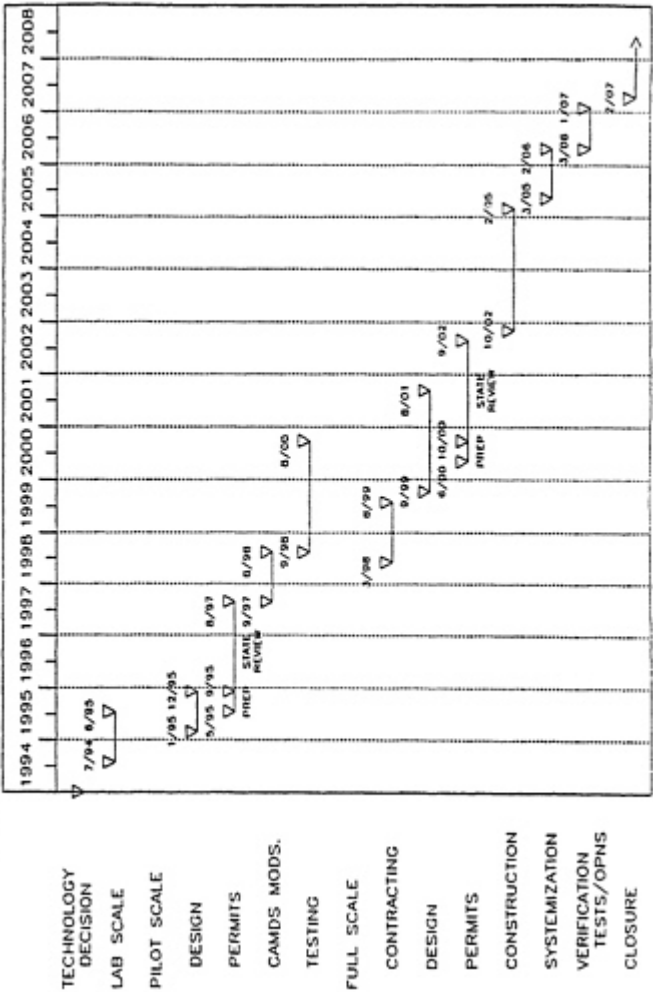
**CASE 1**

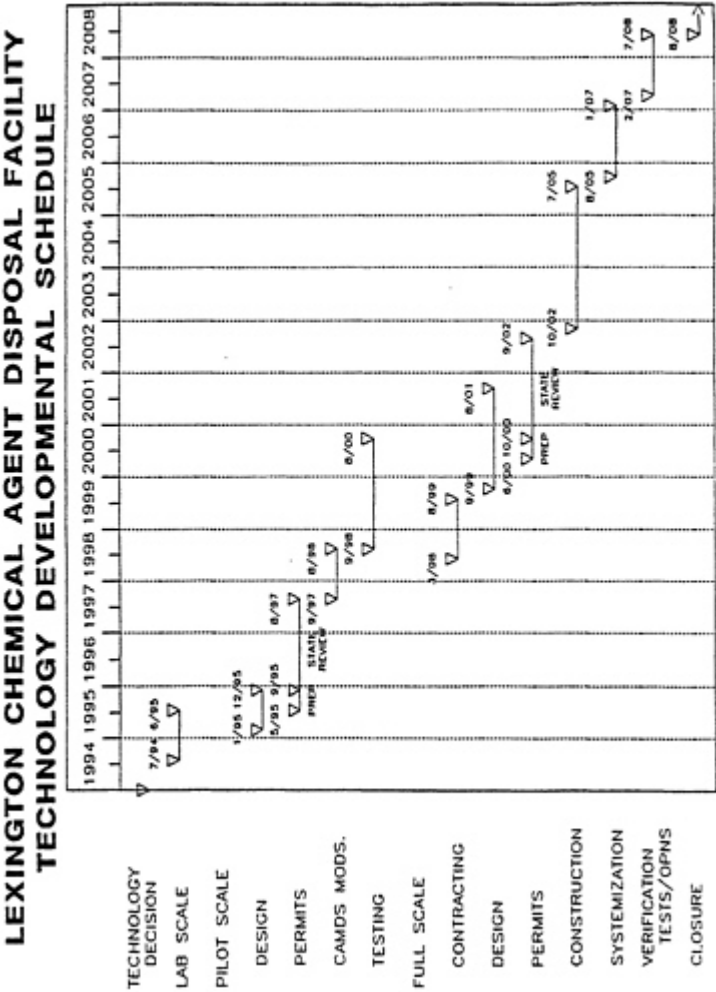
**IMPLEMENT AN ALTERNATIVE TECHNOLOGY**

ABERDEEN CHEMICAL AGENT DISPOSAL FACILITY  
TECHNOLOGY DEVELOPMENTAL SCHEDULE



NEWPORT CHEMICAL AGENT DISPOSAL FACILITY  
TECHNOLOGY DEVELOPMENTAL SCHEDULE

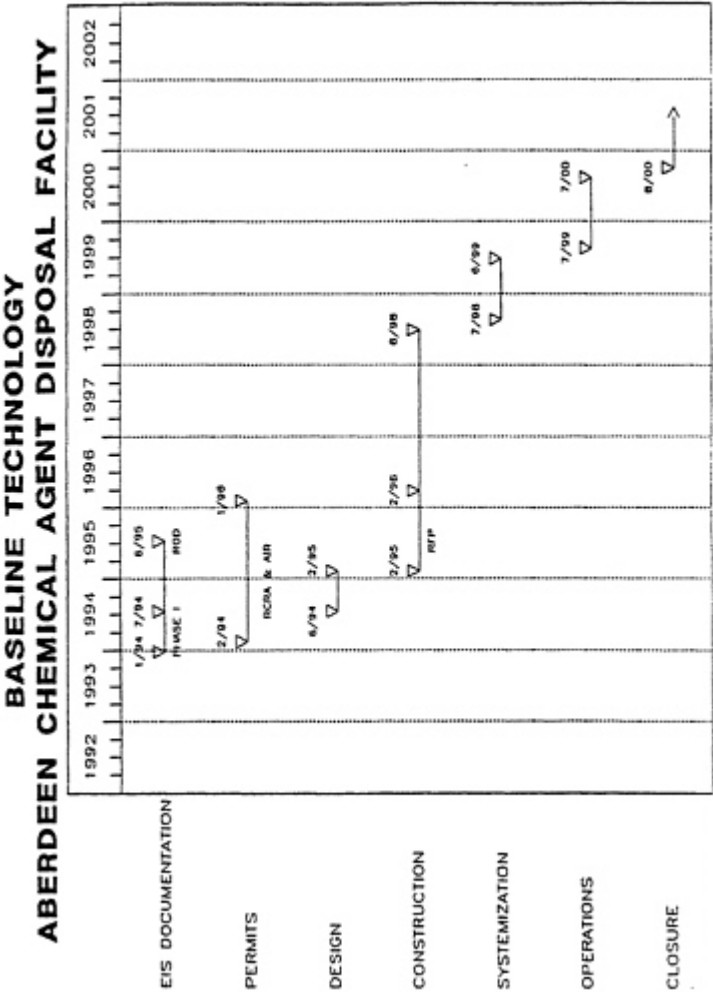


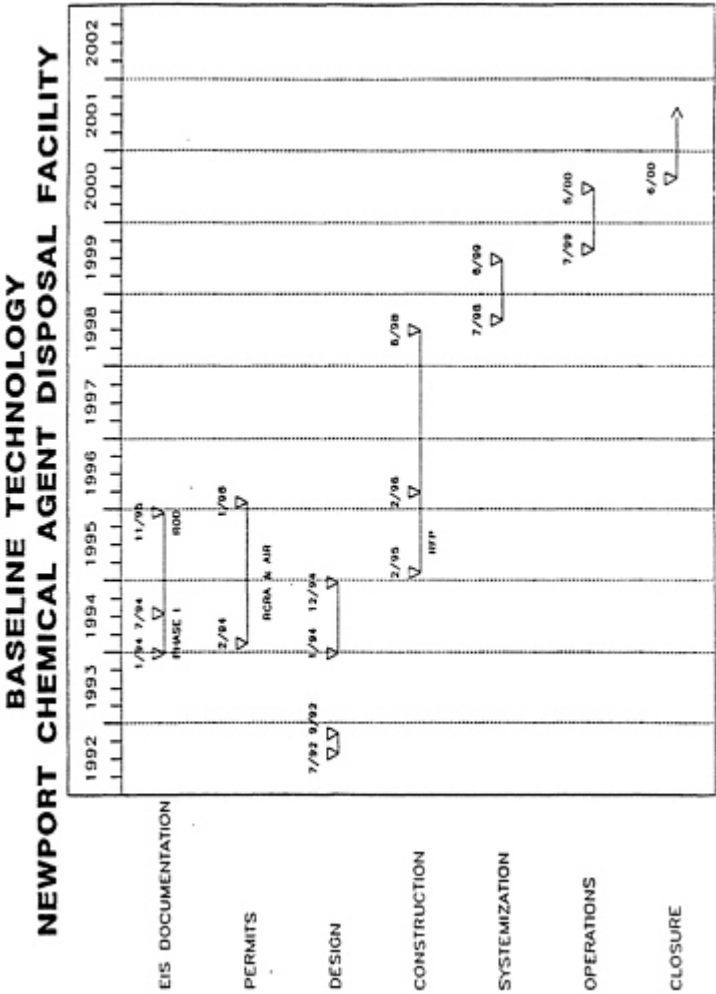


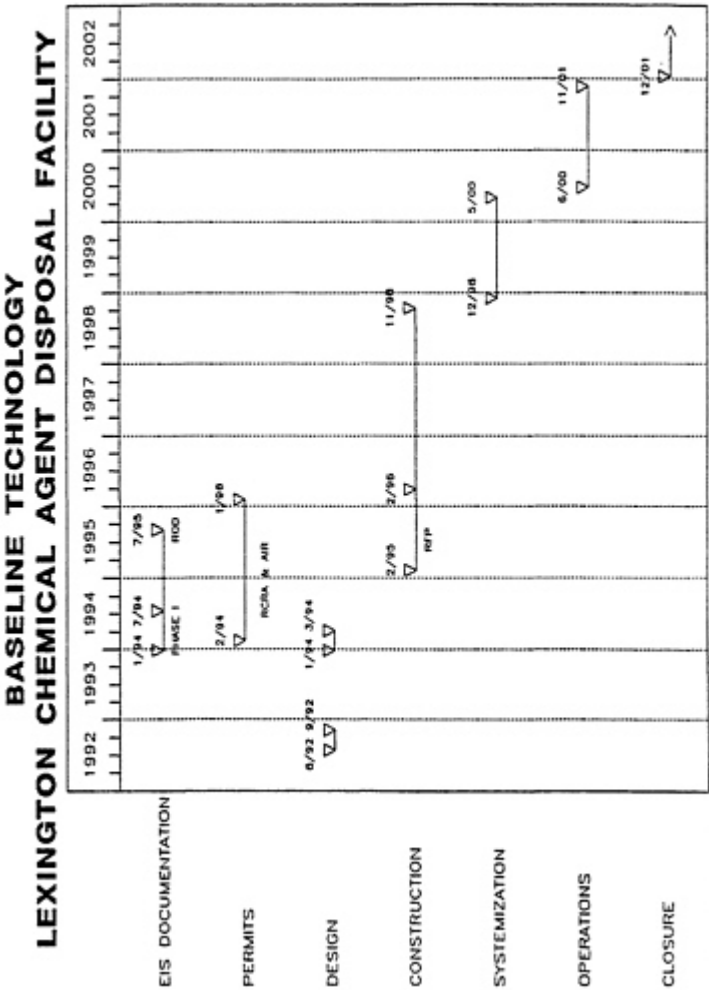
**CASE 2**

**PROCEED WITH BASELINE TECHNOLOGY AFTER DELAY FOR  
ALTERNATIVE TECHNOLOGY REVIEW**









SFIL-CME-M (50q)

29 July 1992

INFORMATION PAPER

SUBJECT: Chemical Agent Monitoring Limits

1. Purpose: To provide information to the National Research Council's Committee on Alternative Technology Committee relative to air monitors detection limits for lethal Chemical agents.

2. Facts.

a. Agent monitoring standards are targeted to achieve a reliable of agent concentrations limits in air. The airborne agent standards are based on analyses and extrapolations of agent toxicological data. This applies to General Population Levels (GPL), Time Weighted Average (TWA) exposures of unprotected workers (long term) and High Level Exposure (HLE) of unprotected workers (short term). The latter is equivalent to the immediately-dangerous-to-life-and-health (IDLH) concentration. The Allowable Stack Concentration (ASC) is based on an achievable level of agent in incinerator exhausts from a well-designed and well-operated incinerator. Worst case air modelling of ASC emission from the plant exhaust stacks results in air concentrations well below the GPL at all detail installation boundaries. The ASC is the only one of the four critical standards which is not based on toxicological analyses. A fifth plant air control standard, described as the maximum allowable concentration of agent in air to which workers in protective clothing (the demilitarization protective ensemble or DPE) can be exposed, is based simply on the test limits of the DPE.

b. Minimum detection limits (MDL) for GB, VX and HD using the Automatic Chemical Agent Monitoring System (ACAMS) and the Depot Area Air Monitoring System (DAAMS) are derived from precision and accuracy studies and are updated monthly based on responses from quality control challenges. Statistical analyses of instrument responses to a range of challenges are used to produce a regression curve with 95% confidence bounds. The MDL is defined as the lowest true agent concentration that, 50% of the time, results in 97.5% confidence that the agent will be detected. Current operational data from JACADS and CAMDS produced the following MDL for the ACAMS and the DAAMS for each of the three lethal chemical agents.

MINIMUM DETECTION LIMITS FOR ACAMS (mg/m<sup>3</sup>)

Agent	ASC	TWA	HLE
GB	0.000030	0.000010	0.020
VX	0.000039	0.0000013	0.0026
HD	0.006	0. 0006	0. 0006

SFIL-CME-M (50q)			
SUBJECT: Chemical Agent Monitoring Limits			
MINIMUM DETECTION LIMITS FOR DAAMS (mg/m <sup>3</sup> )			
Aent	ASC	TWA	HLE
GB	0.000009	0.000003	0.006
VX	0.00012	0.00004	0.0008
HD	0.003	0.0003	0.0003

1 June 1992

## INFORMATION PAPER

SUBJECT: Disposal of Wastes from the JACADS Facility

1. Purpose: To respond to four questions raised by the National Research Council's Alternative Technology Committee.

2. Responses to the NRC Committee's questions were prepared by the operating contractor for the Army's Program Manager for Chemical Demilitarization. Questions and responses are as follows:

a. Question. What are the costs, permits, etc. related to waste shipments from Johnston Island?

Response. JACADS hazardous wastes are classified into two categories-process wastes and non-process wastes. Process wastes are generated as a direct result of the incineration processes. wastes are generated from general maintenance of the facility.

Process wastes (hazardous or non-hazardous) are normally shipped to (Chem-Waste Management Inc. 's Kettleman Hills Facility to California. In the case where the Brine Reduction Area (BRA) cannot be operated, then brines may be sent to them-Waste Management's Corpus Christi, Texas, deep well injection disposal facility. Non-process wastes are shipped to the defense Reutilization and Marketing Office (DRMO) facility in Hawaii.

JACADS wastes are accepted by these Treatment, Storage, and Disposal Facilities (TSDFs) after the wastes have been Characterized ("profiled") by JACADS Environmental personnel and verified by the TSDF laboratory personnel. profiling involves sampling, analyses, and data reporting of the wastes to be disposed. Waste permits are called profiles. Every waste is profiled before it gets accepted for disposal by the TSDFs.

The cumulative cost of JACADS process wastes disposed through the Chem-Waste contract through April, 1992 is approximately \$1,015,000. The cost for JACADS non-process waste disposed through January, 1992 is approximately \$124,000. The total cost for JACADS wastes from the start to now is approximately \$1,139,000.

This total reflects only the cost of disposal at the TSDFs. It does not include the water shipment transportation incurred by Matson Navigation Company.

b. Question. What are the transportation criteria and any restrictions placed upon these shipments?

Response. Title 49 of the Code of Federal Regulations (Department of Transportation) are followed for shipment of the wastes through water and over

SAIL-PMM  
SUBJECT: Disposal of Wastes from the JACADS Facility  
land. The only restrictions pertain to weight limitations and section of incompatible wastes in sea nets or conexes.

c. Question. What are the rules for shipment and landfill disposition of 3X material?  
Response. Before any 3X materials are shipped off-island, the U.S. Army Safety Department Headquarters must approve release. specific existing procedures or to-be-generated procedures followed for all 3X items to be disposed. All 3X materials approved for disposal are sent to Chem-Waste at Kettleman Hills.

d. Question. What are landfill costs currently being  
Response. costs differ for each type of JACADS waste. This is dependent on what type of pre-treatment is necessary before actual landfilling or deep-well injecting of the particular JACADS waste.

Listed below are current examples of process and non-process wastes and their disposal costs.

<u>Process Wastes</u>	
DFS Ash and Metal Residue	\$367/ton
BRA Salts	\$130/drum
3X DPE Suits	\$50/drum
Brines	\$.60/gallon
<u>Non-Process Wastes</u>	
Corrosives (Acids/Caustics)	\$2/pound
Contaminated oil	\$1/pound
Glycols	\$1/pound
Paint, solids	\$.50/pound

Detailed breakdown of the costs are provided for each type of waste in the contracts with (hem-Waste and with DRMO-Hawaii.

ACTION OFFICER: JOSEPH S. STANG  
OFFICER: DONALD L. PUGH

## D

### Biographical Sketches

**Dr. John P. Longwell, Chairman**

Dr. Longwell was graduated with a bachelor of science degree from the University of California, Berkeley, and with a doctor of science degree in chemical engineering from Massachusetts Institute of Technology. His distinguished career in research and engineering with Exxon Research and Engineering Company involved management of several research divisions and culminated with the position of senior scientific advisor for four years. Since 1977 Dr. Longwell has been E.R. Gilliland Professor of Chemical Engineering at Massachusetts Institute of Technology. His research interests for the last decade have been primarily related to his activities as Associate Director of the M.I.T. Center for Environmental Health Sciences, with special focus on generation and health effects of combustion products. He is a member of the National Academy of Engineering the American Institute of Chemical Engineers, and the American Chemical Society.

**Dr. George Apostolakis**

Dr. Apostolakis was graduated with a degree in electrical engineering from the National Technical University, Athens, Greece, and with a masters degree in engineering science and a doctorate in engineering science and applied mathematics from the California Institute of Technology. He is currently a professor in the Mechanical, Aerospace and Nuclear Engineering Department, at the University of California, Los Angeles. He has been a consultant to numerous national and state agencies, as well as to public and private businesses in the area of risk assessment and analysis, particularly as applied to all types of energy production and hazardous waste elimination. Dr. Apostolakis also has participated in the activities and deliberations of countless national and international committees, societies, and conferences. He has published extensively in his field of risk assessment and analysis. He has a particular interest in mathematical methods for risk and reliability



assessment of complex technological systems; uncertainty analysis; decision analysis; and application of probabilistic models to safety and reliability analyses of nuclear reactors, chemical process systems, space systems, and the control of hazardous substances.

**Dr. Joseph Frederick Bunnett**

Dr. Bunnett was graduated with a bachelor of arts degree from Reed College and with a doctorate from the University of Rochester. He has been the recipient of several fellowships, including two Fulbrights and one Guggenheim. Briefly a research chemist for the Western Pine Association, he joined the faculty of Reed College in 1946. This was followed by positions at the University of North Carolina from 1952 to 1958 and Brown University from 1958 to 1966, including Chairman of the Chemistry Department from 1961 to 1964. From 1966 to the present he has been a faculty member of the University of California, Santa Cruz (emeritus since 1991). He was founding editor of the *Journal: Accounts of Chemical Research*, and served as its editor for 20 years. He has been elected to the American Academy of Arts and Sciences and is a Fellow in the American Association for the Advancement of Science. As a member of the International Union of Pure and Applied Chemistry (IUPAC), he has occupied many diverse senior and executive positions. With a particular research interest in organic reaction mechanisms, as well as in the elimination of chemical weapons, Dr. Bunnett comes to the Alternatives Committee as the Chairman of the IUPAC Task Force on Scientific Aspects of the Destruction of Chemical Warfare Agents.

**Dr. Peter S. Daley**

Dr. Daley was graduated with bachelor of science and master of science degrees in chemical engineering from Cornell University and with a doctoral degree in environmental engineering from the University of Florida. He spent 20 years in the United States Air Force in a wide variety of environmental and environmental engineering assignments, culminating a distinguished career with his appointment as Director of Environmental Policy for the Department of Defense. There he directed the department's environmental policy and activities and was its spokesman to Congress and the press regarding environmental matters. He recently was appointed Vice President for Environment and Technology for Waste Management International, London, leaving the position of Senior Director of Research and Development at Waste Management, Inc., where his efforts were concentrated on methods

for treating, stabilizing, destroying and handling chemical wastes and on resource recovery and waste reduction.

**Mr. Gene H. Dyer**

Mr. Dyer was graduated with a bachelor of science degree in chemistry, mathematics, and physics from the University of Nebraska. Over a 12-year period he worked for General Electric as a process engineer, the U.S. Navy as a Research and Development project engineer, and the U.S. Atomic Energy Commission as a project engineer. He then began a more than 20-year career with the Bechtel Corporation in 1963. First a consultant on advanced nuclear power plants and later a program supervisor for nuclear facilities, he then served as manager of the Process and Environmental Department from 1969 to 1983. This department provided engineering services related to research and development projects, including technology probes, environmental assessment, air pollution control, water pollution control, process development, nuclear fuel process development, and regional planning. He culminated his career at Bechtel by serving as a senior staff consultant for several years, with responsibility for identifying and evaluating new technologies and managing their further development and testing for practical applications. He is a member of the American Institute of Chemical Engineers, and a registered Professional Engineer.

**Dr. David S. Kosson**

Dr. Kosson was graduated with a bachelor of science degree in chemical engineering, a masters degree in chemical and biochemical engineering, and a doctorate in chemical and biochemical engineering from Rutgers, The State University of New Jersey. He joined the faculty at Rutgers in 1986 and was made an associate professor with tenure in 1990. He teaches graduate and undergraduate chemical engineering courses. In addition, he is the projects manager for the Department of Chemical and Biochemical Engineering, where considerable work is under way in developing microbial, chemical, and physical treatment methods for hazardous waste. He is responsible for project planning and coordination, from basic research through full-scale design and implementation. Dr. Kosson is a participant in several Environmental Protection Agency Advisory Panels involved in waste research and is the Director of the Physical Treatment Division of the Hazardous Substances Management Research Center in New Jersey. He is a prolific writer in the fields of chemical engineering and waste management and treatment. He is a member of the American Institute of Chemical Engineers.

**Dr. Walter Grant May**

Dr. May was graduated with a bachelor of science degree in chemical engineering and master of science degree in chemistry from the University of Saskatchewan and with a doctor of science degree in chemical engineering from the Massachusetts Institute of Technology. He joined the faculty of the University of Saskatchewan as a professor of chemical engineering in 1943. In 1948, he began a distinguished career with Exxon Research and Engineering Company, where he was a Senior Science Advisor from 1976 to 1983. He was Professor of Chemical Engineering at the University of Illinois from 1983 until his retirement in 1991. There he conducted courses in process design, thermodynamics, chemical reactor design, separation processes, and industrial chemistry and stoichiometry. Dr. May has published extensively, served on the editorial boards of *Chemical Engineering Reviews* and *Chemical Engineering Progress*, and obtained numerous patents in his field. He is a member of the National Academy of Engineering and a fellow of the American Institute of Chemical Engineers, and he has received special awards from the American Institute of Chemical Engineers and the American Society of Mechanical Engineers. He has a particular interest in separations research work.

**Dr. Matthew Meselson**

Dr. Meselson was graduated with a bachelor of philosophy degree from the University of Chicago and a doctorate in physical chemistry from California Institute of Technology. Following a brief term with the faculty at Caltech, he joined the faculty at Harvard University, where since 1976 he has been the Thomas Dudley Cabot Professor of the Natural Sciences. Dr. Meselson is the recipient of numerous awards for distinguished accomplishment, including the National Academy of Sciences Prize for Molecular Biology; the Scientific Freedom and Responsibility Award of the American Association for the Advancement of Science; honorary doctorate degrees from the University of Chicago, Yale, and Princeton; a MacArthur fellowship; and many others. He is a member of the National Academy of Sciences and the Institute of Medicine, a fellow of the American Association for the Advancement of Science, and member of numerous national and international honorary societies. For almost 30 years Dr. Meselson has had an interest in the arms control of chemical and biological weapons and has served as a consultant on this subject to various government agencies.

**Dr. Henry Shaw**

Dr. Shaw was graduated with a bachelors degree in chemical engineering from City College of New York, a masters degree in chemical engineering from the New Jersey Institute of Technology, and a master of business administration degree and a doctorate in physical chemistry from Rutgers University. From 1957 to 1965 Dr. Shaw worked as a nuclear chemical engineer for Babcock and Wilcox Company and for Mobil Oil Corporation. Then, over a period of 20 years, he rose from research engineer to Manager of the Environmental Research Area of the Exxon Research and Engineering Company. In this latter position, his responsibilities included conducting research on global environmental problems such as acid precipitation and atmospheric build-up of CO<sub>2</sub>. In 1986 Dr. Shaw was appointed Professor of Chemical Engineering in the Department of Chemical Engineering, Chemistry and Environmental Science at the New Jersey Institute of Technology. In addition to his teaching responsibilities, Dr. Shaw was the director of a multi-university study involving the New Jersey Institute of Technology, Massachusetts Institute of Technology, Ohio State University, and Pennsylvania State University that established the Industry/University Cooperative Research Center for Emissions Reduction. Dr. Shaw is also supervising research on the thermal destruction of hazardous and toxic wastes using plasmas and catalytic oxidation and the aqueous scrubbing of acid rain precursors. He is a fellow of the American Institute of Chemical Engineers and a member of the American Association for the Advancement of Science, the American Chemical Society, and the American Society for Engineering Education.

**Dr. Thomas O. Tiernan**

Dr. Tiernan was graduated with a bachelor of science degree in chemistry from the University of Windsor in Windsor, Ontario, and with master of science and doctoral degrees in chemistry from Carnegie-Mellon University. He worked for the United States Air Force for 15 years as a research chemist, including 8 years as the director of the Gaseous Excitation and Ionization Processes Group, Aerospace Research Laboratories, where his work primarily involved radiation chemistry, radiation effects, and ion and electron collision processes. In 1975, he joined the faculty of Wright State University as Professor of Chemistry. Concurrently, he was Director of Brehm Laboratory from 1976 to 1987, and has been Director of the Toxic Contaminant Research Program from 1987 to the present. His laboratory was involved in the earliest work to develop techniques for measuring ultra-low levels of chlorinated dioxins. Today it is involved in base-catalyzed decomposition, or dehalogenation, processes that are principally concerned with chlorinated

aromatics, such as PCBs, chlorinated dioxins, chlorinated dimethyl furans, as well as a large number of pesticides and solvents. The recipient of numerous grants, and a prodigious writer in his field, Dr. Tiernan has attained many special honors and awards. He is a fellow of the American Institute of Chemists and a member of the American Chemical Society, the American Physical Society, the American Society for Mass Spectrometry, and the American Society for Testing Materials.

**Dr. Barry Martin Trost**

Dr. Trost was graduated with a bachelor of arts degree from the University of Pennsylvania, and with a doctorate from Massachusetts Institute of Technology. He joined the faculty of the University of Wisconsin, rising in a very short time to full Professor of Chemistry, and later to chairman of the department. In 1987, he was appointed Professor of Chemistry at Stanford University and became the Job and Gertrud Tamaki Professor of Humanities and Sciences in 1990. He has received appointments as Visiting Professor and Lecturer at numerous universities throughout the United States, Canada, and Western Europe. He has very actively participated on the editorial and editorial advisory boards of many books and journals. His many awards and honors include early election to the National Academy of Sciences, Fellow of the American Association for the Advancement of Science, the American Chemistry Society Awards in Pure Chemistry and for Creative Work in Synthetic Organic Chemistry, and recently the Dr. Paul Janssen Prize for Creativity in Organic Synthesis. Dr. Trost has been a consultant to industry, a prodigious author, and a member of numerous committees, panels, juries, and delegations serving the academic and scientific communities involved in chemistry. His special interests are organic reactions and processes.

**Dr. James Robert Wild**

Dr. Wild was graduated with a bachelor of arts degree from the University of California, Davis, and with a doctorate in cell biology from the University of 238 California/Riverside. Following service as a research microbiologist-biochemist at the U.S. Navy Medical Research Institute, he joined the faculty at Texas A&M University in 1975 as an Assistant Professor of Genetics. He was an Associate Professor of Biochemistry and Genetics from 1980 to 1984 and was appointed a Professor of Biochemistry and Genetics in 1984. In addition to being an extremely active teacher, he has served the university in increasingly responsible positions, including as Chairman of the Intercollegiate Faculty of Genetics from 1984 to 1987, Professor and Interim Head of the

Department of Biochemistry and Biophysics from 1986 to 1990, and Executive Associate Dean/Associate Dean for Academic Programs of the College of Agriculture and Life Sciences from 1988 to the present. Dr. Wild has conducted and directed extensive genetic and biochemical research and has published many articles and participated in countless seminars and invited presentations. He holds a particular interest in the design of biological systems that might positively contribute to the enormous problem of environmental cleanup.

E

Technology Developers That Supplied Information

In addition to the presentations at the committee's workshop (see [Appendix F](#)), material was received by the committee on a variety of technologies. The committee considered this material in its work but not all the material received was necessarily germane to the committee's interests. Materials were received from the following:

AEA Technology

Dounreay  
Thurso  
Caithness KW14 7TZ  
Contact: Dr. W. Batey

Ag(II) process

This process generates highly oxidizing species in an electrochemical cell to treat organic wastes and oxidize them to carbon dioxide and water.

BOVAR Corporation

10200 Richmond Avenue  
Suite 150  
Houston, TX 77042 (713) 789-1084  
Contact: Hamish Adam, General Manager

Lewisite Neutralization Technology

This process is carried out in four steps: reaction of lewisite with an oxidizing agent; removal of residual oxidizing agent; decomposition of the products of lewisite oxidation through addition of NaOH; and chemical fixation of the products of acid decomposition to prevent leaching of arsenic salts.

**Dynecology Incorporated**

611 Harrison Avenue                      The Toxiplex Slagging Gasification Process for the Thermal Destruction of Chemical Warfare Agents  
Harrison, NY 10528  
(914) 967-8674  
Contact: Helmut W. Schulz

This is a gasification process (with steam and oxygen) that provides for the conversion of a broad spectrum of toxic and refractory organic substances into a clean fuel or synthesis gas.

**Elkem Technology**

P.O. Box 4376 Torshov                                              Electric Arc Furnaces  
N-0402 Oslo 4  
Norway  
Contact: Arne K. Stoye

Information was provided on the Elkem Multi-purpose Furnace<sup>®</sup>, an electric smelting technology.

**Electrochemical Oxidation Systems**

3445 Greer Road                                              Mediated Electrochemical Oxidation Processes for Chemical Weapons Materials  
Palo Alto, CA 94303-4210  
(415) 494-6982  
Contact: Norvell Nelson, President

In this electrochemical process, very reactive high-oxidation-state metal ions are generated that react either directly or indirectly with organic materials.

**Florida International University**

Drinking Water Research Center                                              High-energy Electron Beam Irradiation for the Removal of Toxic and Hazardous Organic Chemicals from Water and Wastewater  
  
University Park Campus  
Miami, FL 33199  
(305) 348-2826  
Contact: William J. Cooper, Director and Associate Professor

In this process, high-energy electrons impact an aqueous solution, generating reactive transient species that destroy hazardous contaminants.



**Gene Syst International, Inc.**

9326 Fairfax Street  
Alexandria, VA 22309  
(703) 780-8821  
Contact: James A. Titmas

Supercritical-Water Oxidation

Information supplied on the application of supercritical-water oxidation (SCWO) to destroy various organic contaminants including a below-ground SCWO technology.

**HALLIBURTON NUS Environmental Corporation**

Environmental Technologies Group  
5950 North Course Drive  
P.O. Box 721110  
Houston, TX 77272  
(713) 561-1556  
Contact: Roberto E. Frulla, Executive Vice President

Ultrox UV/Oxidation Process

This process dilutes chemical agent(s) into water, and then destroys the highly diluted chemical agent(s) by oxidizing them at ambient temperature in an ULTROX<sup>®</sup> ultraviolet light and hydrogen peroxide reactor.

**Highly Filled Materials Institute**

Stevens Institute of Technology  
  
Castle Point  
Hoboken, NJ 07030  
(201) 216-8225/(201) 216-5119  
Contacts: Professor Dilhan M. Kalyon, Professor Suphan Kovenklioglu

Concomitant Chemical Neutralization of Chemical  
Ammunitions and Encapsulation of Neutralization  
Products Using Twin Screw Extrusion

This process describes a system for using a neutralizing agent and then encapsulating the products in a polymeric matrix. A mechanical system for accomplishing this is described.

**IIT Research Institute**

10 West 35th Street  
Chicago, IL 60616-3799  
(312) 567-4000  
Contact: Alan Snelson, Ph.D., Science  
Advisor, Chemical Sciences Section

Ozone/UV/Fluorocarbon Solvent System

This is a non-aqueous method for biological or chemical decontamination. Ozone is dissolved in a fluorocarbon solvent, and ultraviolet radiation is used to decompose chemical warfare materials.

**Lawrence Livermore National Laboratory**

Department of Chemistry and Materials Science  
Livermore, CA  
(510) 423-6649  
Contact: John F. Cooper

Oxidation Using Catalyzed Peroxy Disulfate and Peroxide

This direct chemical oxidation process proposes using alternate treatments with catalyzed peroxydisulfate (persulfate) and catalyzed hydrogen peroxide in a dosed, aqueous-phase, ambient temperature system.

**Lawrence Livermore National Laboratory**

University of California  
P.O. Box 808, L-619  
Livermore, CA 94550  
Contact: Stephen M. Matthew, Ph.D.,  
Senior Physicist

Radiolytic Decomposition of Hazardous Wastes and Chemical Weapon  
Surrogates

In this process, it is proposed that radiation, either from a cobalt source or from X-rays generated from an electron accelerator, be used to detoxify chemical warfare agents. The proposal is to destroy these chemicals without removal from weapons.

**Lapidus & Associates**

Suite 1210  
Allegheny Building  
429 Forbes Avenue  
Pittsburgh, PA 15219  
(412) 261-9222  
Contact: Robert A. Lapidus

Self-Cooled Containment Building

The Self-Cooled Containment Building was developed to deal with air pollution and heat generated in coke battery operations. The containment building is designed to provide complete containment of any pollution products of combustion or any chemicals that have not been treated in the combustion phase.

**MRK, Inc.**

2602 Main Street  
Baker, LA 70714  
(504) 344-5063  
Contact: C.C. Efferson

Closed Loop Incineration Process

A potential Closed Loop Incineration System (CLIS) that utilizes known technology to recycle the maximum amount of flue gas and converts the remaining exit flue gas into a usable product.

**Plasma Energy Applied Technology, Inc.**

4914 Moores Mill Road  
Huntsville, AL 35811  
(205) 859-3006  
Contact: William C. Bums, PE,  
Vice President & General Manager

Plasma Waste Energy Waste Processing System

A system that uses a plasma torch to thermally treat wastes, converting inorganic material to a vitrified glass-like solid and organic matter to a gas composed of simple molecules such as hydrogen and carbon monoxide.

**Plasma Systems Incorporated**

10103 Sanders Court  
Great Falls, VA 22066  
(804) 448-1633  
Contact: Steve Horvath, Tony Gedeon

"Plasmadestruct" Process for Destruction of Chemical Weapons

"Plasmadestruct" is a patented process for the thermal destruction and vitrification of hazardous wastes. It is a pyrolytic process utilizing non-transferred arc plasma generators as a heat source to gasify and thermally destroy complex organic compounds.

**Tech Three Inc.**

2519 P Street, NW  
Washington, DC 20007  
(202) 338-1278  
Contact: John Page, President

Attributes of Ozone as a Highly Effective Oxidizer

The "Electromagnetically and Sonically Enhanced Ozone Oxidation Process" routes a liquid medium through an electrostatic treater. It is then routed into an injection chamber where ozone that has been electrostatically treated and magnetically enhanced is injected. It then goes to a chamber with sonic probes that agitate the medium. Heavy metals are filtered out.

**Toxco**

P.O. Box 396  
Claremont, CA 91711  
(714) 624-4010  
Contact: William J. McLaughlin, President

Neutralization of Lithium-Filled Containers

This process involves immersion of munitions in liquid argon or nitrogen, shredding of the munitions, chemical neutralization, and incineration of the metal casing.

## F

### Committee Meetings and Activities

#### 1. Committee Meeting, March 9-10, 1992, Washington, D.C.

The following presentations were made to the committee:

- (a) "Introduction to the Chemical Demilitarization Program," Brig. Gen. Walter L. Busbee, Program Manager for Chemical Demilitarization, U.S. Army.
- (b) "Description of Agents/Munitions," Mr. Mark Evans, Office of the Program Manager for Chemical Demilitarization, U.S. Army.
- (c) "History and Program Rationales of the Demilitarization Program," Mr. Charles Baronian, Office of the Program Manager for Chemical Demilitarization, U.S. Army.
- (d) "Current Status of Demilitarization Facilities: Johnson Atoll Chemical Agent Disposal System (JACADS) and Tooele Chemical Agent Disposal Facility (TOCDF)," Maj. Paul E. Wojciechowski, Office of the Program Manager for Chemical Demilitarization, U.S. Army.
- (e) "Description of the Demilitarization Processes-Baseline Process and Cryofracture Process," Mr. Robert P. Whelen, Office of the Program Manager for Chemical Demilitarization, U.S. Army.
- (f) "Safety Requirements for Design," Mr. Robert Perry, Office of the Program Manager for Chemical Demilitarization, U.S. Army.
- (g) "Agent and Non-Agent Monitoring Program Requirements: Destruction Standards and Classification of Agent, Munitions, Dunnage, Metal Parts," Mr. Donald Pugh, Office of the Program Manager for Chemical Demilitarization, U.S. Army.

- (h) "Treaty Status and Requirements," Brig. Gen. Walter L. Busbee, Program Manager for Chemical Demilitarization, U.S. Army.

**2. Committee Meeting and Workshop, June 3-5, 1992, Washington, D.C.**

The following presentations were made to the committee at its workshop:

- (a) "Enzyme System for Degrading G-agents," Dr. Joseph J. DeFrank, U.S. Army Chemical Research and Development Engineering Center (CRDEC).
- (b) "Combined Chemical/Bacterial Degradation of Sulfur Mustard," Dr. Steve Harvey, U.S. Army CRDEC.
- (c) "Use of Microbial, Bacterial and Enzyme-based Systems in Detoxification of Organophosphate Insecticides," Dr. Jeffrey S. Karns, U.S. Department of Agriculture (USDA) Pesticide Laboratory.
- (d) "Development of Enzyme-based Bioremediation Systems for Nerve Agent Destruction," Dr. Clement E. Furlong, University of Washington.
- (e) "Bioreactor Scale-up and Design," Dr. Ronald Unterman, Envirogen, Inc.
- (f) "Bioremediation Opportunities and Challenges," Dr. Jonathan Mielenz, COGNIS, Inc.
- (g) "Complex Environmental Toxins Subject to Bioremediation," Dr. Fran Kremer, U.S. Environmental Protection Agency.
- (h) "General Chemistry of Nerve Agents," Dr. Joseph Epstein, U.S. Army CRDEC.
- (i) "Destruction of Mustard and Nerve Agents," Dr. Fred Menger, Emory University.
- (j) "Iodoscarboxylates as Catalysts for the Destruction of Reactive Phosphates," Dr. Robert Moss, Rutgers, State University of New Jersey.

- (k) "Army Experience with Neutralization at Rocky Mountain Arsenal," Mr. Edward Coale and Mr. Stephen DePew, Office of the Program Manager for Chemical Demilitarization, U.S. Army.
- (l) "Russian Experience in Chemical Agent Destruction," Dr. Joseph F. Bunnett, University of California, Santa Cruz.
- (m) "Wet Air Oxidation Destruction," Dr. William Copa, Zimpro Passavant Environmental Systems, Inc.
- (n) "Hydrogenation Processes," Mr. Don Hedden, UOP.
- (o) "High Temperature Steam Reforming," Mr. Terry Galloway, Synthetica Technologies, Inc.
- (p) Supercritical Water Oxidation
  - (i) "Overview of Supercritical Water Oxidation," Dr. Jefferson Tester, Massachusetts Institute of Technology.
  - (ii) "Supercritical Water Oxidation Industrial Design," Dr. Glenn Hong, MODAR, Inc.
  - (iii) "DARPA Supercritical Water Oxidation Program," Mr. Michael Spritzer, General Atomics.
- (q) "Review of Fluid-Bed Combustion Applications," Dr. Frances Holm, Chemical Waste Management, Inc.
- (r) "Molten Metal Applications via the Catalytic Extraction Process," Dr. Christopher J. Nagel, Molten Metal Technology.
- (s) "Review of Molten Salt Technologies," Dr. Lawnie H. Taylor, Department of Energy.
- (t) "The Adams Process for Conversion to a Sulfur Polymer," Dr. Edgar Berkey, Center for Hazardous Materials Research, and Mr. James Hendricks, Burns and Roe.
- (u) Plasma Technologies
  - (i) "Plasma Arc Process," Dr. Dale L. Keairns, Westinghouse Electric Corporation.

- (ii) "A Plasma Centrifugal Furnace," Mr. Max Schlienger, RETECH, Inc.
- (iii) "Carbon Arc Destruction Technology," Dr. Charles H. Titus, Electro-Pyrolysis, Inc.
- (v) "United Kingdom Experience," Mr. Ron G. Manley, Chemical and Biological Defence Establishment.
- (w) "The Canadian Experience," Dr. John McAndless, Defence Research Establishment, Suffield.
- (x) The Iraq Experience, Dr. Richard S. Magee, New Jersey Institute of Technology.

The workshop was attended by committee members, guest speakers, and observers, as follows:

**COMMITTEE MEMBERS**

Dr. John P. Longwell, <i>Chairman</i>	Massachusetts Institute of Technology
Dr. George Apostolakis	University of California, Los Angeles
Dr. Joseph F. Bunnett	University of California, Santa Cruz
Dr. Peter S. Daley*	Waste Management International
Dr. Gene H. Dyer	Bechtel Corporation, <i>Retired</i>
Dr. David S. Kosson	Rutgers, The State University of New Jersey
Dr. Walter G. May	University of Illinois
Dr. Matthew Meselson	Harvard University
Dr. Henry Shaw	New Jersey Institute of Technology
Dr. Thomas O. Tiernan	Wright State University
Dr. Barry M. Trost	Stanford University
Dr. James R. Wild	Texas A & M University

**GUEST SPEAKERS**

<i>Biological</i>	
Dr. Joseph J. DeFrank	U.S. Army Chemical Research and Development Engineering Center (CRDEC)
Dr. Clement E. Furlong	University of Washington



Dr. Steve Harvey	U.S. Army Chemical Research and Development Engineering Center (CRDEC)
Dr. Jeffrey S. Karns	USDA Pesticide Laboratory
Dr. Fran Kremer	U.S. Environmental Protection Agency
Dr. Jonathan Mielenz	COGNIS, Inc.
Dr. Ronald Unterman	Envirogen, Inc.
<u>Chemical</u>	
Dr. Joseph Epstein	U.S. Army Chemical Research and Development Engineering Center, (CRDEC), <i>Retired</i>
Professor Fred Menger	Emory University
Professor Robert Moss	Rutgers, The State University of New Jersey
Mr. Edward Coale	Office of the Program Manager for Chemical Demilitarization, U.S. Army
Mr. Stephen DePeW	Office of the Program Manager for Chemical Demilitarization, U.S. Army
<u>Medium Temperature</u>	
Dr. William Copa	Zimpro Passavant Environmental Systems, Inc.
Dr. Terry Galloway	Synthetica Technologies, Inc.
Dr. Dave Hazelbeck	General Atomics
Mr. Don Hedden	UOP
Dr. Glenn Hong	MODAR, Inc.
Mr. Michael Modell*	Modell Development Corporation
Mr. Michael Spritzer	General Atomics
Dr. Jefferson Tester	Massachusetts Institute of Technology
<u>High Temperature</u>	
Dr. Edgar Berkey	National Environmental Technology Applications Corporation, University of Pittsburgh
Mr. James Hendricks	Burns and Roe
Dr. Francis W. Holm	Chemical Waste Management, Inc.
Dr. Dale L. Keairns	Westinghouse Electric Corporation

Mr. Howard Miller	Chemloop, L.P.
Dr. Christopher J. Nagel	Molten Metal Technology
Mr. Max Schlienger, P.E.	RETECH, Inc.
Mr. Lawnie H. Taylor	Department of Energy
Dr. Charles H. Titus	Electro-Pyrolysis, Inc.
<i>Foreign</i>	
Dr. Richard S. Magee	New Jersey Institute of Technology
Mr. Ron G. Manley	Chemical and Biological Defence Establishment, United Kingdom
Dr. John McAndless	Defense Research Establishment, Canada

OBSERVERS

Mr. Robert Bell	Senator Sam Nunn's office, Senate Armed Services Committee
Dr. Mark A. Brown	Office of Technology Assessment
Dr. Eileen Choffnes	Senate Government Affairs Committee
Dr. Shyam V. Dighe	Westinghouse Electric Corporation
Dr. Dupont Durst	U.S. Army Chemical Research, Development and Engineering Center
Mr. Jeffrey Gaines	U.S. Environmental Protection Agency
Dr. Victor Gatto	Molten Metal Technologies
Ms. Sebia Hawkins	Greenpeace
Mr. Tom Hess	Office of the Assistant Secretary of the Army
Mr. Bob Hukill	Legal Representative
Dr. Paul Johnston	Greenpeace/Exeter University, United Kingdom
Mr. Mark Kagan	Committee for National Security
Ms. Linda Koplovitz	Concerned Citizens for Maryland's Environment, Inc.
Dr. Raymond A. MacKay	Clarkson University
Dr. Stephen M. Matthews	Lawrence Livermore National Laboratory
Mr. Doug Medville	The MITRE Corporation
Dr. David Morrison	The MITRE Corporation
Dr. Walter Mulbry	U.S. Department of Agriculture Pesticide Degradation Lab

Mr. Phillip W. Murphy	Arkansas's Department of Pollution Control and Ecology
Mr. John Nunn	Legal Representative
Dr. Robert C. Oliver	Institute for Defense Analyses
Dr. Jisook Park	Synthetica Technologies, Inc.
Mr. Howard Podell	Chemloop, L.P.
Dr. Michael A. Rigdon	Institute for Defense Analyses
Dr. David Ross	SRI International
Mr. Robert Sabia	Bums & Roe
Mr. Ross Sheldon	Synthetica Technologies, Inc.
Ms. Donna Smatlack	Massachusetts Institute of Technology
Mr. Larry Sotsky	U.S. Army Armament Research, Development and Engineering Center
Dr. Joseph Soukup	Science Applications International Corporation
Dr. Jeremy L. Sprung	Sandia National Laboratories
Dr. Gregory Steele	Indiana Department of Health
Mr. Jeff Surma	Battelle Pacific Northwest Laboratories
Dr. Robert Swank, Jr.	U.S. Environmental Protection Agency
Mr. Ross Vincent	RVC Associates
Mr. Craig E. Williams	Kentucky Environmental Foundation
Mr. George Wilson	Office of Congressman Jim Jontz
Dr. J. Kenneth Wittle	Electro-Pyrolysis, Inc.
Dr. Yu-Chu Yang	U.S. Army Chemical Research and Development Engineering Center

**INVITED OBSERVERS WHO WERE UNABLE TO ATTEND**

Mr. Alvin Bowles	Maryland's Hazardous and Solid Waste Management Administration
Mr. Jeffrey Denit	U.S. Environmental Protection Agency
Mr. Dennis R. Downs	Utah's Bureau of Solid and Hazardous Waste
Ambassador Charles Flowerree	Committee for National Security
Mr. Jerome Hauer	Indiana Emergency Management Agency
Mr. Phillip L. Hicks	Alabama Emergency Management Agency

Dr. Vernon N. Houk, M.D.  
Ms. Valerie Hudson  
Mr. Tom Inch  
Dr. Sheridan Johnston  
Mr. Dennis Kwiatkowski  
Ms. Myra Thompson Lee  
Mr. Paul Lurk  
Ms. Jamie E. Miranda  
Mr. Alfred Picardi  
Dr. Helmut W. Schulz  
Ms. Joan Sowinski  
Dr. I. J. Wilk  
Mr. James Lee Witt  
House of Representatives  
The Honorable Glen Browder  
The Honorable Larry J. Hopkins  
The Honorable John T. Myers  
The Honorable Beryl F. Anthony  
The Honorable Ben Campbell  
The Honorable James V. Hansen  
The Honorable Bob Smith  
The Honorable Jim Jontz  
The Honorable Les Aspin  
The Honorable Bill Dickinson  
The Honorable John Murtha  
The Honorable Wayne Gilchrest  
United States Senate  
The Honorable John Glenn  
The Honorable Paul S. Sarbanes  
The Honorable Barbara Mikulski

National Center for Environmental Health and Injury Control  
Kentucky's Department of Environmental Protection  
BP America  
Sandia National Laboratories  
Federal Emergency Management Agency  
Oregon Emergency Management  
U.S. Department of Energy  
Texaco, Inc.  
Consultant  
Dynecology, Inc.  
Colorado Department of Health  
Brine Cell, Inc.  
Arkansas Office of Emergency Services  
Demilitarization Site  
Anniston Army Depot, Alabama  
Lexington Blue Grass Army Depot, Kentucky  
Newport Army Ammunition Plant (AAP), Indiana  
Pine Bluff Arsenal, Arkansas  
Pueblo Depo Activity, Colorado  
Tooele Army Depot, Utah  
Umatilla Depot Activity, Oregon  
Newport AAP, Indiana  
Chairman, House Armed Services Committee  
Anniston Army Depot, Alabama  
Defense Appropriates Committee  
Aberdeen Proving Ground, Maryland  
Demilitarization Site  
Member, Senate Armed Services Committee  
Aberdeen Proving Ground, Maryland  
Aberdeen Proving Ground, Maryland

The Honorable Howell T. Heflin	Anniston Army Depot, Alabama
The Honorable Richard C. Shelby	Anniston Army Depot, Alabama
The Honorable Wendell H. Ford	Lexington Blue Grass Army Depot, Kentucky
The Honorable Mitch McConnell	Lexington Blue Grass Army Depot, Kentucky
The Honorable Richard G. Lugar	Newport AAP, Indiana
The Honorable Dan Coats	Newport AAP, Indiana
The Honorable Dale Bumpers	Pine Bluff Arsenal, Arkansas
The Honorable David Pryor	Pine Bluf Arsenal, Arkansas
The Honorable Hank Brown	Pueblo Depot Activity, Colorado
The Honorable Timothy E. Wirth	Pueblo Depot Activity, Colorado
The Honorable Jake Gain	Tooele Army Depot, Utah
The Honorable Orrin G. Hatch	Tooele Army Depot, Utah
The Honorable Mark P. Hatfield	Umatilla Depot Activity, Oregon
The Honorable Bob Packwood	Umatilla Depot Activity, Oregon
The Honorable Sam Nunn	Senate Armed Services Committee
The Honorable Daniel Inouye	Chairman, Defense Appropriations Committee

- 3. Committee Meeting, September 3-4, 1992, Washington, D.C.
- 4. Committee Meeting, October 22-23, 1992, Washington, D.C.
- 5. Committee Meeting, November 19-20, 1992, Washington, D.C.
- 6. Committee Meeting, April 21-23, 1993, Washington, D.C.

\* unable to attend

G

Technology Status Worksheet

*This technology worksheet was used as a guide by committee members in collecting information. It was also given as an information collection guide to the technology developers.*

For use as a supplement to the written presentation handout.

Use extra sheets as necessary and refer to the topic number/letter.

**Process:**

**Reviewer:**

TOPIC	COMMENTS
<b>1. Technology Description</b>	
a. Narrative/Conceptual Flow Sheet	
b. Proposed advantages	
<b>2. Data Base Status</b>	
a. Chemistry/Physics fundamentals	
b. Stoichiometry/kinetics	
<b>3. Special Considerations</b>	
a. Hazardous/unusual reagents	
b. High temperature/pressure	
c. Corrosion/materials of construction	
d. Fouling/plugging	
e. Changing reactivity or selectivity	
f. Related equipment technology status	

TOPIC	COMMENTS	
g. Process stability/temperature excursions/explosion possibility		
h. Extent to which process can be expected to achieve acceptable level of destruction -- will additional or further treatment by other methods be required		
<b>4. By-products and Waste Streams</b>		
a. Types/composition/quantities (gaseous, liquid, solid)		
b. Normal/Upset conditions		
c. Pollution control systems requirements Types/dynamics required/availability/performance		
<b>5. Availability of Analytical Techniques for Monitoring</b>		
a. Process monitoring		
b. Environmental monitoring of processing area		
<b>6. Current Development Status</b>		
Concept/laboratory/pilot plant/demonstration/commercial		
<b>7. Extrapolation to an ability for destruction of chemical agents</b>		
a. Technical basis		
b. Probable limits (3X, 5X)*		
c. Development required to demonstrate this extrapolation		
<b>8. Areas of proposed applicability (check appropriate areas)</b>		
Feed Stream	3X	5X
-- Bulk liquid		
-- Metal parts decontamination		
-- Energetics		
-- Dunnage		
-- Wastes from other "front end" processes		
-- Hazardous chemicals other than the chemical agents (e.g. PCBs)		

TOPIC	COMMENTS
<b>9. Further tasks and time required to develop/ demonstrate prior to pilot plant level (The additional time to production level will be estimated).</b>	
<b>10. Costs to the extent known, with emphasis on special costs such as reagents, materials of construction and waste disposal.</b>	

\*3X: Decontamination to the extent that material can be transported as toxic waste but still must be under government control.  
5X: Complete decontamination and can be released from government control.



## H

### Excerpt from the U.S. Army's 5X Decontamination Review

*The following is the text from a memorandum on 5X decontamination for the Chief of the Engineering and Technology Division, U.S. Army, from Barbara A. Kuryk; Chief of the Process Development Branch. Graphical and tabular attachments to that memorandum are not included.*

1. A review of documentation concerning 5X decontamination has been completed per your request. A list of the references that were reviewed is provided at enclosure 1. The information reviewed includes literature searches, test reports, general background documentation, and correspondence. This review focused on three aspects of 5X decontamination: related background information, 5X criteria evaluation, and 5X testing.
2. An understanding of the definition of 5X decontamination and the knowledge of the standard Army criteria for 5X decontamination was necessary to review the documentation. Decontamination to the 5X level indicates the equipment or facilities have been completely decontaminated, are free of agent and may be released for general use or to the public (reference 18). The current standard Army criteria to meet the 5X requirement is to maintain the temperature of the article at 1000°F for 15 minutes ensuring agent destruction (reference 27).
3. Related Background Information. The background topics reviewed are related to 5X decontamination and either support the 5X criteria or are the basis for other studies. The topics of primary interest are laboratory scale incineration studies and hot air decontamination studies.
  - a. Incineration Studies. The incineration studies that were found dealt with the incineration of the nerve agents GB and VX. This information was reviewed to find background substantiation for the 1000°F and 15 minute criteria.

- (1) References 4, 6, and 7 are studies done at Aberdeen Proving Grounds in the early 1970's. The purpose of the three studies was to prove the agents GB and VX could successfully be destroyed by incineration. In all three cases operating temperatures exceeded the 1000°F standard by a minimum of 300°F. The reactor residence time, however, was of the order of one second or less. At these operating conditions the agent destruction was better than 99.9% consistently.
- (2) The aforementioned studies referred to previous work done by Baier and Weller (reference 28) and work done by Reeves and Kurtz (reference 29) on the thermal destruction of the chemical agent GB. The range of operating conditions for this work were 750°F to 1200°F and residence times of 0.13 sec to 2.7 sec. Two approaches to the thermal destruction of GB were investigated; thermal decomposition in a nitrogen atmosphere and catalytic oxidation. The results are presented in Table 1 [Table 1 of the original memorandum is not included here.]. Baier and Weller determined from their data that the decomposition of GB follows first order kinetics. Based on their work, calculations predict a detoxification of 99.99% in 0.1 sec at 1000°F.
- b. Hot Air Decontamination Studies. The topic of hot air decontamination could not be fully reviewed given time and resource constraints. The information presented in reference 22 indicates the relationship between surface temperature and agent removal has been investigated. Agent removal of 99% or better has been achieved with surface temperatures of 500°F for 90 seconds. Further investigation of the hot air decontamination studies is required to determine to what extent they support the 5X criteria.
4. 5X Criteria Evaluation. A limited number of studies that test the Army's standard for 5X decontamination has been done. The studies completed to date conclusively support the 5X criteria. The most comprehensive work was done by Southern Research Institute (SoRI) (a subcontractor to General Atomics) in support of the cryofracture/incineration development program. Prior to the SoRI study, testing was conducted on the thermal detoxification of M55 Rockets. Brief synopses of these studies follow.
  - a. M55 Rocket Tests. The objective of this study was to verify that samples of the M55 rocket immersed in agents GB and VX can be detoxified at 1000°F and to determine the required residence time.
- (1) Test Procedure. Representative sections of the aluminum warhead and the fiberglass reinforced plastic (FRP) launch robe were immersed in either GB or VX and heated to 1000°F. The GB samples were

maintained at 1000°F for periods of 1, 3, 5 and 15 minutes. The VX samples were maintained at 1000°F for periods of 2 and 15 minutes. After the constant temperature period the samples were isolated and a set of two bubblers were used for agent detection. The minimum detectable levels for GB and VX using this method are  $0.625 \times 10^{-4} \text{ mg/m}^3$  and  $0.125 \times 10^{-4} \text{ mg/m}^3$ , respectively. The results for each agent type will be discussed individually.

- (2) VX Results. No VX was detected for samples with residence times of either 2 or 15 minutes. These results indicate the 5X criteria is adequate for VX.
  - (3) GB Results. Residence time of 5 minutes or less were determined to be inadequate for the detoxification of GB. In each case one bubbler detected GB at concentrations several times above the detectable level, while the second bubbler was below the detectable level. No agent was detected after a residence time of 15 minutes. The results indicate a 15 minute residence time is adequate for the detoxification of GB. The minimum time of 5X decontamination of GB contaminated items cannot be determined from the M55 rocket study since no times between 5 and 15 minutes were tested.
- b. SoRI Work. The study conducted by SoRI includes a literature review and laboratory scale studies. General Atomics also wrote a 5X Thermal Task Report evaluating the literature review and the laboratory studies performed by SoRI.
- (1) Literature Review. The literature reviewed by SoRI were studies of the thermal decomposition of chemical agents GB, VX, and HD. The topics reviewed include the mechanism for decomposition, the kinetics of decomposition, and the decomposition products. The most important information presented in the review are the actual test results and the time versus temperature predictions based on analysis of the data. The findings concerning each chemical agent will be discussed individually.
  - (a) The chemical agent GB has been more extensively studied than the other chemical warfare agents. A study as early as 1954 by Reeves and Kurtz resulted in the 100% decomposition of GB at 560°C (1040°F) in 1.08 seconds. Predictions based on the kinetic work performed by Baier and Weller indicate complete decomposition of GB can be accomplished at 395°C (743°F) in 1.3 seconds. The data presented and the predictions from the kinetic analysis all support the 5X criteria.

- (b) A limited number of studies has been devoted to the thermal decomposition of the chemical agent VX. The studies reviewed by SoRI are inconclusive. Inadequate residence times (on the order of milliseconds) resulted in incomplete decomposition. At no temperature was the percent of VX decomposition greater than 71.8%. No predictions based on kinetic analysis were presented. The data presented is insufficient to make a supportive case for the 5X criteria.
- (c) Several studies have been performed on the thermal decomposition of HD. The main emphasis of a large portion of the work was determining the decomposition products of HD; however, some work was done on the time versus temperature relationship for decomposition. All the actual data presented are at temperatures of 400°C (752°F) or lower and residence times less than 0.5 seconds. At 400°C and 0.41 seconds 98.5 to 98.8% of the HD is decomposed. Based on the data collected, the decomposition of HD would be complete after 2.2 seconds at 400°C. The data presented substantiates the 5X criteria.
- (2) Laboratory Studies. The SoRI laboratory studies involved the pyrolysis of the chemical agents GB, HD, and VX. The tests were developed to simulate worst case conditions of agent being trapped in a confined space such as a crack or crevice. A quantity of agent was confined in a closed reaction vessel and the reaction vessel placed in a furnace. The operating temperature ranged from 330°C (626°F) to 660°C (1220°F), and the residence time varied from 0 to 60 minutes. The reaction vessel was submerged in liquid nitrogen to stop any further decomposition and the quantity of residual agent was determined. The results for each agent will be discussed individually.
- (a) GB Results. A definition of residence time is necessary to discuss the GB test results as well as the other agent tests. The residence time, for this study, is the time the reaction vessel spends in the furnace. There has been no adjustment for a heat up period of the reaction vessel, although the cool down period is not included in the residence time. The data for the GB tests are presented in Table 2 [Table 2 of the original memorandum not included here.]. The vessel temperature was never maintained at exactly 583°C (1000°F). At a furnace temperature of 549°C (1020°F) and a vessel maximum temperature of 498°C (928°F) a 99.998% destruction of GB was attained in 10 minutes. A plot of the data at furnace temperatures of 549°C and 457°C is provided in Figure 1 [Figure 1 of the original memorandum not included here.]. An extrapolation of the time versus GB found curves indicates complete GB destruction after 15 minutes at either temperature. The data, although not collected at 1000°F, indicate the 5X criteria is valid for GB.

- (b) VX Results. The data for VX tests are presented in Table 3 [Table 3 of the original memorandum not included here.]. At furnace temperatures of 554°C (1029°F) and 618°C (1144°F) the maximum vessel temperatures approach the 1000°F criterion. The two points of most interest are a maximum vessel temperature of 514°C (957°F) and of 527°C (981°F). The residence times for these temperatures are 7 and 5 minutes respectively, and the percent destruction are 99.9988 and 99.9942, respectively. Plots of the time versus VX found at various temperatures are presented in Figure 2 [Figure 2 of the original memorandum not included here.]. Extrapolation of the course of the curves at furnace temperatures of 460°C (860°F), 554°C (1029°F), and 618°C (1144°F) to a time of 15 minutes indicates essentially complete destruction of VX. These results indicate the 5X criteria is valid for the agent VX.
  - (c) HD Results. The data for the HD tests are presented in Table 4 [Table 4 of the original memorandum not included here.]. The results of the HD tests are far less conclusive than the results for the VX and GB. The sampling techniques were inadequate to measure quantities of HD below 80 micrograms, only confirming agent destruction to 99.6% of the HD samples. This level of destruction was achieved at residence times as short as 6 minutes and maximum vessel temperatures as low as 320°C (608°F). Although the data does not conclusively Confirm the 5X criteria for HI), the data does strongly support the criteria.
4. 5X Testing.
- a. A 5X testing program is currently on going at the Chemical Agent Munitions Disposal System (CAMDS). The effort is directed towards proving out the capability of the Metal Parts Furnace (MPF) to accomplish 5X decontamination. Simulant tests have been run and the indication is that the 5X criteria can be met by the MPF. A shielding system has been developed to more uniformly heat ton containers and thereby relieve a problem overloading the system due to rapid vaporization of the simulant. Additional simulant test will be run in late April or early May 1989 prior to any agent testing.
  - b. The Johnston Atoll Chemical Agent Destruction System (JACADS) furnaces will be subjected to 5X decontamination validation during systemization. These tests will be conducted in FY1989-1990.

5. Conclusions.

- a. Background information in the areas of agent incineration, agent thermal decomposition, and hot air decontamination provide an experimental and theoretical basis for the 5X decontamination criteria.
  - b. A limited amount of testing has been performed specifically directed at proving the current 5X criteria are valid. The testing which has been done strongly supports the 5X criteria.
  - c. The current CAMDS MPF test programs have, to date, demonstrated the capability to maintain the temperature and time criteria of 5X decontamination. Further CAMDS and JACADS testing will provide increased confidence in the criteria.
6. The point of contact for the action is Mr. Donald Macfarlane, extension 2514/2361.
7. encls  
BARBARA A. KURYK Chief, Process Development  
Branch

**ENCLOSURE 1: REFERENCE LIST**

1. Literature Review of Thermal Decomposition Studies of the Agents GB, VX and HD. Special Report to GA Technologies, Inc. Gary D. Sides, Ralph B. Spafford, 28 September 1984.
2. 5X Thermal Task Report, GA Report No. 908182, 3 September 1986.
3. Analysis of Decontaminating Packing Containers for the Kits Demilitarization Project, 7 December 1981.
4. Incineration of VX and Containment of Gaseous Products, H.F. Hildebrandt, T.R. Gervasoni, J.A. Baker, CPT, CmlC, March 1972.
5. Detailed Test Report-GB Challenge Testing of the CAMDS Deactivation Furnace System, David L. Daughdrill, August 1977.
6. Incineration of GB and Containment of Gaseous Products, October 1970, D.L. Pugh, J.A. Baker, 1LT, CmlC, T.R. Gervasoni, H.F. Hildebrandt.
7. Pilot-Scale Incineration of GB and VX and the Containment of Gaseous Products, Dennis J. Wynne, May 1973.
8. Test Report for Deactivation Furnace System Agent Challenge Test, Test No. 04-25, N.R. Jarret, 3 June 1981.
9. Correspondence from Frank Rinker of Maumee Research and Engineering, Incorporated to A1 Moore of CAMDS, Subject: CAMDS Metal Parts Furnace (MPF) 5X Testing-Vapor Combustion Furnace Flue Arrangement, 10 May 1988.
10. Correspondence from Frank Rinker of Maumee Research and Engineering, Inc to A1 Moore of CAMDS, subj: CAMDS MPF Safety Trip Report/Meeting, 3/14/88 minutes 22 March 1988.
11. Test Plan for 5X Testing with Projectiles and Bulk Containers. Test Plan No. 05-53, Ron Payeur and Kerm Jackson, 21 March 1988.
12. Test Report for 5X Testing with Projectiles and Bulk Containers. Test Report No. 05-53, Kerm Jackson and Frank Rinker, 1 August 1988.

13. Test Report for BB#4 Deactivation Furnace Scrubber (DFS) Thermal Detoxification of M55 Rockets, Test No. CAMDS 03-5, 14 April 1975.
14. Test Plan for 5X Decontamination Study, GA document 907582, 14 August 1984.
15. Pyrolysis of Isopropyl Methylphosphonofluoridate (GB), GA Document No. 909007.
16. Pyrolysis of BIS (Z-Chloroethyl) Sulfide (HD), GA Document No. 908193.
17. Pyrolysis of O-Ethyl S-(2-Diisopropyl-aminoethyl Methylphosphonothiolate) (VX). GA Document 909008.
18. TB 700-4, Decontamination of Facilities and Equipment, Army Technical Bulletin, October 1978.
19. GB Incineration Tests at CAMDS, Prepared by R.M. Parsons, January 1984.
20. VX Incineration Tests at CAMDS, Prepared by R.M. Parsons, August 1984.
21. Safety Design Requirements for JACADS, Prepared by R.M. Parsons, 17 January 1983.
22. Presentation Outline, Surface Temperature: The Critical Parameter in Decontamination by Forced Hot Air and other Surface-Heating Methods, Hugh Carlon, 22 April 1988.
23. Chemical Stockpile Disposal Program, Chemical Agent and Munitions Disposal, Summary of the U.S. Army's Experience, 21 September 1987.
24. RCRA Permit
25. MFR, subj: Technical Paper Defining Operating Conditions for the Incineration of the Chemical Agents GB, H, and VX, 7 May 1984.
26. Analysis and Testing of the CAMDS and JACADS Metal Parts Furnace for the Demilitarization of Chemical Warfare Munitions, Dr. Deane A. Horne, Mr. Franklin G. Rinker, Maumee Research and Engineering, Inc., Dr. Ronald L. Fournier, University of Toledo, and Mr. Kerm Jackson, CAMDS.



27. AMC-R 385-131.

28. Catalytic and Thermal Decomposition of Isopropyl Methyl Fluoromethylphosphonate. Industrial and Engineering Chemistry, Process Design and Development, Vol 6, No. 3, Baier, R.W. and Weller, S.W., July 1967.

29. Thermal Decomposition of GB, CRLR393, Reeves, A.M. and Kurtz, M.C., August 1954.

I

IONIZING RADIATION

TECHNOLOGY DESCRIPTION

Material to be irradiated is moved remotely inside a shielded chamber (cave) in containers or pumped in a pipe past an electron beam, an irradiation device containing a specific gamma radiation source such as Co-60, or a mixed radiation source such as a spent nuclear reactor fuel element to chemically change the contents to less complex materials and gases. The irradiations start at room temperature and pressure. However, the material irradiated may be heated slightly by the absorption of radiation and pressure may increase from the production of radiolytic gases. If the absorbed dose is sufficient to destroy the agent in the containers, then the containers can be sampled and either irradiated again or disposed of conventionally.

DEVELOPMENT STATUS

Techniques such as those needed for agent destruction are not developed. Irradiation techniques for much lower dose rates than those required by the Army's Chemical Weapons Disposal Program have been developed in the food preservation industry and for the production of specialty polymers. A considerable development effort would be required to obtain 99.9999 percent destruction of agent, including the certification that the containers are safe for direct handling.

APPLICATIONS TO CHEMICAL WEAPONS DESTRUCTION

There are no reports in the technical literature indicating that full destruction of chemical agent has been achieved with ionizing radiation. Certain surrogates such as carbon tetrachloride, chloromethane, trichloroethylene, and hexachloroethane, have been irradiated with 9 MeV X-rays or 700 keV gamma rays to doses of 1,400 rads. In general, these

compounds were destroyed to better than 85 percent but not better than 99 percent. Compounds containing carbon-phosphorus bonds were harder to destroy. Furthermore, it is not known whether the products from irradiations are indeed less hazardous than the feed materials.

The major advantage of the radiation technique is that disassembly may not be required to render the contents of rockets or mines harmless. However, there is no experimental evidence indicating that such a level of destruction has been achieved.

### **BY-PRODUCTS AND WASTE STREAMS**

After irradiation, the components containing agent, propellant, or munitions will need to be analyzed to ascertain that they may be opened and the products of radiation collected for conventional destruction. Conventional destruction includes any of the oxidation techniques such as molten salt, high temperature steam, fluidized-bed oxidation, or catalytic oxidation. Note that these munitions containers may be under substantial pressure from radiolytic production of gases in the closed containers. Leakage of these gases and containment become major concerns. It is very doubtful that complete destruction of agent is achievable (i.e., 99.9999 percent). It is not dear what the radiation products will be. It is possible that two phases will be recovered, namely, a radiolytic gas and polymerized solids.

### **ADVANTAGES AND DISADVANTAGES**

The procedures for destroying agent by using penetrating nuclear radiation such as gamma rays or X-rays have the advantage that they may not need reverse assembly of weapons. There should be no thermal effects, thus reducing the possibility of explosions.

The disadvantages of irradiations of other than penetrating radiation is that disassembly will be required. Thus, mixed radiation from spent fuel elements, electron irradiation, or beta rays will require less absorbing matter between the radiation and the agent. Other disadvantages are that radiation embrittlement of containers may become a problem at very high absorbed doses, and in conjunction with radiolytic gases, containers may have to withstand high stresses in embrittled containers.

**DEVELOPMENT NEEDS**

Radiation devices that can emit high-energy ionizing radiation at high dose rates may need to be developed. This is needed to fully destroy the agents in their containers in a reasonable amount of time. Remote handling and sampling become secondary development criteria. Finally, the contents of the irradiated containers should be non hazardous and be able to be transported or otherwise destroyed on site. This final destruction would need to be experimentally verified because the composition of the products may be different from that obtained from other methods of destruction.

## J

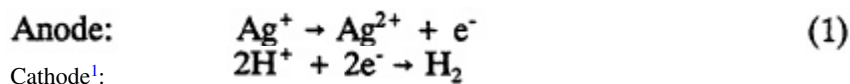
## Electrochemical Oxidation

## TECHNOLOGY DESCRIPTION

Electrochemical oxidations have been developed for many of organic chemical syntheses. The electrochemical cells used are based in general on designs that have been developed for the chlor-alkali industry or for Monsanto's acrylonitrile/adiponitrile process. Processes have been developed for carrying the oxidation to completion, with all of the carbon in the original hydrocarbon converted to  $\text{CO}_2$ . The complete oxidation process appears to be best carried out by using a combination of electrolysis and chemical reaction.

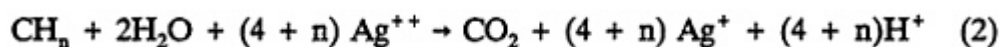
The mediated electrochemical oxidation (MEO) process was developed by AEA Technology (formerly the Atomic Energy Authority of Great Britain). An electrolysis cell is used to generate an active metal ion,  $\text{Ag}^{2+}$  in the MEO process. The metal ion is the active chemical agent; it may react directly with the organic material to be destroyed or it may first react with water to form hydroxyl radicals, which in turn oxidize the material.

The electrolytic cells used have two compartments usually with a permeable membrane between; the cathode is in one compartment, the anode in the other. Highly engineered cells have been developed that, for example, incorporate a large electrode surface area and minimize electrical resistance heating losses. The use of silver as the mediating ion requires a cation selective membrane (see Eq. 1 for the electrode reactions).



The  $\text{Ag}^{2+}$  ion is very reactive. Water can be dissociated and organic material reacted with oxygen from the water. The  $\text{Ag}^{2+}$  ion is reduced to  $\text{Ag}^+$ . A typical hydrocarbon oxidation might appear as follows:

<sup>1</sup> This is the preferred cathode reaction, but see below.



The  $\text{H}^+$  ions created in the process migrate to the cathode possibly to form  $\text{H}_2$  gas; the  $\text{Ag}^+$  ions are reoxidized at the anode to  $\text{Ag}^{2+}$ .

In principle the only products of a hydrocarbon oxidation will be  $\text{CO}_2$  and  $\text{H}_2$ . Heteroatoms in organic compounds are also oxidized: sulfur to sulfate, phosphorus to phosphate, nitrogen atoms to molecular nitrogen or N-oxides, chlorine to molecular chlorine, and fluorine to fluoride and molecular fluorine. Gaseous products ( $\text{CO}_2$ ,  $\text{N}_2$ ,  $\text{NO}$ ,  $\text{Cl}_2$ ) are withdrawn; the other materials remain in the electrolyte and must be recovered from the solution.

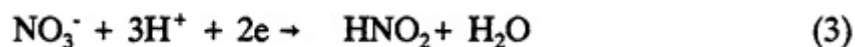
The two components of the process, electrolysis and chemical reaction, may be combined in one vessel or separated into two. That is, the organic may be added directly to the oxidizing fluid of the anode compartment. Alternatively, the oxidizing anode fluid may be pumped to a separate vessel to contact the organic material to be destroyed.

### STATUS AND DATABASE

The electrolytic cells required are well developed. The cell size required (e.g., area of anode) would be large but in the range of industrial experience.

There has been a substantial research effort on electrolytic decontamination processes, generally for small flow rates as for air purification. Various mediating ion couples have been used: cerium (II/IV), iron (II/III), or chromium (III/VI). The AEA Technology process using silver as the mediating ion has been developed to at least pilot plant scale of a few hundred pounds per day. It has been used to oxidize uranium during separations processing of plutonium from uranium. It has been tested at small scale for the destruction of solvents.

The metal ions differ in their reactivity and ability to oxidize. Silver is very reactive at moderate temperature (less than  $100^\circ\text{C}$ ). It has been used with nitric acid (10 percent by weight) as the electrolyte. The primary cathode reaction is then reduction of nitrate ion instead of  $\text{H}_2$  production:



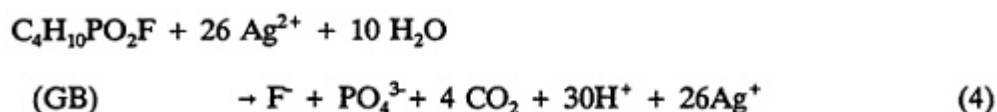
This has the advantage of reducing the voltage required (reducing power); but it has the disadvantage of an additional chemical step to reoxidize the nitrous acid or recover  $\text{NO}_x$  in the cathode gas. Other metal ions are less reactive; they require a longer time to complete the oxidation or higher temperature. An experimental process using iron, for example, is reported to operate at  $180^\circ\text{C}$ ; the vessel pressure would have to exceed 10 bars to prevent boiling.

Alternative nonaqueous electrolytes could be considered, such as propylene carbonate, or dimethyl sulfoxide (DMSO).

### APPLICATION TO CHEMICAL WEAPONS DESTRUCTION

The MEO process has not been tested with chemical agents. Related compounds have been oxidized in small scale test work: two phosphate esters, tributyl phosphate and tritolyl phosphate; and a compound related to mustard, 2-chloroethyl ethyl sulfide. High conversions were obtained.

Complete oxidation of organic compounds requires the transfer of a large number of electrons, commonly four for every carbon atom for example. The overall chemical reaction for oxidation of GB would be (in principle):



The transfer of 26 electrons per mole of GB destroyed (Eq. 4) translates into a very large electric current flow and power consumption. For the destruction of 1 ton per day of GB:

- A current flow of about 200,000 amps for a 24-hour period would be required.
- The electrode potential of the  $\text{Ag}^+/\text{Ag}^{2+}$  couple is 1.98 V; with allowance for electrical heating losses and electrode over voltages, the cell voltage would be expected in the range of 4 to 5 V. The power consumption for a 4 V cell would then be 800 kW for 24 hours.
- The usual electrode current density is limited to 200 A/square foot; thus the anode area requirement would be 1,000 square feet.

The usual industrial arrangement is to operate several cells in series. In that way the current flow can be reduced (which is preferable) while the overall voltage is increased; the power consumption stays the same.

No data are available on the rates of the chemical reactions. Very high conversion levels are required, so that the concentration of chemical agent in the reacting mixture must be very low. The size of reactor needed to meet the destruction rate required under these conditions is not known.

### ADVANTAGES AND DISADVANTAGES

The MEO process operates at a temperature of less than 100°C, and at atmospheric pressure. It is stable in operation over long time periods; perturbations of flow, temperature, or electrolyte composition do not cause adverse reactions. The reactivity of the chemical process can be controlled to a degree by control of the temperature. The process can be stopped by terminating power input to the cell.

The amount of organic material held up in the cell or the chemical reactor at any time is very small. The process is continuous and agent would be destroyed as fast as it is fed; the concentration in the exit stream would be very low, corresponding to 99.9999 percent destruction.

The process is energy intensive. The estimated electric energy requirement (800 kW for 24 hours to destroy 1 ton of GB) is several-fold larger than the heat of combustion of the agent. Part of this energy goes into the production of H<sub>2</sub> (or HNO<sub>2</sub>), but most of it must be removed as heat. This large heat flow must be removed at low temperature-less than 100°C-to prevent the electrolyte from boiling.

The electric energy is provided as a very large current flow, at low voltage. This power will require a substantial substation of transformers, rectifiers, and large busbars to carry the necessary current, which are standard electrolysis equipment.

The presence of heteroatoms, such as fluorine, sulfur, or phosphorus, complicates the operation because they remain in the electrolyte solution as fluoride, sulfate, or phosphate ions. For a steady-state operation they must be removed continuously. In the process, the metal mediating ion, (e.g., silver) also would be withdrawn and lost to the reactor. It would be separated and recovered from the other materials of the spent electrolyte. The amount of mediating ion to be recovered will depend on its concentration in the solution, which will in turn depend on important system variables the chemical reaction rate and the concentration of oxidizing ion required to achieve the organic destruction and the flow past the anode to re-oxidize the ion (i.e., Ag<sup>+</sup> going to Ag<sup>2+</sup>). This ion loss cannot be predicted but could be substantial: several hundred pounds of silver per ton of GB destroyed, for example.

The process would be applicable only to agent and not to metal parts, energetics, or dunnage.

### SPECIAL CONSIDERATIONS

Problems can develop that set operating limits on the processes:

- The anode requires a reasonably uniform concentration of the



reduced ion species; this is usually supplied by a high flow rate of electrolyte.

- The organic being decomposed may go through a polymerization resulting in insoluble materials; the membrane may be plugged as one of the undesirable consequences. The organic concentration must be kept low. Miscellaneous materials in the feed also may cause membrane fouling, e.g., alkaline earth elements or thickening compounds sometimes present in nerve agent.
- The chlorine present in mustard may precipitate silver (as silver chloride) unless concentrations are kept very low. A mediating ion other than silver may be necessary for this case. Cobalt has been suggested as a probable substitute.
- The very large destruction efficiency needed may be difficult to achieve in a completely mixed reactor. Reaction rate information is needed.
- The differing solubilities in aqueous medium of GB, VX, and HD may or may not require different reactor configurations. Although HD has low solubility, the amount in solution must in any case be kept low. Test work will be needed to determine whether HD destruction would require a two-phase reactor. (Most organic oxidations have had two-phases.)

### BY-PRODUCTS AND WASTE STREAMS

The principal gas streams produced are carbon dioxide and hydrogen. Some contamination with nitrogen oxides, chlorine, or carbon monoxide should be expected. This would be particularly true with silver as the mediating ion.

An electrolyte solution of strong acid, containing most of the heteroatoms in the feed as well as mediating metal ion, will be produced. Suitable recovery for all these materials must be provided.

### DEVELOPMENT NEEDS

The nature and size of the chemical reactor will need to be determined through development.

Electrolytic reactions are generally limited by transport and other physical properties, such as solubility. They resemble combustion reactions in this regard. Reaction rate data do not appear to be available; destruction levels of 99.9999 percent will need rate data for reactor design. The choices of mediating ion and reaction conditions such as temperature, ion concentration, and organic species concentration, will need to be developed.

A substantial research and development program should be anticipated.

K

Additional Data and Material Balances for Wet Air Oxidation, Supercritical Water Oxidation, and the Synthetica Detoxifier

WET AIR OXIDATION

An approximate material balance has been calculated with estimates for the size of equipment and the product streams.

The numbers are based on the following:

- feed: 1,000 kg of GB;
- oxygen: 25 percent excess over theoretical;
- enriched air:  $O_2/N_2 = 1/1$ ;
- NaOH added to produce a 3 M solution after reaction (this large an excess of NaOH may not be needed.);
- 20 percent of C-H in the feed is left as sodium acetate; and
- the  $CO_2$  content of the gas is an estimate and is not based on equilibrium with liquid.

Feed:

- |   |         |                        |
|---|---------|------------------------|
| • | GB:     | 1,000 kg (7.14 kg mol) |
| • | Water:  | 19,000 (1056 kg mol)   |
| • | NaOH:   | 4,770 (119.2 kg mol)   |
| • | $O_2$ : | 50.7 kg mol            |
| • | $N_2$ : | 50.7 kg mol            |

Gas phase:

- |   |          |                                    |
|---|----------|------------------------------------|
| • | $O_2$ :  | 16.0 percent by volume (dry basis) |
| • | $N_2$ :  | 81.7 percent by volume             |
| • | $CO_2$ : | 2.3 percent by volume              |
| • | CO:      | 500 ppm                            |

- Hydrocarbons: 500 ppm
  - Volume (dry basis): 62.1 kg tool  
=  $1.52 \times 10^3 \text{ m}^3$  @  $P = 1 \text{ bar}$  and  $T = 25^\circ\text{C}$
  - $\text{H}_2\text{O}$  in gas phase at reactor conditions  $\approx 62 \text{ kg mol}$
- Liquid phase:
- |                             |           |
|-----------------------------|-----------|
| $\text{H}_2\text{O}$ :      | 19,118 kg |
| $\text{NaF}$ :              | 300 kg    |
| $\text{Na}_3\text{PO}_4$ :  | 1,171 kg  |
| $\text{Na}_2\text{CO}_3$ :  | 2,271 kg  |
| $\text{CH}_3\text{COONa}$ : | 234 kg    |
| $\text{NaOH}$ :             | 1,799 kg  |
|                             | 24,893 kg |

Reactor volume (assuming feed = 1,000 kg GB/day, 0.5 V/h/V):

- $2.6 \text{ m}^3$
- (i.e., length = 7 m; diameter = 0.68 m)

The calculations demonstrate that the volumes of material to be handled and the inorganic residue are many times greater than the volume of original agent to be destroyed.

The calculations also demonstrate that it would be quite practical to operate as a closed system with material released from the process only after analysis. For example:

- basis: 1,000 kg GB/day;
- liquid holdup for 8 hours retention time = 8,300 kg (approximately  $8 \text{ m}^3$ ); and
- gas holdup for 8 hours retention, at  $25^\circ\text{C}$  and 60 bars (typical pressure):  $8.4 \text{ m}^3$  (dry basis).

Holdup volumes of both liquid and gas for 8-hour retention times are modest. The compositions shown above will change under upset conditions.

- A low inlet temperature will quench the reaction, leading to little oxygen consumption and little organic destruction.
- A high inlet temperature will yield more complete oxidation to  $\text{CO}_2$  and  $\text{H}_2\text{O}$  and possibly an undesirable temperature excursion.

Both conditions will lead to a shutdown. In the first case, the unreacted material is recycled to a feed tank.

SUPERCritical WATER OXIDATION

Supercritical water oxidation has been applied experimentally a number of materials. (See [Table K-1](#))

Process Material Balance

Estimated feed and product analyses and flow rates are shown below for destruction of 1,000 kg of GB. The case assumes a first-stage hydrolysis with NaOH followed by supercritical water oxidation of the hydrolysis product. Excess sodium hydroxide would be used in the hydrolysis reactor; this excess is then consumed in the oxidation reactor. The NaOH is limited, however, so that CO<sub>2</sub> remains in the gas phase. (This is in contrast to the wet air oxidation case shown previously, where a large excess of NaOH was used for pH control and most of the CO<sub>2</sub> ended up in solution as sodium carbonate.) Oxygen-enriched air (O<sub>2</sub>/N<sub>2</sub> = 1:1) is assumed with 25 percent excess O<sub>2</sub>. The GB is 15 percent by weight of the feed solution.

The over-all reaction assumed is

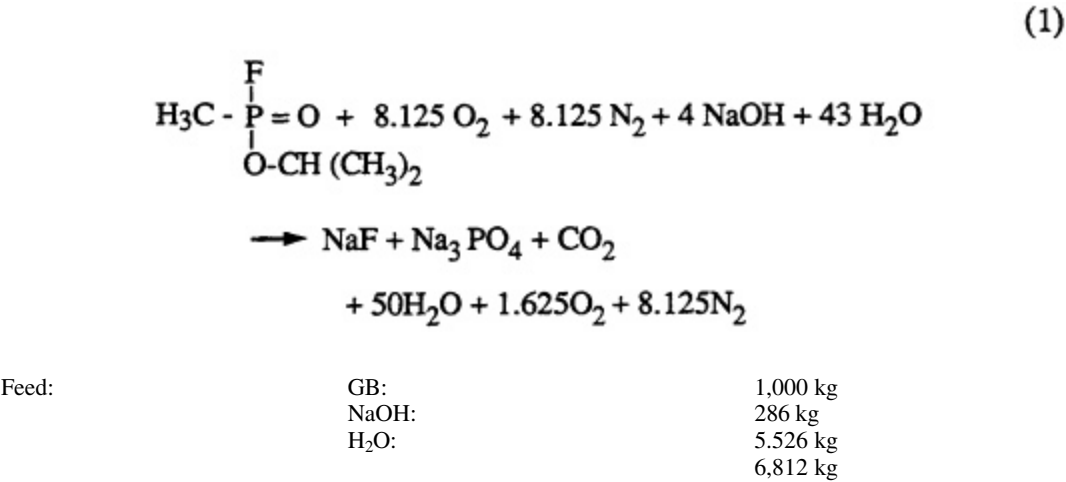


TABLE K-1 Chemicals Successfully Treated by Supercritical Water Oxidation and Typical Destruction Efficiencies<sup>a</sup>

Organic Compound	Bench Scale	Pilot Scale	Destruction Efficiency <sup>b</sup> , %
Acetic acid	x		
Acetylsalicylic acid (aspirin)	x		
Ammonia		x	>99.71
Aroclors (PCBs)	x	x	>99.995 <sup>c</sup>
Benzene	x		
Biphenyl	x		99.97
Butanol	x		
Carbon tetrachloride		x	>96.53 <sup>c</sup>
Carboxylic acids	x		
Carboxymethyl cellulose	x		
Cellulose	x		
Chlorinated dibenzo- <i>p</i> -dioxins	x		>99.9999
Chlorobenzene		x	
Chloroform		x	> 98.83 <sup>c</sup>
2-Chlorophenol		x	> 99.997 <sup>c</sup>
<i>o</i> -Chlorotoluene	x	x	>99.998 <sup>c</sup>
Cyanide		x	
Cyclohexane	x		99.97
DDT	x		99.997
Decachlorobiphenyl	x		
Dextrose	x		99.6
Dibenzofurans	x		
3, 5-Dibromo-N-cyclohexyl-N-methyltoluene- $\alpha$ , 2-diamine	x		
Dibutyl phosphate	x		
Dichloroacetic acid	x		
Dichloroanisole	x		
Dichlorobenzene	x		
4, 4'-Dichlorobiphenyl	x		99.993
1, 2-Dichloroethylene	x		99.99
Dichlorophenol	x		
Dimethyl sulfoxide		x	
Dimethylformamide		x	
4, 6-Dinitro- <i>o</i> -cresol	x		
2, 4-Dinitrotoluene	x		99.9998

Organic Compound	Bench Scale	Pilot Scale	Destruction Efficiency <sup>b</sup> , %
Dipyridamole	x		
Ethanol	x		
Ethyl acetate		x	
Ethylene chlorohydrin	x		
Ethylene glycol	x		>99,9998 <sup>c</sup>
Ethylenediamine tetraacetic acid	x		
Fluorescein	x	x	>99,9992 <sup>c</sup>
Hexachlorobenzene	x		
Hexachlorocyclohexane	x	x	>99,9993 <sup>c</sup>
Hexachlorocyclopentadiene	x		99,99
Isooctane	x		
Isopropanol	x	x	
Mercaptans	x		
Methanol	x	x	
Methyl cellosolve	x		
Methylene chloride	x	x	
Methyl ethyl ketone	x		99,993
Nitrobenzene		x	>99,998 <sup>c</sup>
2-Nitrophenol	x		
4-Nitrophenol	x		
Nitrotoluene	x		
Octachlorostyrene	x		
Octadecanoic add magnesium salt	x		
Pentachlorobenzene	x		
Pentachlorobenzonitrile	x		
Pentachloropyridine	x		
Phenol	x		
Sodium hexanoate	x		
Sodium propionate	x		
Sucrose	x		
Tetrachlorobenzene	x		

Organic Compound	Bench Scale	Pilot Scale	Destruction Efficiency <sup>b</sup> , %
Tetrachloroethylene	x	x	99.99
Tetrapropylene H	x		
Toluene	x		
Tributyl phosphate	x		
Trichlorobenzenes	x		99.99
1, 1, 1-Trichloroethane	x	x	>99.99997 <sup>c</sup>
1, 1, 2-Trichloroethane		x	>99.981 <sup>c</sup>
Trichloroethylene	x		
Trichlorophenol	x		
Trifluoroacetic acid	x		
1, 3, 7-Trimethylxanthine	x		
Urea	x		
<i>o</i> -Xylene	x		99.93

Complex Mixed Wastes/Products (Bench-Scale Tests)

Adumbran	Human waste
<i>Bacillus stearothermophilus</i> (heat-resistant spores)	Ion exchange resins (styrene-divinyl benzene)
Bran cereal	Malaria antigen
Carbohydrates	Olive oil
Casein	Paper
Cellulosics	Protein
Coal	Sewage sludge
Coal waste	Soybean plants
Corn starch	<i>Sulfolobus acidocaldarius</i>
Diesel fuel	Surfactants
<i>E. Coli</i>	Transformer oil <sup>d</sup>
Endotoxin (pyrogen)	Yeast

**Inorganic Compounds (Bench-Scale Tests)<sup>c</sup>**

Alumina	Magnesium phosphate
Ammonium chloride <sup>d</sup>	Magnesium dulfate
Ammonium sulfate	Mercuric chloride
Boric acid	Potassium bicarbonate <sup>d</sup>
Bromides	Potassium carbonate <sup>d</sup>
Calcium carbonate <sup>d</sup>	Potassium chloride <sup>d</sup>
Calcium chloride <sup>d</sup>	Potassium sulfate <sup>d</sup>
Calcium oxide <sup>d</sup>	Silica
Calcium phosphate <sup>d</sup>	Sodium carbonate <sup>d</sup>
Calcium sulfate <sup>d</sup>	Sodium chloride <sup>d</sup>
Fluorides	Sodium hydroxide <sup>d</sup>
Heavy metal oxides	Sodium nitrate
Hydrochloric acid <sup>d</sup>	Sodium nitrite
Iron	Sodium sulfate <sup>d</sup>
Iron oxide <sup>d</sup>	Sod
Lithium sulfate	Sulfur, elemental
Magnesium oxide	Titanium dioxide

<sup>a</sup> Sources: Thomason et al. (1990), Thomason and Modell (1984), Modell (1985, 1989), and unpublished data from MODAR, Inc.  
<sup>b</sup> No entry for destruction efficiency indicates that a quantitative determination was not reported.  
<sup>c</sup> Compound undetectable in effluent; quoted efficiency is based on analytical detection limit.  
<sup>d</sup> Pilot-scale tests were also performed successfully.  
<sup>e</sup> Inorganic compounds were not destroyed but the process was operated successfully with those compounds present.



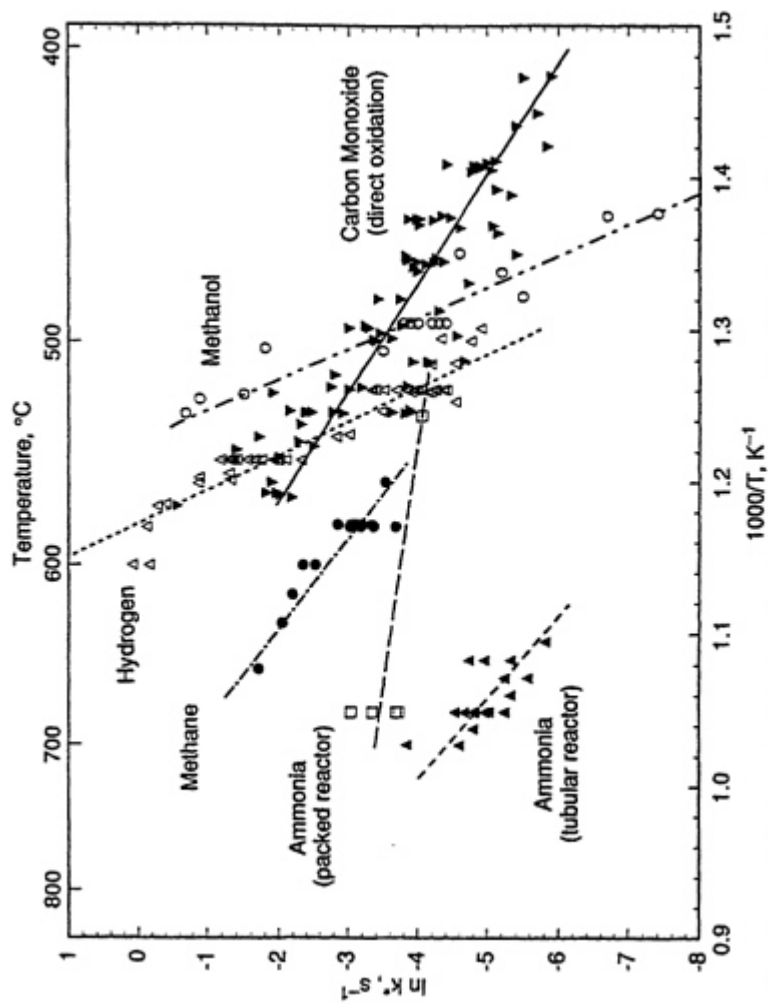


FIGURE K-1 Apparent first-order Arrhenius plot for oxidation of model compounds in supercritical water at 24.6 MPa. Source: Tester et al. (1991), Tester (1992).

Gas products:	O <sub>2</sub> :	12 percent
	N <sub>2</sub> :	59 percent
	CO <sub>2</sub> :	29 percent
	Volume = 2,400.5 m <sup>3</sup> at 25°C, 1 atm.	
Liquid product:	H <sub>2</sub> O:	81.4 percent by weight
	NaF:	3.8 percent by weight
	Na <sub>3</sub> PO <sub>4</sub> :	14.8 percent by weight
	Mass = 1,106 kg	

The product volumes are small enough to be easily retained long enough for analysis before discharge to the atmosphere.

For example, for destruction of 1,000 kg GB/day and an 8-hour retention time of products:

- gas volume (eight hours) at P = 250 bars, 25°C: 3.2 m<sup>3</sup>;
- liquid (eight hours): 368 kg (about 0.368 m<sup>3</sup>); and
- upset conditions would lead to off-specification liquids, as well as possibly to off-specification gases.

Provision for recycling would be required. A standard gas polishing unit, e.g., catalytic oxidation or carbon adsorption, would ensure gas quality before release.

SYNTHETICA DETOXIFIER

Heat and Material Balances

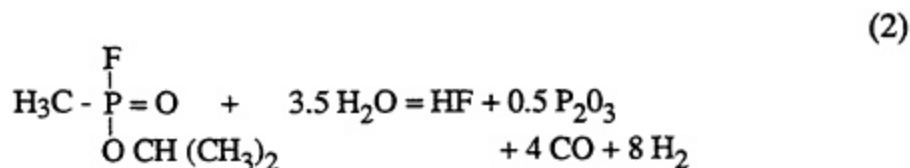
Measured or design heat and material balances have not been disclosed. Estimates have been made, based in large part on operating conditions that have been presented:

- Temperatures in the moving bed evaporator (MBE):  
1300°F (705°C) bottom  
800°F (427°C) top
- Detoxification unit: T = 2400°F (1316°C)
- Adsorption beds: T = 350°F (177°C)

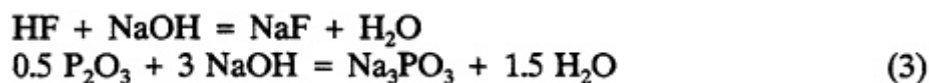
Agent GB has been chosen for the calculated balances.

The reactions desired in the Moving Bed Evaporator (MBE) are steam reforming and acid gas neutralization. The precise alkaline agent has not been specified; NaOH is shown in the equation below for illustration only.

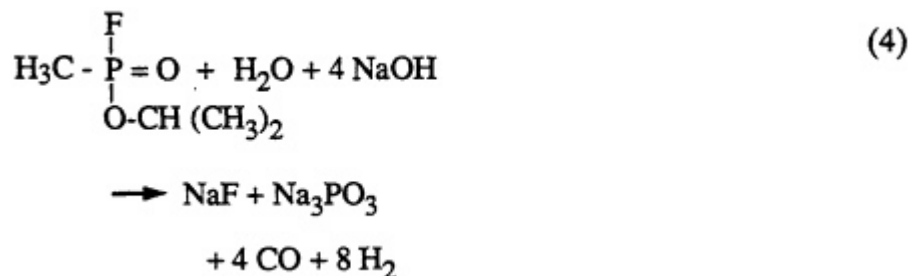
Steam reforming:



Neutralization:



The overall reaction in the MBE is then the sum of these:



The gas product shown is CO and H<sub>2</sub>. Excess H<sub>2</sub>O is required for the reaction, however, to reduce some stable hydrocarbons to very low concentrations, (e.g., methane, ethylene, benzoyl chloride). Additional steam will then lead to the water gas shift reaction to form CO<sub>2</sub>:



Equilibrium for this reaction is favorable at the temperature of the MBE (800°F outlet). The equilibrium shifts at higher temperature, however, so that little CO<sub>2</sub> should remain in the gas leaving the high-temperature detoxifier.

Estimated heat and material balances are shown below (see [Figure K-2](#)). These values are based on estimates and assumptions that may not conform to "Synthetica" operating practice, but that practice has not been fully disclosed.

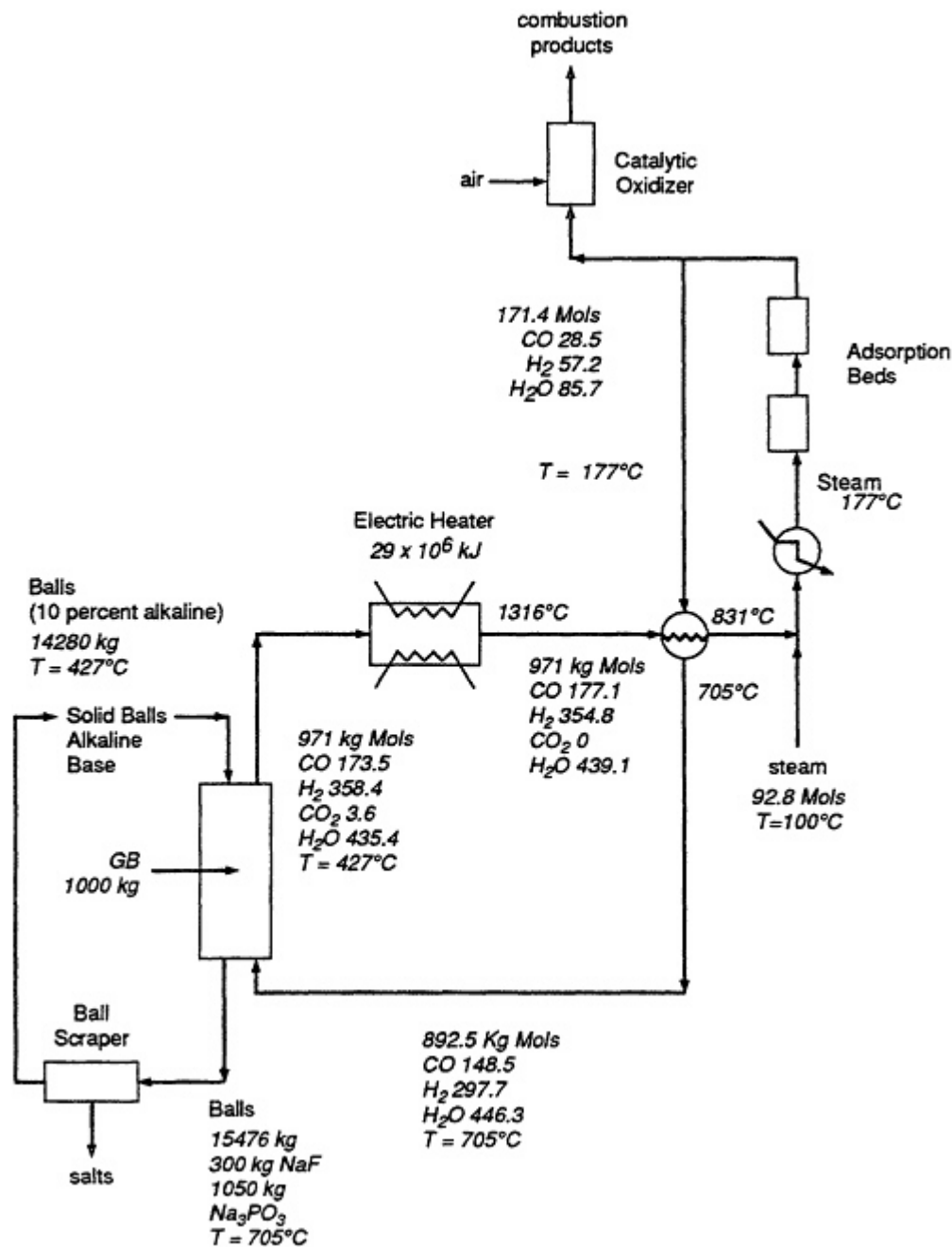


FIGURE K-2 Heat and material balances for the Synthetica System.

Basis: 1,000 kg GB destroyed.

Gas composition to the MBE (assumed):

CO:	16.7 percent
H <sub>2</sub> :	33.3 percent
H <sub>2</sub> O:	50 percent

Solid balls fed to the top of the MBE:

Alkali: 10 percent by weight of (assumed NaOH)

Alumina: 90 percent by weight

Temperature = 800°F (427°C)

The unit could be operated as an enclosed system; the gas volumes to be held up would be substantial, however, because the unit operates at atmospheric pressure.

- The product gas going to catalytic oxidation is shown as 171.4 tool, at 177°C. Assuming an 8-hour hold-up (24-hour operation) and that the holdup gas would be cooled to 40°C, the hold-up volume requirement would be 1,600 m<sup>3</sup>. This would consist primarily of CO and H<sub>2</sub>; most of the water would have been condensed.
- The solid balls from the moving bed evaporator would mount to 4,830 kg over an 8-hour period (again assuming 24-hour operation).

Electric power consumption in the detoxification reactor is large-estimated at 335 kW (24-hour operation). Some of the heat supplied is recovered in a series of heat exchangers. The heat requirement of the cold stream is much less than the heat content of the hot stream, however. Less than one-half of the hot stream enthalpy change is recovered; the rest is removed by addition of 100°C steam and by external cooling.

The MBE requires heat; the reaction is endothermic, and the solid balls are heated in their passage through the unit. Sixty percent of the heat goes for heating the solids; 40 percent supplies the endothermic heat of reaction.

The solids removed with the circulating balls consist of 1,356 kg of sodium fluoride and sodium phosphite together with a small amount of excess caustic. The sodium phosphite will require further oxidation to the phosphate for stability.

The composition of the circulating gas is the product gas (CO/H<sub>2</sub> ratio = 1/2) with 50 percent steam. The steam supply has been selected to be in 100 percent excess over the stoichiometric requirement. The product gas to the final catalytic oxidation unit has 50 percent steam as a

consequence. (If the circulating gas had been chosen to be primarily CO and H<sub>2</sub> and steam had been limited to near stoichiometric, this product gas would have contained about 10 percent steam.) The excess steam will be useful, however, in mediating the temperature in the catalytic oxidation unit. This temperature must be kept low to avoid formation of NO<sub>x</sub> and to maintain catalytic activity. The oxidation temperature would be very high without the diluent steam.

The flow rate of the circulating gas is calculated to be 50 m<sup>3</sup>/minute. A reasonable diameter for the moving bed evaporator would then be 1.9 m; the superficial gas velocity would be 0.3 m/second (i.e., 1 ft/second).

The absorption beds would be expected to be about the same diameter, i.e., 1.9 m.

No effort has been made to prepare a material and energy balance for propellant or explosive. It would be very different. Their decomposition would be highly exothermic, and the electric power requirement of the detoxification reactor would be greatly reduced. Little acid gas would be formed, and solid salt formation would be negligible.

## References and Bibliography

- Adams, H.W. 1990. Processes for Destruction of Toxic Organic Chemicals and the Resultant Inert Polymer By-Product. U.S. Patent 4,921,936 (May 1).
- Anderson, R.S., H.D. Durst, and W.G. Landis. 1988. Organofluorophosphatehydrolyzing activity in an estuarine clam Rangia cuneata. Comp. Biochem. Physiol. 91:575-578.
- Aune, J.A. 1991. Cost-Efficient Solutions To Solid Waste Treatment Through Metals Recovery Combined With Ultimate Thermal Destruction. Oslo, Norway: Elkem Technology.
- Attaway, H., J.O. Nelson, A.M. Baya, M.J. Voll, W.E. White, D.J. Grimes, and R.R. Colwell. 1987. Bacterial detoxification of diisopropyl fluorophosphate. Appl. Environ. Microbiol. 53:1685-1689.
- Barner, H.E., C.Y. Huang, T. Johnson, G. Jacobs, M.A. Martech, and W.R. Killilea. 1991. Supercritical water oxidation: an emerging technology. Presented atACHEME, June 9, 1991. J. Haz. Mat. In press.
- Baronian, C. 1992a. Information sent to Dr. John P. Longwell, Chairman (August 7). Letter. See Appendix C.
- Baronian, C. 1992b. Presentation to the National Research Council's Committee on Review and Evaluation of the Army Chemical Stockpile Disposal Program. Washington, D.C., October 9, 1992.
- Baronian, C., and P.E. Wojciechowski. 1992. Presentation to the committee at its meeting, Washington, D.C., March 9-10, 1992.

- Barrass, R.C. 1992. Information sent to Dr. Matthew Meselson, committee member (December 3). Letter.
- Bartlett, P.D., and C.G. Swain. 1949. Kinetics of hydrolysis and displacement reactions of  $\beta$ ,  $\beta'$ -dichlorodiethyl sulfide (mustard gas) and of  $\beta$ -chloro- $\beta'$ -hydroxydiethyl sulfide (mustard chlorohydrin). *J. Am. Chem. Soc.* 71:1406-1415.
- Beaudry, W.T., J.H. Buchanan, D.K. Rohrbaugh, J.B. Samuel, L.L. Szafraniec, and J.R. Ward. 1992. Analysis of Decontaminated Solutions of G Agents to Detect Reformation of Agent. Report from the Chemical Research, Development and Engineering Center (CRDEC), Aberdeen Proving Ground, Md.
- Berkey, E., and J. Hendricks. 1992. The Adams Process for conversion to a sulfur polymer. Presentation at the committee's workshop, Washington, D.C., June 3-5, 1992. See Appendix F. Information also available from Chemloop, L.P., Applied Research Center, University of Pittsburgh.
- Bronson, R. 1992. Personal communication with Mr. Gene H. Dyer, committee member. Chicago Bridge and Iron Company, Chicago.
- Broomfield, C.A., J.S. Little, D.E. Lenz, and R. Ray. 1989. Organophosphorus acid anhydride hydrolases that lack chiral specificity. Pp. 79-89 in *Enzymes Hydrolyzing Organophosphorus Compounds*, E. Reiner, W.N. Aldridge, and F.C.G. Hoskin, eds. Chichester, U.K.: Ellis Horwood Ltd.
- Buckingham, J., ed. 1982. *Dictionary of Organic Compounds*. 5th ed. Vol. 2:2381. London: Chapman and Hall.
- Caldwell, S.R., and F.M. Rauschel. 1991. Detoxification of organophosphate pesticides using a nylon based immobilized phosphotriesterase from *Pseudomonas diminuta*. *Appl. Biochem. Biotechnol.* 31:59-73.
- Chettur, G., J.J. DeFrank, B.J. Gallo, F.C.G. Soskin, S. Mainer, F.M. Robbins, K.E. Steinmann, and J.E. Walker. 1988. Soman-hydrolyzing and-detoxifying properties of an enzyme from a thermophilic bacterium. *Fundam. Appl. Toxicol.* 11:373-380.
- Coale, E., and S. DePew. 1992. Presentation at the committee's workshop, Washington, D.C., June 3-5, 1992. See Appendix F.



- Compton, J.A.F. 1987. Military Chemical and Biological Agents: Chemical and Toxicological Properties. Caldwell, N.J.: Telford.
- Conference on Disarmament. 1981. CD/173, Geneva (April 3).
- Conference on Disarmament. 1991. CD/CW/WP.367, Geneva (October 7).
- Conference on Disarmament. 1992. CD/CW/WP.374, Geneva.
- Cooper, J.F. 1992. Destruction of Chemical Warfare Agents by Oxidation Using Catalyzed Peroxydisulfate and Peroxide in a Closed System. Technical Memorandum. Lawrence Livermore National Laboratory, Livermore, Calif. (December 21).
- Copa, W.M. 1992. Personal communication. Zimpro, Inc. Rothschild, Wisc.
- Copa, W.M., and W.B. Gitchel. 1989. Wet oxidation. Pp. 8.77-8.90 in Standard Handbook of Hazardous Waste Treatment and Disposal, H.M. Freeman, ed. New York: McGraw-Hill.
- Copa, W.M., and R.W. Lehmann. 1992. Wet-air oxidation for the destruction of chemical agents. Presentation at the committee's workshop, Washington, D.C., June 3-5, 1992. See Appendix F.
- Crosby, D.G. 1990. Applications of photocatalysis to pesticide residues in the field. Paper presented to Symposium on Advanced Oxidation Processes, Toronto, June 4-5, 1990.
- Dave, K.L., C.F. Miller, and J.R. Wild. 1993. Characterization of the organophosphorus hyclolases and the genetic manipulation of the phosphotriesterase from Pseudomonas diminuta. Chem. Biol. Interact. In press.
- DeFrank, J.J. 1991. Organophosphate cholinesterase inhibitors: detoxification by microbial enzymes. In IUCCP Symposium on Bioremediation and Biotechnology. Texas A&M University, Bryant College Station, Tex.
- DeFrank, J.J., and T.C. Cheng. 1991. Purification and properties of an organophosphorus acid anhydrase from a halophilic bacterial isolate. J. Bacteriol. 173:1938-1943.
- de Jong, L.P.A., C.V. Dijk, and H.P. Benschop. 1989. Stereoselective hydrolysis of soman and other chiral organophosphates by mammalian

- phosphorylphosphatases. Pp. 65-78 in *Enzymes Hydrolysing Organophosphorus Compounds*, E. Reiner, W.N. Aldridge, and F.C.G. Hoskin, eds. Chichester, U.K.: Ellis Horwood Ltd.
- Department of Defense Authorization Act 1986, Public Law No. 99-145, Statute 99, Stat.583 (1985).
- Dumas, D.P., S.R. Caldwell, J.R. Wild, and F.M. Raushel. 1989a. Purification and properties of the phosphotriesterase from *Pseudomonas diminuta*. *J. Biol. Chem.* 33:19659-19665.
- Dumas, D.P., J.R. Wild, and F.M. Raushel. 1989b. Diisopropylfluorophosphate hydrolysis by a phosphotriesterase from *Pseudomonas diminuta*. *Biotechnol. Appl. Biochem.* 11:235-243.
- Dumas, D.P., H.D. Durst, W.G. Landis, F.M. Raushel, and J.R. Wild. 1990. Inactivation of organophosphorus nerve agents by the phosphotriesterase from *Pseudomonas diminuta*. *Arch. Biochem. Biophys.* 227:155-159.
- Durst, H.D. 1992. Comments at the committee's workshop, Washington, D.C., June 3-5, 1992.
- Durst, H.D., E.W. Sarver, H.W. Yurow, W.T. Beaudry, P.A. D'Eramo, D.M. Jackson, H. Salem, J.B. Samuel, L.L. Szafraniec, F.P. Ward, and J.R. Ward. 1988. Support for the Delisting of Cecontaminated Liquid Chemical Surety Materials as Listed Hazardous Waste from Specific Sources (State) MD02 in COMAR 10.51.02.16-1. Report CRDEC-TR-009. Aberdeen Proving Ground, Md.: U.S. Army Armament Munitions Chemical Command.
- Ember, L.R. June 29, 1992. Army's plans for destroying chemical weapons likely to be waylaid. *Chemical and Engineering News*. 19-20.
- Environmental Protection Agency (EPA). 1991. The Superfund Innovative Technology Evaluation Program: Technology Profiles, Fourth Edition (November). EPA/540/5-91/008. Cincinnati: Risk Reduction Engineering Laboratory.
- Enzminger, J.D., D. Robertson, R.C. Ahlert, and D.S. Kosson. 1987. Treatment of Leachates/Liquids from Land Disposal Sites. *J. of Haz. Mat.* 14(1):83-101.

- Epstein, J. 1992a. Briefing presented to the committee at its workshop, Washington, D.C., June 3-5, 1992. See Appendix F.
- Epstein, J. 1992b. Telephone conversations with Dr. Joseph F. Bunnett, committee member (July 11 and August 30).
- Epstein, J., V.E. Bauer, M. Saxe, and M.M. Demek. 1956. The chlorine-catalyzed hydrolysis of isopropyl methylphosphonofluoridate (Sarin) in aqueous solution. *J. Am. Chem Soc.* 78:4068-4071.
- Epstein, J., G.T. Davis, L. Eng, and M.M. Demek. 1977. Potential hazards associated with spray drying operations. *Environ. Sci. Technol.* 11:70-75.
- Evans, M. 1993. Information supplied by the Program Manager for Chemical Demilitarization. Aberdeen, Md.
- Farrauto, R. 1992. Personal communication with Dr. Henry Shaw, committee member. Engelhard, Menlo Park, Edison, N.J.
- Flamm, K.J., Q. Kwan, and W.B. McNulty. 1987. Chemical Agent and Munition Disposal; Summary of the U.S. Army's Experience. Report SAPEO-CDE-IS-87005. Available from Program Manager for Chemical Demilitarization, Aberdeen Proving Ground, Md.
- Fossey, R.D., D.A. Summers, J.G. Blaine, and L.J. Tyler. 1991. Son of wombat (lessons learned in the development of an automated explosive removal system). Pp. 479-485 (Chapter 33) in *Jet Cutting Technology: Proceedings of the 10th International Conference*. Amsterdam: Elsevier Science.
- Froelich, E.M. 1990. The perox-pure<sup>TM</sup> oxidation system: a comparative study. Presented to Symposium on Advanced Oxidation Processes, Toronto, June 4-5, 1990.
- Froment, D. 1993. Briefing of the Task Force on Scientific Aspects of the Destruction of Chemical Warfare Agents of the International Union of Pure and Applied Chemistry. Salisbury, U.K., February 23, 1993.
- Frye, G.C., S.J. Martin, R.W. Cernosek, and K.B. Pfeifer. Portable acoustic wave sensor systems for on-line monitoring of volatile organics. *Int. J. of Environmentally Conscious Manufacturing*. In press.

- Furlong, C.E., R.J. Richter, C. Chaplin, and J.W. Crabb. 1991. Purification of rabbit and human serum paraoxonase. *Biochemistry* 30:101433-10140.
- Galloway, T.R. 1992. Personal communication with Dr. Walter May, committee member.
- Galloway, T.R. 1989. Thermolytica Detoxifier Performance. Final Report, California Hazardous Waste Reduction Grant Program, Contract No. 86-T0119 A-1. California State Department of Health Services, Alternative Technology Section (August 15).
- Gan, K.N., A. Smolen, H.W. Eckerson, and B.N. LaDu. 1991. Purification of human serum paraoxonase/arylesterase: evidence for one esterase catalyzing both activities. *Drug. Metab. Disp.* 19:100-106.
- General Atomics. 1982. Research and Development Services for Mechanical Process Development/Laboratory Studies in Support of the Munition/Agent Process Development Program. Phase I Final Report. No. GA-A16891, GACP 23-216. Vol. I. Books 1-4. Technical Report. San Diego: General Atomics Company.
- Goodman, A. and A. Gilman. 1985. *The Pharmacological Basis for Therapeutics*. 7th ed. New York: McGraw-Hill.
- Gordon, M.R. September 2, 1992. Negotiators agree on accord to ban chemical weapons. *New York Times*.
- Greenhalgh, R., and M.A. Weinberger. 1967. The selective phosphorylation of ethanolamine. *Can. J. Chem.* 45:495-500.
- Harkness, D.R. 1986. Bacterial growth on aminoalkylphosphonic acids. *J. Bacteriol.* 92:623-627.
- Harvey, S.P., and J.J. DeFrank. 1992. Biodegradation of chemical warfare agents: demilitarization applications. *Proceedings of the 1992 Conference on Chemical Warfare Research*. In press.
- Hassett, C., R.J. Richter, R. Humbert, C. Chaplin, J.W. Crabb, C.J. Omiecinski, and C.E. Furlong. 1991. Characterization of cDNA encoding rabbit and human serum paraoxonase: the mature protein retains its signal sequence. *Biochemistry* 30:10141-10149.

- Hedden, D. 1992. Hydrogenation processes. Presentation at the committee's workshop, Washington, D.C., June 3-5, 1992. See Appendix F.
- Helling, R.K. 1986. Oxidation Kinetics of Simple Compounds in Supercritical Water: Carbon Monoxide, Ammonia and Ethanol. Ph.D. dissertation. Department of Chemical Engineering, Massachusetts Institute of Technology, Cambridge, Mass.
- Helling, R.K., and J.W. Tester. 1987. Oxidation of simple compounds and mixtures in supercritical water. *Energy Fuels* 1:417.
- Helling, R.K., and J.W. Tester. 1988. Oxidation of simple compounds and mixtures in supercritical water: carbon monoxide, ammonia and ethanol. *Environ. Sci. Technol.* 22:1319.
- Hickinbottom, W.J. 1957. *Reactions of Organic Compounds*. London: Longmans, Green & Co.
- Ho, M.-D. 1992. Personal letter to Mr. Gene H. Dyer, committee member, from ProxAir, Inc. (Linde), along with a set of brochures (October 20).
- Hoke, R.C., H. Shaw, and A. Skopp. 1972. A regenerative limestone process for fluidized bed coal combustion and desulfurization. Presented at the Third International Conference on Fluidized Bed Combustion, College Comer, Ohio, October 29-November 1, 1972.
- Holgate, H.R., and J.W. Tester. 1991. Fundamental kinetics and mechanisms of hydrogen oxidation in supercritical water. Presentation at the Second International Conference on Supercritical Fluids, Boston, May 20-22, 1992. Cambridge Science Technology. Submitted.
- Hoskin, F.C.G. 1990. An organophosphorus detoxifying enzyme unique to squid. Pp. 469-480 in *Squid as Experimental Animals*, D.L. Gilbert, W.J. Adelman, Jr., and J.M. Arnold, eds. New York: Plenum Press.
- Hoskin, F.C.G., and A-H. Roush. 1982. Hydrolysis of nerve gas by squid-type diisopropyl phosphorofluoridate hydrolyzing enzyme on agarose resin. *Science* 215:1255-1257.
- International Agency for Research on Cancer (IARC). 1975. IARC monographs on the evaluation of carcinogenic risk of chemicals to man. Vol. 9, Some Aziridines, N-, S- and O-Mustards and Selenium. Lyon: IARC.

- Irvine, R.L., and L.H. Ketchum. 1989. Sequencing batch reactions for biological wastewater treatment. *CRC Crit. Rev. Environ. Control* 18:255-294.
- Jody, B.J., G. Chettur, R.J. Dihu, M. Schurger, and R.H. Snow. 1983. Development of Chemical Processes for Chemical Demilitarization-Phase I. Report to U.S. Army Toxic and Hazardous Materials Agency. Chicago: IIT Research Institute.
- Kalfadelis, C.D. 1977. An environmental assessment of 638 MWe molten carbonate fuel cell power plant. Pp. 681-688 in *Proceedings of the Twelfth Intersociety Energy Conversion Engineering Conference*, G. Ciprios, H.H. Horowitz, and H. Shaw, eds. Vol. 1.
- Kaplan, D.L. 1993. Biotechnology and bioremediation for organic energetic compounds. In *Organic Energetic Compounds*, P. Marinkas, ed. Nova Science. In press.
- Kalyon, D.M. 1992. Information submitted to the committee from the Highly Filled Materials Institute, Stevens Institute of Technology, Hoboken, N.J. See Appendix E.
- Keairns, D.L., D.F. McLaughlin, and S.V. Dighe. 1992. Westinghouse Plasma System for Chemical Demilitarization. Presentation at the committee's workshop, Washington, D.C., June 3-5, 1992. See Appendix F.
- Kearney, P.C., J.S. Karns, M.T. Muldoon, and J.M. Ruth. 1986. Coumaphos disposal by combined microbial and UV-ozonation reactions. *Agric. Biol. Chem.* 34:702-706.
- Landis, W.G. 1991. Distribution and nature of the aquatic organophosphorus acid anhydases: enzymes for organophosphate detoxification. *Rev. Aquatic Sci.* 5:267-285.
- Landis, W.G., and J.J. DeFrank. 1991. Enzymatic hydrolysis of toxic organo fluorophosphate compounds. Pp. 183-201 in *Biotechnology and Biodegradation: Methods and Applications in Biodegradation*, D. Kamely, A. Chakrabarty, and G.S. Omenn, eds. The Woodlands, Tex.: Portfolio Publishing.
- Landis, W.G., D.M. Haley, M.V. Haley, D.W. Johnson, H.D. Durst, and R.E. Savage. 1987. Discovery of multiple organofluorophosphate hydrolyzing

- activities in the protozoan, *Tetrahymena thermophila*. J. Appl. Toxicol. 7:35-71.
- Lee, C.C. 1989. Plasma systems. Pp. 8.169-8.177 in Standard Handbook of Hazardous Waste Treatment and Disposal, H. M. Freeman, ed. New York: McGraw-Hill.
- Leonov, G.S. 1991. Complex for the destruction of faulty chemical munitions (KUASI). Report presented to a United Nations committee on chemical demilitarization; also presented to Dr. Joseph F. Bunnett, committee member, Moscow (December).
- Lepore, J.V., R.C. Ahlert, and D.S. Kosson. 1990a. Migration and treatment of a dense aqueous contaminant source and plume. Haztech International Conference, Houston, May, 1990.
- Lepore, J.V., L.H. Turner, and D.S. Kosson. 1990b. Process development for in-situ remediation of a highly contaminated groundwater plume. J. Haz. Mat. 25:289-307.
- Lepore, J.V., R.C. Ahlert, and D.S. Kosson. 1991. Migration and treatment of a dense aqueous contaminant source and plume. J. Env. Sci. Health, Part A, 26(1).
- Lepore, J.V., R.C. Ahlert, and D.S. Kosson. 1989. Migration and treatment of a dense aqueous contaminant source and plume. American Chemical Society 199th National Meeting, Dallas, April, 1989.
- Lester, G. 1992. Personal communication with Dr. Henry Shaw, committee member. Allied-Signal Inc., Des Plaines, Ill.
- Lewis, V.E., W.J. Donarski, J.R. Wild, and F.M. Raushel. 1988. The mechanism and stereochemical course at phosphorus of the reaction catalyzed by a bacterial phosphotriesterase. Biochemistry. 27:1591-1597.
- Liljegren, R. 1992. Personal communication with Mr. Gene H. Dyer, committee member. Brown Minneapolis Company, Minneapolis.
- Liota, R., and J. Santos. 1978. Fluidized-Bed Incinerator for Disposal of Propellants and Explosives. U.S Army Research and Development Command. Large Caliber Weapon Systems Laboratory. Technical Report ARLCD-TR-78032 (October). Dover, N.J.

- Little, J. S., C.A. Broomfield, M. K. Fox-Talbot, L. J. Boucher, B. MacIver, and D.E. Lenz. 1989. Partial characterization of an enzyme that hydrolyzes sarin, soman, tabun, and diisopropyl phosphorofluoridate (DFP). *Biochem. Pharmacol.* 38:23-29.
- Mackness, M.I., and C.H. Walker. 1981. A-esterase activity in the lipoprotein fraction of sheep serum. *Biochem. Pharmacol.* 30:903-906.
- Magee, E.M., C.E. Jahnig, and H. Shaw. 1974. Evaluation of Pollution Control in Fossil Fuel Conversion Process; Gasification; Section 1: Koppers-Totzek Process. U.S. Department of Commerce, National Technical Information Service, PB #231,675, 53 p. (Also EPA-650/2-74-009a and EXXON/GRU.3DJ.74).
- Main, A.R. 1960. The differentiation of the A-esterases in sheep serum. *Biochem. J.* 75:188-195.
- Manley, R. 1992a. Briefing presented to the committee's workshop, Washington, D.C., June 3-5, 1992. See Appendix F.
- Manley R. 1992b. Information sent to Mr. Donald L. Siebenaler, Senior Staff Officer, Board on Army Science and Technology, National Research Council (October 16). Letter.
- Martens, H. 1992. Information sent to Dr. Matthew Meselson, committee member (October 27). Letter.
- Matthews, S.M. 1992. Briefing to the committee on activities at Lawrence Livermore National Laboratory at the committee's workshop, Washington, D.C., June 3-5, 1992. See Appendix F.
- Mazur, A. 1946. An enzyme in animal tissues capable of hydrolysing the phosphorus fluorine bond of alkyl fluorophosphates. *J. Biol. Chem.* 164:271-289.
- McAndless, J. 1992a. Briefing presented at the committee's workshop, Washington, D.C., June 3-5, 1992. See Appendix F.
- McAndless, J. 1992b. Information sent to Mr. Donald L. Siebenaler, Senior Staff Officer, Board on Army Science and Technology, National Research Council (October 14).



- McDaniel, C.S., LL Harper, and J.R. Wild. 1988. Cloning and sequencing of a plasmid-borne gene (opd) encoding a phosphotriesterase . J. Bacteriol. 170:2306-2311.
- Menger, F.M., and A.R. Elrington. 1991. Organic reactivity in microemulsion systems. J. Am. Chem. Soc. 113:9621-9624.
- Menke, J.L., H.M. Carlson, M.H. Flinn; S.R. MacRae, D.M. Medville, and D.J. Triplet. 1991. Evaluation of the GB Rocket Campaign: Johnston Atoll Chemical Agent Disposal System Operational Verification Testing (June). MTR-91W00039. McLean, Va.: MITRE Corporation.
- MITRE Corporation. 1993. Preliminary Draft: Summary Evaluation of the Johnston Atoll Chemical Agent Disposal System: Operational Verification Testing. (April 13). McLean, Va.: MITRE Corporation.
- MODAR, Inc. 1992. Unpublished data. Natick, Mass.
- Modell, M. 1985. Processing Methods for the Oxidation of Organics in Supercritical Water. U.S. Patent 4,543,190 (September 24).
- Modell, M. 1989. Supercritical water oxidation. Pp. 8.153-8.168 in Standard Handbook of Hazardous Waste Treatment and Diposal, H.M. Freeman, ed. New York: McGraw-Hill.
- Moss, R.A., K.W. Alwis, and J.-S. Shin. 1984. Catalytic cleavage of active phosphate and ester substrates by iodoso-and iodoxybenzoates. J. Am. Chem. Soc. 106:2651-2655.
- Mounter, L.A., R.F. Baxter, and A. Chanutin. 1955. Dialkylfluorophosphatases of microorganisms. J. Biol. Chem. 215:699-704.
- MRK, Inc. 1992. Information submitted to the committee on the MRK Potential Closed Loop Incineration System (CLIS). See Appendix E.
- Mulbry, W.W., and J.S. Karns. 1989a. Parathion hydrolase specified by the Flavobacterium opd gene: relationship between the gene and protein. J. Bacteriol. 171:6740-6746.
- Mulbry, W.W., and J.S. Karns. 19891. Purification and characterization of three parathion hydrolases from Gram-negative bacterial strains. Appl. Environ. Microbiol. 55:289-293.

- Munnecke, D.M. 1976. Enzymatic hydrolysis of organophosphate insecticides, a possible pesticide disposal method. *Appl. Environ. Microbiol.* 32:7-13.
- Nagel, C.J. 1992. Molten metal applications via the catalytic extraction process. Presented at the committee's workshop, Washington, D.C., June 3-5, 1992. See Appendix F. Information also available from Molten Metal Technology, Cambridge, Mass.
- Namba, T. 1971. Cholinesterase inhibition by organophosphorus compounds and its clinical effects. *Bull. World Health Organ.* 44:289-307.
- National Academy of Sciences (NAS). 1969. Report of the Disposal Hazards of Certain Chemical Warfare Agents and Munitions. Ad Hoc Advisory Committee of the National Academy of Sciences. Washington, D.C.: National Academy Press.
- National Defense Authorization Act Fiscal Year 1989. Public Law No. 100-456. Statute 102, Stat. 1918 (1988).
- National Defense Authorization Act Fiscal Year 1991. H.R. 4739, Public Law No. 101-510 (1990).
- National Defense Authorization Act for Fiscal Year 1993. S. 3114. Congressional Record, Vol. 138, No. 129 (September 21, 1992).
- National Research Council (NRC). 1984. Disposal of Chemical Munitions and Agents. Committee on Demilitarizing Chemical Munitions and Agents. Washington, D.C.: National Academy Press.
- National Research Council (NRC). 1991. Demilitarization of Chemical Weapons by Cryofracture: A Technical Assessment. Washington, D.C.: National Academy Press.
- National Research Council (NRC). 1993. Review of Monitoring Activities within the Chemical Demilitarization Program. Committee on Review and Evaluation of the Army Chemical Stockpile Disposal Program. Washington, D.C.: National Academy Press.
- Office of Technology Assessment (OTA), U.S. Congress. 1992. Disposal of Chemical Weapons: An Analysis of Alternatives to Incineration. Background Paper. Washington, D.C.: U.S. Government Printing Office.

- PEIS. 1988. See U.S. Department of the Army Chemical Stockpile Disposal Program Final PEIS, 1988.
- Picardi, A., P. Johnston, and R. Stringer. 1991. Alternative Technologies for the Detoxification of Chemical Weapons: An Information Document. Prepared for Greenpeace International, Washington, D.C. (May 24).
- Reichert, C. 1975. Study of Mustard Destruction by Hydrolysis. Report DRES-TN-329. Defence Research Establishment, Suffield Ralston, Canada.
- Schlienger, M.P. 1992. Plasma Centrifugal Furnace, Retech, Inc. Presentation at the committee's workshop, Washington, D.C., June 3-5, 1992. See Appendix F.
- Schowaneck, D., and W. Verstraete. 1990a. Phosphonate utilization by bacterial cultures and enrichments from environmental samples. *Appl. Environ. Microbiol.*, 56:895-903.
- Schowaneck, D., and W. Verstraete. 1990b. Phosphonate utilization by bacteria in the presence of alternative phosphorus sources. *Biodegradation* 1:43-53.
- Schulz, H.W. 1992. Materials submitted to the committee. Dynecology, Inc., Harrison, N.Y. See Appendix E.
- Scientists Against Nuclear Arms (SANA). 1991. The Destruction of Chemical Weapons. Report. N.S.W., Australia.
- Serdar, C.M., D.C. Murdock, and M.F. Rohde. 1989. Parthion hydrolase gene from *Pseudomonas diminuta* MG: subcloning, complete nucleotide sequence, and expression of the mature portion of the enzyme in *Escherichia coli*. *Biotechnology* 7:1151-1155.
- SFIL-CMT. 1992. Information sent to Mr. Donald L. Siebenaler, Senior Staff Officer, Board on Army Science and Technology, National Research Council (October 4). Letter.
- Shaw, H., and E.M. Magee. 1974a. Evaluation of Pollution Control in Fossil Fuel Conversion Processes; Gasification; Section 1: Lurgi Dry Ash Process, EPA-650/2-74-009c, 70 p. (NTIS PB-237, 694).

- Shaw, H., and E.M. Magee. 1974b. Technology needs for pollution abatement in fossil fuel conversion processes. Pp. 309-313 in Symposium Proceedings: Environmental Aspects of Fuel Conversion Technology. St. Louis, 1974. U.S. Environmental Protection Agency, Environmental Protection Technology Series, Report EPA-650/2-74-118.
- Shaw, H., Y. Wang, T.C. Yu, and A.E. Cerkowicz. 1992. Catalytic oxidation of trichloroethylene and methylene chloride with noble metals. Pp. 358-379 in American Chemical Society (ACS) Advances in Chemistry Series No. 518: Emerging Technologies for Hazardous Waste Management III, D.W. Tedder and F.G. Pohland, eds. ACS symposium, Atlanta, October 1-3, 1991. Washington, D.C.: American Chemical Society.
- Smolen, A., H.W. Eckerson, K.N. Gan, N. Hailat, and B.N. LaDu. 1991. Characteristics of the genetically determined allozymic forms of human serum paraoxonase/arylesterase. *Drug. Metab. Disp.* 19:107-112.
- Snow, R. 1992. Personal communication with Dr. Walter G. May, committee member. Illinois Institute of Technology Research Institute, Chicago.
- Southwest Research Institute (SRI). 1992. Results of the RCRA Trial Burn with VX Feed for the Liquid Incinerator at the Johnston Atoll Chemical Agent Disposal System. Final Report prepared for the Program Manager for Chemical Demilitarization Environmental and Monitoring Division. (June 23). SRI-APC-92-384-7530. 11. 1-I-R3, Birmingham.
- Sun, Y., and J.J. Pignatello. 1993. Photochemical reactions involved in the total mineralization of 2, 4-D by  $\text{Fe}^{3+}/\text{H}_2\text{O}_2/\text{UV}$ . *Environ. Sci. Technol.* 27,2:304-310.
- Taylor, L. 1992. Molten salt technologies: destruction of chemical warfare agents, propellants, and munitions. Presentation at the committee's workshop, Washington, D.C., June 3-5, 1992. See Appendix F.
- Tester, J.W. 1992. Supercritical-water oxidation. Presentation at the committee's workshop, Washington, D.C., June 3-5, 1992. See Appendix F.
- Tester, J.W., H.R. Holgate, F.J. Armellini, P.A. Webley, W.R. Killilea, G.T. Hong, and H.E. Barrier. 1991. Supercritical water oxidation technology: a review of process development and fundamental research. Pp. 35-76 in the American Chemical Society (ACS) Symposium Series No. 518:

- Emerging Technologies for Hazardous Waste Management III, D.W. Tedder and F.G. Pohland, eds. ACS symposium, Atlanta, October 1-3, 1991. Washington, D.C.: American Chemical Society.
- Thomason, T.B., G.T. Hong, K.C. Swallow, and W.R. Killilea. 1990. The MODAR supercritical water oxidation process. Pp. 3142 in Innovative Hazardous Waste Treatment Technology Series, Vol. 1: Thermal Process, H.M. Freeman, ed. Lancaster, Pa.: Technomic.
- Thomason, T.B., and M. Modell. 1984. Supercritical water destruction of aqueous wastes. *Haz. Waste* 1:453.
- Tires, C.H. 1992. A graphite electrode DC arc furnace system for disposal of chemical munitions. Presentation at the committee's workshop, Washington, D.C., June 3-5 1992. See Appendix F.
- Toler, I.J. 1990. War gases in the Second World War. *British Army Rev.* August: 67-72.
- Upadhye, R.S., M.G. Adamson, J.F. Cooper, and A.K. Lee. 1992. An investigation of the need for the hold, test and release (HT&R) option for the Rocky Flats Fluidized Bed Unit (FBU). Lawrence Livermore National Laboratory, June.
- USATHAMA. 1982. Long Range Chemical Demilitarization Concept Study-Revised. Aberdeen Proving Ground, Md.: U.S. Army Toxic and Hazardous Materials Agency.
- USATHAMA. 1983. Final Demilitarization Plan for Operation of the Chemical Agent Munitions System (CAMDS) at Tooele Army Depot, Ut. Aberdeen Proving Ground, Md.: U.S. Army Toxic and Hazardous Materials Agency.
- U.S. Army Corps of Engineers. 1987. Chemical Stockpile Disposal Program Process Criteria Development for Tooele Army Depot Onsite Option. Proposal for Program Manager for Chemical Munitions. Contract No. DACA87-86-C0084, Huntsville, Ala.
- U.S. Department of the Army. 1974. Chemical Agent Data Sheets, Vol. 1. Technical Report, EO-SR-74001 (Edgewood Arsenal Special Report). Alexandria, Va.: Defense Technical Information Center.

- U.S. Department of the Army. 1988. Chemical Stockpile Disposal Program Final Programatic Environmental Impact Statement (PEIS). Available from Program Manager for Chemical Demilitarization, Aberdeen Proving Ground, Md.
- U.S. Departments of the Army and Air Force. 1975. Military Chemistry and Chemical Compounds. Field Manual No. 3-9, Air Force Regulation No. 355-7. (October 30) Washington, D.C.: U.S. Department of the Army Headquarters.
- U.S. Department of the Army. 1989. SAIL-PMT-E, 5X Decontamination Review (March 27). Available from the Process Development Branch. See Appendix H.
- U.S. Department of the Army. 1991. Annual Status Report on the Disposal of the Lethal Chemical Stockpile (December 15). Available from the Program Manager for Chemical Demilitarization, Aberdeen Proving Ground, Md.
- Vogel, G.A. 1989. Hazardous-waste management capacity. Pp. 2.21-2.31 in Standard Handbook of Hazardous Waste Treatment and Disposal, H.M. Freeman, ed. New York: McGraw-Hill.
- Wang, Y., H. Shaw, and R. J. Farrauto. 1992. Catalytic oxidation of trace concentrations of trichloroethylene over 1.5% platinum on  $\gamma$ -alumina. Pp. 125-140 in American Chemical Society Symposium Series No. 495: Catalytic Control of Air Pollution: Mobil and Stationary Sources, R.G. Silver, J.E. Sawyer, and J.C. Summers, eds. Fourth Chemical Congress of North America, New York, August 25-30, 1991. Washington D.C.: American Chemical Society.
- Ward, F.P. 1991. Military applications of biodegradation. Pp. 147-154 in Biotechnology and Biodegradation: Methods and Applications in Biodegradation, D. Kamely, A. Chakrabarty, and G.S. Omenn, eds. The Woodlands, Tex.: Portfolio Publishing.
- Ward, J.R., and R.P. Seiders. 1984. On the activation energy for the hydrolysis of bis(2-chloroethyl)sulfide. *Thermochim. Acta* 81:343-348.
- Ward, R. 1992. Personal telephone communication with Mr. Gene H. Dyer, committee member (November 12). U.S. Army Research, Development and Engineering Center, Edgewood, Md.

- Whitehouse, L.W., and D.J. Ecobichon. 1975. Paraoxon formation and hydrolysis by mammalian liver. *Pestic. Biochem. Physiol.* 5:314-322.
- Wojciechowski, P.E. 1992. Presentation to the committee at its meeting, Washington, D.C., March 9-10, 1992.
- Yang, Y.-C. 1992a. Personal communication to Dr. Joseph F. Bunnett, committee member (December 11).
- Yang, Y.-C. 1992b. Personal communication to Dr. Joseph F. Bunnett, committee member (October 16).
- Yang, Y.-C. 1992c. Briefing presented at a meeting of a subgroup of the committee, Aberdeen Proving Ground, Md., October 1, 1992.
- Yang, Y.-C. 1992d. Comments to the committee at its workshop, Washington, D.C., June 3-5, 1992. See Appendix F.
- Yang, Y.-C., J.A. Baker, and J.R. Ward. 1992. Decontamination of chemical warfare agents. *Chem. Rev.* 92:1729-1743.
- Yang, Y.-C., L.L. Szafraniec, W.T. Beaudry, and D.K. Rohrbaugh. 1990a. Oxidative detoxification of phosphonothiolates. *J. Am. Chem. Soc.* 112:6621-6627.
- Yang, Y.-C., L.L. Szafraniec, W.T. Beaudry, and J.R. Ward. 1990b. Nucleophile-Assisted Hydrolysis of Mustard. Report DRDEC-TR-216. Aberdeen Proving Ground, Md.: U.S. Army Armament Munitions Chemical Command.
- Yang, Y.-C., J.R. Ward, R.B. Wilson, W. Burrows, and J.S. Winterle. 1987. On the activation energy for the hydrolysis of bis(2-chloroethyl) sulfide II. *Thermochim. Acta* 114:313-317. *Chem Abst.* 107:38979.
- Yu, T.C., H. Shaw, and R.J. Farrauto. 1992. Catalytic oxidation of trichloroethylene over PdO catalyst on  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>. Pp. 141-152 in American Chemical Society Symposium Series No. 495: Catalytic Control of Air Pollution: Mobil and Stationary Sources, R.G. Silver, J.E. Sawyer, and J.C. Summers, eds. Fourth Chemical Congress of North America, New York, August 25-30, 1991. Washington, D.C.: American Chemical Society.

Zech, R., and K.D. Wigand. 1975. Organophosphate-detoxiating enzymes in E. coli. gelfiltration and isoelectirc focusing of DFPase, paraoxonase and unspecific phosphohydrolases. *Experientia* 31:157-158.

Zimmerman, F.J. 1958. New waste disposal process. *Chem. Engineering* August: 117-120.

Zimmerman, J.K., and T.M. Brown. 1986. Partial purification of rabbit serum arylesterhydrolase. *J. Agric. Food Chem.* 34:515-520.





## Index

### A

- Aberdeen Proving Ground (Maryland), 24, 27*t*, 49, 50*f*, 51*t*, 52*t*, 221*t*, 223*t*, 224*t*, 226*f*, 230*f*
- Acetylcholine, 41-42
- Acetylcholinesterase, 41 n.5, 41-42
- Acid-catalyzed hydrolysis, 114-115
- Acid chorinolysis, 111, 117
- Activated-carbon filtering
- action of, 107
  - in baseline technology, 17, 18, 28-29, 108
  - of chlorinated dioxin, 86
  - disposal of waste from, 107-108
  - role of, 13, 14, 19, 20, 106-107, 108, 194-195
  - in storage and certification, 88
  - in wet-air oxidation, 144
- Adams process
- advantages, 183
  - applications, 182-183
  - chlorinated compounds in, 182
  - development status, 180-182
  - disadvantages, 183
  - research needs, 183-184
  - technology of, 180, 181*f*
  - waste streams in, 183
- Advanced Research Projects Agency, 135, 148
- Afterburner processing
- in alternative technologies, 19, 205
  - in baseline approach, 2, 19, 24, 194, 203, 205
  - catalytic oxidation for, 13, 19, 174, 176, 192, 205
  - chlorinated dioxin synthesis in, 86
  - in high-temperature pyrolysis, 12
  - molten salt systems for, 19, 205
  - role of, 19, 21, 205, 207
  - supercritical water oxidation for, 11, 19
  - techniques, 19, 21, 199, 207
  - in thermal treatment, 97-98
- Alcohol, 113 n.1
- GB neutralization in, 113-114, 186
  - in low-temperature detoxification, 6, 113-114, 186
  - in neutralization process, 62, 186
- Alkanes, C<sub>2</sub>-C<sub>7</sub>, 148
- Alternative technologies
- afterburners in, 19, 205
  - assessment of, 2-3, 5, 34-36, 83-84, 92-94, 259-261
  - categories of, 6, 185
  - cost considerations, 5, 91-92
  - development/demonstration times, 4-5, 20, 89-90, 91*t*
  - development of, 29-30
  - energy consumption in, 92
  - hazardous byproducts from, 85-86
  - high-temperature, low-pressure oxidation, 12-13
  - high-temperature, low-pressure pyrolysis, 12
  - low-temperature, low-pressure, liquid-phase detoxification, 6-10, 16, 109-110
  - low-temperature, low-pressure, liquid-phase oxidation, 10-11, 16, 109-110
  - metal parts in, 21, 207
  - moderate-temperature, high-pressure oxidation, 11, 16
  - monitoring of, 87
  - non-viable, 35
  - in other countries, 62, 74
  - sources for, 2, 34-35
  - for Strategy 1, 15-17, 32-33, 200-201
  - for Strategy 2, 17-19, 33-34, 201-205, 202*t*
  - summary of processes, 7-9*t*, 187-189*t*
  - toxic air emissions in, 19-20, 205-206
  - use of, 3, 29
  - See also specific technology*
- Aluminum, in M55 rockets, 97
- Ambrose, James R., 31, 210

- Ammonia  
   in GB detoxification, 113  
   sodium metal ha, 122  
   in supercritical water oxidation, 148  
 Ammonium peroxydisulfate, 120  
 Anniston Army Depot, 27*t*, 50*f*, 51*t*, 52*t*  
 Army Research Office, 135, 148  
 Artillery, 42, 44*f*, 47*t*, 48*t*  
 Aryl chlorides, 114  
 Atomic Energy Commission, 171  
 Atomization, 103  
 Azoxy compounds, 114
- B**
- Baseline technology  
   activated-carbon filters in, 17, 18, 108  
   afterburners in, 2, 19, 24, 194, 203, 205  
   augmentation strategies, 17, 18  
   development of, 24-26  
   efficiency of, 26 n.4  
   elements of, 23, 24, 25*f*  
   energetics in, 203-204, 204*t*  
   gas waste in, 24, 28, 104, 194, 203-204  
   implementation schedule, 230-232*f*  
   liquid waste in, 196  
   metal parts in, 24, 98, 193, 203-204, 204*t*  
   munitions disassembly in, 77-78  
   objections to, 2, 30  
   operational verification testing of, 24-26  
   process of, 1-2, 3, 94, 203  
   storage and certification in, 88  
 Benzene, 148  
 Binary chemical weapons, 1 n.1, 22 n.1  
 Biological processes  
   applications, 10-11, 110, 126-128, 136, 190  
   batch bioreactor size, 134  
   concerns about, 127  
   diffusional limitations, 85  
   in direct destruction of agents, 128-130, 133-134  
   for energetics, 132  
   enzyme-based capabilities, 129*t*, 130  
   for GB reaction products, 131-132  
   in initial detoxification, 127  
   methane by-products, 132  
   for mustard agents, 132  
   oxygen dilution of emissions from, 135  
   processing time in, 133-134  
   for reaction products, 131-32, 134-135  
   research needs in, 21, 109-110, 132-134, 206  
   for VX reaction products, 131-132  
   waste from, 132, 134-135  
   for wet-air oxidation wastes, 144, 145  
   whole cells method, 133  
 bis(2-chloroethyl)sulfide, 38  
 Blister agents. *See* Mustard agents  
 Bombs, 42, 42 n.6, 44*f*, 45*f*, 47*t*  
   *See also* Munitions  
 Bulk material  
   biodegradation of, 131  
   chemical processes for, 111  
   high-temperature systems for, 204  
 Bursters, 48, 48 n.7, 77  
 Butyl alcohol, 119  
 By-products  
   of Adams process, 180, 183  
   of biological processes, 127, 131  
   of catalytic fluidized-bed oxidation, 170  
   chlorinated dioxins, 85-86  
   in electrochemical oxidation, 278  
   in HD-peracid interaction, 120  
   of hydrogenation processes, 178-179  
   hydrogenation processing of, 176, 178  
   of indirect heating, 97  
   of ionizing radiation procedure, 272  
   of molten metal pyrolysis, 153, 156  
   of sodium hydroxide neutralization of GB, 112-113  
   in sodium hydroxide neutralization of VX, 113-114  
   of supercritical water oxidation, 151  
   valuable, 92, 179  
   water as, 101-102  
   of wet-air oxidation, 144  
   *See also* Reaction products;  
   Waste streams/management
- C**
- Calcium carbonate, 76, 99  
 Calcium fluoride, 99  
 Calcium hydroxide, 6, 10, 99  
   HD reaction with, 119, 186  
 Calcium salts, 77  
 Canada, 62, 63*t*, 64*t*, 65*t*, 113  
 Carbon dioxide, 76, 190  
   lime in capturing, 20, 104, 106, 196, 205  
   salt waste formation and, 99, 193  
   storage systems, 88-89, 105

- Catalytic extraction, 153
- Catalytic fixed bed, 13, 192
- Catalytic fluidized-bed oxidation
- advantages, 170-171
  - application, 170
  - bed composition, 169, 170, 171
  - development status, 170
  - disadvantages, 171
  - explosives destruction in, 169-170
  - process, 169-170
  - research needs, 171
  - waste streams in, 170
  - See also High-temperature, low-pressure oxidation
- Catalytic hydrogenation. See Hydrogenation processes
- Catalytic oxidation advantages, 175-176
- as afterburner, 19, 205
  - applications, 174, 175, 176
  - development status, 175
  - disadvantages, 176
  - process, 174-175
  - research needs, 176
  - waste streams, 175
  - in wet-air oxidation, 144
  - See also Catalytic fluidized-bed oxidation; High-temperature, low-pressure oxidation
- Caustic hydrolysis, 29
- Center for Hazardous Material Research, 180
- Ceramic materials, 151
- Chemical Agent Munitions Disposal System (CAMDS) 24, 54, 56*t*, 57*t*, 59*t*, 62
- See also Tooele Army Depot
- Chemical agents
- additives in, 41, 41 n.4
  - breakdown products, 76-77
  - chemical composition of, 1 n.2, 76
  - classes of, 1 n.1, 23
  - demilitarization strategies for, 15-18, 197-200
  - distribution in munitions, 47*t*, 48*t*
  - lethal doses of, 82*t*
  - permissible air concentrations of, 82*t*, 87
  - properties of, 37-41
  - toxicity of, 41-42
  - See also Organophosphate nerve agents; *specific agents*
- Chemical detoxification
- advantages of, 110-111
  - battlefield systems, 111, 123
  - biodegradation of reaction products from, 131-132
  - decontamination standards and, 84, 118
  - diffusional limitations in, 84-85
  - experience with, 6-10
  - of metal parts, 84, 98, 118-119
  - obstacles to, 110
  - reducing agents in organic synthesis, 121-122
  - role of, 20-21, 29, 206
  - See also Hydrolysis; Low-temperature, low-pressure, liquid-phase detoxification; neutralization processes
- Chemical Stockpile Disposal Program (CSDP)
- binary chemical weapons in, 1 n.1
  - completion date, 22, 78-80, 197
  - environmental impact studies for, 26, 28
  - goals of, 1, 31-32, 196-197
  - legislative history, 22, 24-26
  - schedule for, 22, 26, 27*t*, 78-80, 197
  - strategies for complying with, 15-19, 32-34, 197-200
- Chemical stockpiles
- contents of, 1, 23, 37, 49, 52*t*
  - locations of, 1, 26, 49, 50*f*, 51*t*, 52*t*
  - munitions in, 42-49
- Chemical Weapons Convention, 3-4, 22-23, 35
- Chloride ions, corrosion from, 150, 152
- Chlorine/Chlorinated compounds, 6, 77, 85-86, 122
- in Adams process, 182
  - hydrogenation processes for, 176, 177*f*, 178
  - as oxidizing agent for VX, 117
  - salt waste from, 30
  - in supercritical water oxidation, 146, 148
- Chloromethane, 271
- m*-chloroperbenzoic acid, 120
- Circulating Bed Combustor, 169
- Clean Air Act, 145
- Closed-loop gas containment, 14, 18, 28
- See also Storage and certification
- Coal gasification, 160-163
- Commonwealth of Independent States, 22-23, 74, 116
- disposal experiences in, 62, 67*t*, 68*t*
- Concerned Citizens for Maryland's Environment, 36
- Corrosion. See Equipment corrosion
- Cost considerations, 5, 91-92
- cost per pound of agent, 92
  - full-scale production, 220-224

reverse assembly function in, 92  
 technology development, 91-92, 219-220  
 transportation, 33  
 waste shipments from Johnston Atoll, 235-236  
 Coumaphos, 130  
 Cresol, 178  
 Cryofracture process, 24 n3, 95-95, 205

**D**

DeChlor/KGME process, 114  
 Decontamination fluid, 33, 33 n.7, 78, 99, 114, 196 DS2, 114  
 Decontamination standards, 4, 82-83, 84-85  
   Level 1X, 82  
   See also Level 3X decontamination;  
   Level 5X decontamination  
 Demilitarization Protective Ensemble, 81  
 Department of Defense, 135  
 Department of Energy, 148, 171  
 Detection, 84  
   of charcoal bed contamination, 107  
   of chlorinated dioxins, 86-87  
   difficulties in, 84-85  
   false positives in, 87  
   of GB, 84  
   minimum limits of, 233-234  
   process, 87  
   research needs in, 87  
 Detoxification  
   alternative strategies for, 200-202, 201t  
   biological processes for, 126-128  
   of charcoal filter materials, 107-108  
   with deferred oxidation, 20, 32-33, 80, 197-198, 206  
   in demilitarization strategies, 15-18, 197-200  
   of energetics, 16-17, 18-19, 200  
   ionizing radiation for, 122-123  
   low-temperature, liquid-phase processes for, 6-10, 109, 186-190  
   of metal parts, 16, 32-33, 84, 197  
   peroxydisulfate salts in, 124  
   See also Chemical detoxification  
 Development times, 91t, 220, 223-224, 226-228f  
   for alternative technologies, 20, 198, 206, 226-228  
   in assessing alternative technologies, 4-5  
   for cryofracture process, 95-95  
   estimating, 5, 92 n3  
   factors in, 89-90, 217-218  
   opportunities for shortening, 90  
   sodium hydroxide hydrolysis of GB, 200

for wet air oxidation, 146  
 Diethylenetriamine, 114  
 Diisopropyl carbodiimide, 41 n.4  
 Dimethyl sulfoxide, 276  
 Dioxins. See Chlorinated dioxins  
 Dioxins, chlorinated, 85-86  
 Disposal sites, 2, 26  
 Drain-in-furnace, 29  
 DS2, 33 n.7, 114  
 Dunnage, 48-49  
   agent in crevices of, 84-85  
   alternative technologies for, 21, 203, 204t  
   in baseline approach, 24  
   in catalytic fluidized-bed oxidation, 170  
   decontamination strategies, 1, 2, 2 n.3, 16-17, 97  
   low-temperature processes for, 110  
   munitions, 78  
   in Synthetica Steam Detoxifier, 167  
   thermal treatments for, 97

**E**

Edgewood Research, Development and Engineering Center, 24  
 Electric kilns, 12, 18, 191  
 Electro-Pyrolysis, Inc. furnace, 159f  
 Electrochemical oxidation, 206  
   advantages, 277  
   applications, 21, 124, 206, 276  
   development status, 275-276  
   disadvantages, 277  
   energy use in, 277  
   GB in, 276  
   potential operating limits, 277-278  
   process, 124-125, 274-275  
   research needs, 125, 278  
   waste streams in, 278  
 Electrolytic regeneration, 10, 190  
 Elkem Multipurpose Furnace, 153, 155f  
 Elkera Technology, 153  
 Emulsification  
   in HD detoxification, 119-120, 186  
   in low-temperature, low-pressure, liquid-phase detoxification, 10  
 Energetics, 1, 48  
   in Adams process, 182  
   alternative technologies for, 21, 203, 204, 204t  
   in baseline approach, 24, 203-204, 204t

- bioremediation of, [132](#)
- in catalytic fluidized-bed oxidation, [169-170](#)
- detoxification strategies, [16-17](#), [18-19](#), [200](#)
- disposal problems with, [33](#)
- in high-temperature, low-pressure oxidation, [13](#)
- in high-temperature, low-pressure pyrolysis, [191](#)
- in low-temperature oxidation, [11](#)
- mechanical separation of, [96](#)
- in molten salt oxidation, [173](#), [174](#)
- munitions disassembly and, [77-78](#)
- in plasma arc processes, [157](#)
- reaction with potassium hydroxide, [114](#)
- reaction with sodium hydroxide, [114](#)
- in supercritical water oxidation, [11](#), [148](#), [149](#), [150](#), [152](#), [191](#)
- in Synthetica Steam Detoxifier, [166-167](#), [169](#), [291](#)
- thermal treatments for, [97](#)
- in wet air oxidation, [11](#), [141](#), [146](#), [191](#)
- Energy use
  - in Adams process, [183](#)
  - in alternative technologies, [92](#)
  - in electrochemical oxidation, [277](#)
  - in Synthetica Steam Detoxifier, [168](#), [290](#)
- Environmental Protection Agency, [81](#)
- Environmental risk
  - of air emissions, [19-20](#), [205-206](#)
  - permissible agent concentrations in air, [81](#), [82t](#), [87](#)
  - in waste storage, [4](#), [106](#)
- Enzyme-based hydrolysis, [128-130](#)
  - research needs in, [133-134](#)
- Equipment corrosion, [117](#)
  - from acid catalysts, [115](#)
  - in gasification pros, [161](#), [163](#)
  - in supercritical water oxidation, [149](#), [150-151](#), [152](#)
  - in Synthetica Steam Detoxifier, [167](#)
  - in wet air oxidation, [142-143](#)
- Ethanolamine, [6](#), [186](#)
  - in destruction of GB, [62](#), [67t](#), [115-116](#), [131](#), [186](#)
  - in destruction of mustard agents, [62](#), [67t](#), [121](#), [186](#)
  - salt wastes and, [99](#)
- Ethyl-N, N-dimethyl phosphoramidocyanidate. [See](#) GA
- Ethylene glycol, [113](#)
- Explosives. [See](#) Energetics
- F**
- Fenton's reagents, [124](#)
- Flue gas recycling, [102-103](#)
- Fluidized bed oxidation, [12-13](#), [17](#), [18](#), [21](#)
  - [See also](#) Catalytic fluidized-bed oxidation
- Fluoride/Fluorine, [30](#), [77](#), [149](#)
  - in supercritical water oxidation, [150](#), [152](#)
  - in wet air oxidation, [143](#)
- France, [74](#)
- Fuzes, [48](#), [48 n.7](#), [77](#)
- G**
- GA, [23](#), [65t](#)
  - chemical structure, [37](#), [37 n.1](#)
  - lethal doses of, [82t](#)
  - permissible air concentrations, [82t](#), [83](#)
  - storage of, [42](#)
  - toxicity of, [41](#)
- Galson process, [114](#)
- Gas storage
  - advantages of, [19-20](#), [205](#)
  - estimating requirements for, [103-104](#)
  - techniques for, [14](#), [88-89](#), [105-106](#), [195](#)
  - [See also](#) Gas wastes;
  - Storage and certification
- Gas wastes, [4](#), [11](#), [194](#)
  - activated-carbon adsorption for, [14](#), [20](#), [106-108](#), [194-195](#)
  - in Adams process, [180](#), [183](#)
  - afterburner technologies for, [19](#), [21](#), [199](#)
  - in baseline approach, [24](#), [28](#), [86](#), [104](#), [194](#), [203-204](#)
  - in biodegradation of reaction products, [134-135](#)
  - in hydrogenation processes, [178](#), [179](#)
  - in hydrolysis, [33](#)
  - in molten metal pyrolysis, [153](#), [156](#)
  - monitoring technology for, [87](#)
  - in plasma arc processes, [157](#)
  - recirculated, [14](#), [102-103](#)
  - reducing volume of, [14](#), [16](#), [20](#), [102-104](#), [192-193](#), [194](#), [195](#), [205-206](#)
  - strategies for managing, [13-14](#), [16](#), [17-18](#), [18-19](#), [88-89](#), [194](#), [205-206](#)
  - in supercritical water oxidation, [16](#), [151](#), [190](#)
  - in thermal decomposition, [97](#)
  - in wet air oxidation, [16](#), [144](#), [145t](#)
  - [See also](#) Carbon dioxide;
  - Gas storage
- Gasification processes
  - advantages, [163](#)

- applications, 161
- development status, 160
- disadvantages, 163
- research needs, 161, 163
- technology of, 160, 161*t*, 162*t*
- wastes products from, 163
- GB, 1, 20-21, 23
  - acid-catalyzed hydrolysis for, 114-115
  - biodegradation of reaction products from, 131-132
  - chemical neutralization of, 62, 65*t*, 67*t*, 70*t*, 73*t*
  - chemical structure, 37, 37 n.1, 38*f*
  - detection levels, 84, 233-234
  - direct biological destruction of, 128-130, 133-134
  - ethanolamine in destruction of, 62, 67*t*, 115-116, 131, 186
  - lethal doses of, 82*t*
  - level 5X decontamination of, 263-264, 265
  - low-temperature detoxification for, 6, 10, 109, 186
  - moderate-temperature, high-pressure oxidation for, 11
  - nitrogen compounds in, 101
  - organic synthesis agents and, 121-122
  - oxidation reaction for, 276
  - past disposal experiences, 54, 56*t*, 57*t*, 58*t*, 62
  - permissible air concentrations, 82*t*, 83
  - properties, 38, 39-40*t*
  - reaction with alkali in alcohol, 113-114
  - reaction with sodium hydroxide, 112-114, 186, 200
  - salt wastes, 99, 100*t*, 193
  - storage, 42
  - in supercritical water oxidation, 149, 281, 287
  - in Synthetica Steam Detoxifier, 167, 287-291
  - toxicity of, 41
  - wet air oxidation of, after hydrolysis, 141-142, 143, 144
- GD, chemical neutralization of, 67*t*
- General Electric KPEG process, 114
- Germany, 66*t*
- Greenpeace International, 30, 35, 36
- H**
- H, 1, 23
  - lethal doses of, 82*t*
  - low-temperature detoxification for, 109
  - organic synthesis agents and, 121-122
  - past disposal experiences, 54, 55*t*
  - permissible air concentrations, 82*t*
  - with potassium hydroxide in methanol, 113-114
  - properties, 38, 39-40*t*, 41
  - See also Mustard agents
- Hazardous materials, definition of, 37 n.2
- HD, 1, 23
  - calcium hydroxide in detoxification of, 186
  - chemical structure, 38*f*
  - converted to thiodiethanol, 119
  - emulsification, 119-120, 186
  - ethanolamine in detoxification of, 116, 121
  - lethal doses of, 82*t*
  - level 5X decontamination of, 265, 266
  - in low-temperature, liquid-phase detoxification, 6, 10, 118-121, 186
  - minimum detection limits, 233-234
  - nitrogen compounds in, 101
  - past disposal experiences, 61*t*
  - permissible air concentrations, 82*t*
  - properties, 38, 39-40*t*, 41
  - reaction with oxidizing agents, 119-120
  - reaction with peracids, 120
  - solubility, 118, 119
  - See also Mustard agents
- Heteroatoms
  - in Adams process, 183
  - in catalytic fluidized-bed oxidation, 171
  - in electrochemical oxidation, 275, 277
  - in form of stable salts, 76
  - in hydrogenation processes, 176, 179
  - in plasma arc processes, 156
  - in supercritical water oxidation, 146, 149
- Hexachloroethane, 271
- HF. See Hydrofluoric acid
- High-temperature, low-pressure oxidation, 137
  - application of, 12-13, 192, 203
  - summary of processes, 9*t*, 189*t*, 192-193
  - See also Catalytic oxidation;
  - Molten salt oxidation
- High-temperature, low-pressure pyrolysis, 29, 137, 191-192
  - application of, 12
  - gasification processes, 160-163
  - summary of processes, 9*t*, 189*t*
  - See also Molten metal pyrolysis;
  - Plasma arc processes;
  - Synthetica Steam Detoxifier
- HPO<sub>2</sub>, 122
- HT, 1, 23
  - lethal doses of, 82*t*
  - permissible air concentrations, 82*t*

- properties, 38, 39-40*t*, 41
- See also Mustard agents
- Hydrocarbons
  - oxidation of, 274-275
  - in supercritical water oxidation, 146, 149
- Hydrofluoric acid
  - in acid-catalyzed hydrolysis, 115
  - in ethanolamine processing, 115-116
  - in hydrolysis of GB, 113
- Hydrogen, in disposal process, 76
- Hydrogen chloride, 175
- Hydrogen peroxide, 6, 21
  - in chemical oxidation, 124, 206
  - sodium hydroxide and, 116
  - VX in sodium hydroxide and, 116, 186
- Hydrogen sulfide, 175
- Hydrogenation processes, 189*t*
  - advantages, 179
  - applications, 176, 178
  - catalysts in, 178
  - development status, 178
  - process, 176, 177*f*
  - research needs, 179
  - waste streams, 178-179
- Hydrolysis
  - acid-catalyzed, 114-115
  - caustic, 29
  - enzyme-based, 128-130
  - of GB, 112-116
  - of mustard agents, 118-119
  - role of, 3, 32
  - salt wastes from, 100
  - of VX, 116-117
  - waste products from, 3, 33, 100, 110
  - See also Chemical detoxification
- I**
  - In-shell combustion, 29
  - Incineration
    - in baseline technology, 2, 8, 24, 28, 94
    - chlorinated dioxin synthesis in, 85-86
    - of contaminated carbon filters, 107
    - of GB, 62
    - level 5X standard for, 4, 32, 83, 84
    - of M55 rockets, 78
    - nitrogen oxides in, 101
    - opposition to, 28, 30
    - of VX, 62
    - See also, High-temperature, low-pressure oxidation; High-temperature, low-pressure pyrolysis
  - Indirect heating techniques, 97-98
  - International agreements
    - Chemical Weapons Convention, 3-4, 22-23, 197
    - compliance with, 20, 32, 80, 197-198, 206
  - Ionizing radiation, 122-123
    - advantages, 272
    - applications, 271-272
    - development needs, 273
    - development status, 271
    - disadvantages, 272
    - technology, 271
    - waste streams in, 272
  - Iraq, 37, 72*t*, 73*t*
  - Isopropyl methyl phosphonofluoridate. See GB
- J**
  - Johnston Atoll Chemical Agent Disposal System (JACADS), 1, 2, 24-26, 27*t*, 49, 51*t*, 52*t*, 60*t*, 61*t*, 62
    - chlorinated dioxin reaction products in, 86
    - demilitarization process, 77-78, 79*f*
    - gas storage requirements, 104
    - nitrogen oxide generation at, 101
    - solid waste in, 82
    - transportation of waste from, 235-236
- K**
  - Kentucky Environmental Foundation, 36
- L**
  - Land mines, 42, 43*f*, 47*t*, 77
  - Landfill, 33
    - contaminated carbon filters in, 107, 108
    - dunnage materials in, 2 n.3
    - salt wastes in, 99
  - Lawrence Livermore Laboratory, 124
  - Lethal
    - definition of, 37 n.2
    - doses of chemical agents, 82*t*
  - Level 1X decontamination, 82
  - Level 3X decontamination, 4, 82-83, 84
    - of metal, chemical processes for, 98
    - salt wastes, shipment of, 100-101
  - Level 5X decontamination, 4, 32, 83, 84



- data sources, [262-263](#), [266-267](#)
- equivalency, [83](#)
- of GB, [263-264](#), [265](#)
- of HD, [265](#), [266](#)
- indirect heating methods for, [97](#)
- of M55 rocket, [263-264](#)
- of metal wastes, [98-99](#)
- of VX, [263-264](#), [265](#), [266](#)
- for waste salts, [195](#)
- Lewisite (L), [41](#), [42](#), [82t](#)
- Lexington-Blue Grass Army Depot, [27t](#), [30](#), [49](#), [50f](#), [51t](#), [52t](#), [222t](#), [223t](#), [224t](#), [228f](#), [232f](#)
- LiAlH<sub>4</sub>, [122](#)
- Lime, [20](#), [104](#), [205](#)
- Liquid waste, [4](#), [32](#), [196](#)
  - from biological degradation, [134-135](#)
  - biological oxidation for, [10-11](#)
  - in hydrogenation processes, [178-179](#)
  - internal recycling for, [81](#)
  - source of, [15](#)
  - standards for, [81](#)
  - in supercritical water oxidation, [151](#)
  - water, [101-102](#)
- Locations of stockpiles, [1](#), [26](#), [49](#), [50f](#), [51t](#), [52t](#)
- Low-temperature, low-pressure, liquid-phase detoxification
  - applications, [6-10](#), [16](#), [17](#), [32](#), [186](#), [200-201](#)
  - for GB, [112-116](#), [186](#)
  - irreversibility of, [109](#), [186-190](#)
  - for mustard agents, [118-121](#), [186](#)
  - research needs, [10](#)
  - summary of processes in, [7t](#), [187t](#)
  - technology, [6-10](#), [186](#)
  - for VX, [116-117](#), [186](#)
  - See also Biological processes;
  - Chemical detoxification
- Low-temperature, low-pressure, liquid-phase oxidation
  - application, [10-11](#), [16](#)
  - electrochemical, [21](#), [124](#), [206](#), [275-278](#)
  - prospects for, [109](#), [203](#)
  - role of, [123](#), [190](#)
  - summary of processes in, [8t](#), [188t](#)
  - technology, [10](#), [190](#)
  - ultraviolet radiation in, [123](#), [124](#), [125-126](#), [190](#)
  - See also Biological processes;
  - Oxidation processes
- M**
- M34 bomblet dusters, [34](#)
- M55 rockets, [29](#), [33](#), [42](#), [43f](#), [47t](#), [48t](#)
  - disposal productivity, [80](#)
  - in indirect thermal decomposition, [97](#)
  - level 5X decontamination of, [263-264](#)
  - removal of agent from, [77-78](#)
  - sheer machine for, [77](#)
- Marine Protection, Research and Sanctuaries Act, [54](#)
- MC-1 bomb, [42](#) n.6
- Mechanized processes, for disassembly, [96](#)
- Mediated electrochemical oxidation, [124-125](#), [274](#), [277](#)
- Metal parts
  - alternative technologies for, [14](#), [21](#), [203](#), [204t](#), [207](#)
  - in baseline approach, [1-2](#), [14](#), [24](#), [193](#), [203-204](#), [240t](#)
  - in catalytic fluidized-bed oxidation, [170](#)
  - chemical detoxification of, [84](#)
  - detoxification of, [16](#), [32-33](#), [193](#)
  - high-temperature processes for, [12](#)
  - indirect heating of, [97-98](#)
  - low-temperature processes for, [110](#)
  - in molten metal pyrolysis, [19](#), [153](#)
  - oxidation of, [17](#)
  - postprocessing operations, [98-99](#)
  - in supercritical water oxidation, [149](#)
  - in Synthetica Steam Detoxifier, [167](#)
  - thermal treatments for, [19](#), [97](#), [191](#)
- Methane
  - as biological process by-product, [132](#)
  - in supercritical water oxidation, [148](#)
- Methanol, [113](#)
- 2-methoxyethanol, [113](#)
- Methylene chloride, [175](#)
- Mineralization, [17-19](#)
  - alternative strategies, [201-205](#), [202t](#)
  - definition of, [32](#) n.6
  - of gas wastes, [196](#)
  - goals, [33-34](#), [198-200](#), [199f](#)
  - See also Oxidation processes
- Mitre Corporation, [26](#)
- MK-94
  - bomb, [42](#) n.6
- MK-116 bomb, [42](#) n.6
- Moderate-temperature, high-pressure processes, [138](#)
  - application of, [11](#), [16](#), [17](#), [191](#)

- examples of, 137, 190
- process, 11, 190-191
- research needs, 11
- See also Supercritical water oxidation;
- Wet air oxidation
- Molten metal pyrolysis
  - applications, 19, 21, 153, 156, 191
  - development status, 153
  - process, 12, 152-153, 154-155<sup>f</sup>
  - reaction products, 153
  - research needs, 156
  - waste streams, 18
  - See also High-temperature, low-pressure oxidation
- Molten Metal Technology, 153, 154<sup>f</sup>
- Molten salt oxidation, 12-13, 17, 18, 21
  - advantages, 174, 192
  - as afterburner, 19, 205
  - application, 173
  - development status, 171-172
  - disadvantages, 173, 174
  - energetics in, 173, 174, 204
  - energy use, 92
  - process, 171, 173
  - research needs, 174
  - waste streams 173
  - See also High-temperature, low-pressure oxidation
- Mortar cartridges, 42, 47<sup>t</sup>
- Moving bed evaporator, 163-164, 166, 169
- Munitions, 49>42
  - in baseline technology, 77-78
  - composition of, 47<sup>t</sup>, 48<sup>t</sup>
  - dunnage, 78
  - geographic distribution, 49, 50<sup>f</sup>, 51<sup>t</sup>, 52<sup>t</sup>
  - ionizing radiation for, 122-123, 272
  - mechanical disassembly of, 96
  - plasma arc processes for, 157
  - reverse assembly of, 23, 77-78, 80, 92, 94, 95-96, 201
  - storage conditions, 77
  - waste streams, 77-78
  - work environment for disposal of, 78
- Mustard agents
  - action of, 42
  - Army code designations, 23
  - biological processes for, 132
  - calcium chloride generation in disposal of, 99
  - chemical detoxification of, 63<sup>t</sup>, 67<sup>t</sup>, 118
  - chemical properties, 38n.3, 39-40<sup>t</sup>, 41
  - containers for, 16
  - disposal in Iraq, 72<sup>t</sup>
  - gas, 1, 3
  - in gel form, 10, 41, 96
  - hydrolysis of, 118-119
  - long-term exposure to, 42
  - mediated electrochemical oxidation of, 125
  - moderate-temperature, high-pressure oxidation for, 11
  - past disposal experiences, 54, 55<sup>t</sup>
  - permissible air concentrations, 82<sup>t</sup>, 83
  - sodium hypochlorite reactions, 119-120
  - storage of, 42
  - in Synthetica Steam Detoxifier, 169
  - See also H;
  - HD;
  - HT
- N
  - NaBH<sub>4</sub>, 122
  - NaOH. See Sodium hydroxide
  - Napthalene, 148
  - National Academy of Sciences, 29, 54
  - National Aeronautics and Space Administration, 148
  - National Defense Authorization Act, 23 n.2, 30
  - National Environmental Technology Application Corporation, 180
  - National Institute for Occupational Safety and Health, 81
  - National Research Council, 23, 26, 29, 34
  - National Science Foundation, 148
  - Nerve agents. See Organophosphate nerve agents
  - Nervous system, nerve agent action in, 41-42
  - Neutralization processes, 54, 56<sup>t</sup>, 62, 65<sup>t</sup>, 67<sup>t</sup>, 74
    - alkali in alcohol, 113-114
    - ammonia in, 113
    - for GB, 62, 65<sup>t</sup>, 70<sup>t</sup>, 73<sup>t</sup>, 112-114
    - for mustard agents, 63<sup>t</sup>, 67<sup>t</sup>
    - potassium hydroxide in, 113-114
    - for salt wastes, 99
    - See also Chemical detoxification;
    - Ethanolamine;
    - Sodium hydroxide
  - Newport Army Ammunition Plant (Indiana), 26, 27<sup>t</sup>, 49, 50<sup>f</sup>, 51<sup>t</sup>, 221<sup>t</sup>, 223<sup>t</sup>, 224<sup>f</sup>, 227<sup>f</sup>, 231<sup>f</sup>
  - Nickel, in fluidized-bed oxidation, 170, 171
  - Nitrogen
    - in combustion, 102-103
    - in supercritical water oxidation, 148
  - Nitrogen oxides, 101
    - from ethanolamine, 115-116, 121

in supercritical water oxidation, 149  
Norepinephrine, 41

## O

LO-ethyl-S-[2-diisopropyl aminoethyl]  
methylphosphonothiolate. *See* VX  
Occupational, Safety and Health Act, 81  
Ocean dumping, 29, 54  
Office of Naval Research, 135  
Office of Technology Assessment, 30  
Ogden Environmental Services, 169  
Organic synthesis, 121-122  
Organophosphate nerve agents, 23  
biological detoxification of, 127, 129*t*, 130  
chemical composition, 37  
*See also* Chemical agents  
Ortho-iodosobenzoate catalyst, 112  
Oxidation processes  
acidic products of, 98  
carbon dioxide in, 76, 190  
deferred, 20, 32-33, 80, 197-198, 206  
in demilitarization strategies, 2, 17-18, 32, 34, 190  
Fenton's reagents in, 124  
GB in, 276  
lid in, 119-121  
hydrocarbons in, 274-275  
hydrogen peroxide in, 124  
low-temperature, liquid-phase, 109  
nitrogen oxides in, 101  
one-step approaches, 17  
peroxydisulfate salts in, 124  
reducing gas waste volume in, 102-103  
ultraviolet light in, 125-126  
for VX in acid, 117  
*See also* High-temperature, low-pressure oxidation;  
Low-temperature, low-pressure, liquid-phase oxidation;  
moderate-temperature, high-pressure processes  
OXONE, 116, 117, 120  
Oxygen, pure  
in afterburners, 19  
in combustion processes, 11, 13, 196  
in diluting gaseous emissions from bioremediation, 135  
in gas waste management, 14, 16, 20, 196, 203-204  
in high-temperature, low-pressure oxidation, 192-193  
in molten salt oxidation, 173  
in reducing gas waste volume, 102-103, 192-193, 194, 195

research needs, 203  
risks of, 103  
in supercritical water oxidation, 148, 190, 196 n.1  
in waste gas storage, 104, 106  
in wet air oxidation, 143-144, 190  
Ozone, 125-126

## P

Packaging. *See* Dunnage  
Peracids, 120  
Peroxydisulfates, 21, 206  
in low-temperature oxidation, 10, 124, 190  
mustard reactions, 120  
Pesticides, 139  
Phosphorous, 77, 148  
Pilot plants, 89, 91*t*  
Adams process, 180-182, 183  
catalytic fluidized-bed oxidation, 170-171  
development times, 5  
for high-pressure oxidation processes, 11  
molten metal pyrolysis, 156  
molten salt oxidation, 174  
recycled flue gases in, 102-103  
Pine Bluff Arsenal, 27*t*, 50*f*, 51*t*, 52*t*  
Plasma arc processes, 12, 17, 18, 19, 21, 191  
advantages of, 160  
application, 157  
development status, 157  
disadvantages of, 160  
energy use, 92  
oxygen sources for, 157  
process, 156-157, 158-159*f*  
research needs, 160  
waste stream, 157-159  
Poisonous substance, definition of, 37 n.2  
Pollution abatement  
afterburner exhaust, 2  
assessment of systems for, 95  
in baseline approach, 23  
liquid waste in, 196  
toxic air emissions, 19-20  
water wastes in, 101-102  
*See also* Waste streams/management  
Polychlorinated biphenyls, 49, 114, 178  
in plasma arc processes, 157

Polyethylene glycol, 113, 114

Potassium hydroxide

in alcohol, GB reaction with, 113-114, 131

in DeChlor/KGME process, 114

in neutralization of H, 113-114

in polyethylene glycol, 113, 114

Programmatic Environmental Impact Statement, 28, 28 n.5, 31

Propellants. *See* Energetics

Propylene carbonate, 276

Public interest groups, 36

Public opinion

health concerns, 28 n.5

opposition to incineration, 30

Pueblo Depot, 27*t*, 49, 50*f*, 51*t*, 52*t*

Pyrolysis

steam, 29, 192

*See also* High-temperature, low-pressure pyrolysis

## R

Reaction products

bioticgradation of, 126, 127, 131-132, 134-135

in chemical detoxification, 10, 20

in ethanolamine processing, 115-116

GB, 115-116, 131-132

in indirect heating, 97

in low-temperature, low-pressure, liquid-phase detoxification, 10

in neutralization with alkali in alcohol, 113-114

in pyrolysis, 137

in Synthetica Steam Detoxifier, 167, 168

VX, 116, 117, 131-132

*See also* By-products

Recirculated flue gas, 102-103

Resource Conservation and Recovery Act, 81, 145

Reverse assembly, 23, 75, 77-78, 80, 94, 201

cost of, 92

cryofracture alternative, 95-96

mechanical, 96

Rocky Mountain Arsenal, 54, 55*t*, 56*t*

Rutgers University, 135

## S

Safety standards

decontamination levels, 4, 82-83, 84-85

for pure oxygen use, 103

for work environments, 81

Salt wastes, 15, 99, 193-194

in biodegradation of reaction products, 135

composition of, 76

disposal of, 77

drying of, 100

heteroatoms in, 30

in hydrolysis of mustard, 118, 119

level 5X decontamination of, 195

in molten salt oxidation, 171, 173, 174

from neutralization of GB, 99, 193

shipment of, 100-101

in sodium hydroxide neutralization of GB, 112

solubility, 77, 99

source of, 98, 99

in supercritical water oxidation reactor, 149-150, 151, 152

in Synthetica Steam Detoxifier, 167, 168

Satin. *See* GB

Scientists Against Nuclear Arms, 35

(CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>)<sub>3</sub>SnH, 122

Sodium fluoride, 99

Sodium hydroxide, 6, 99

in DS2 decontamination fluid, 114

GB and, 112-114, 186, 200

hydrogen peroxide and, 116

hydrolysis of mustard agents and, 118, 119

in VX detoxification, 116, 186

Sodium hypochlorite, HD and, 120

Sodium metal, 122

Spectrometry, agent-specific, 87

Steam gasification, 12, 17, 21

Steam pyrolysis, 29, 192

Storage

bulk liquid, 42

of chemical munitions, 42-49, 77

of contaminated carbon filter material, 108

*See also* Gas storage;

Storage and certification

Storage and certification, 28, 88, 195

alternatives to, 88-89

need for, 30, 103

retention times, 76, 88-89

Strategy 1, 15-17, 32-33, 197-198, 200-201, 201*t*

Strategy 2, 17-19, 33-34, 198-200, 201-205, 202*t*

Sulfur, 77

in Adams process, 180

dioxide, 175

in hydrogenation processes, 176

in supercritical water oxidation, 148

trioxide, 175

vapor, 76

- Supercritical water oxidation, [11](#), [16](#), [17-18](#), [21](#), [190-191](#), [203](#)  
 advantages of, [151-152](#)  
 as afterburner, [19](#)  
 applications, [146](#), [148](#), [149](#), [282-285t](#)  
 by-products, [151](#)  
 corrosion in, [149](#), [150-151](#), [152](#)  
 development status, [148-149](#), [202t](#)  
 disadvantages of, [152](#)  
 energetics in, [148](#), [149](#), [150](#), [152](#)  
 of GB, [149](#), [281](#), [287](#)  
 kinetic data, [148-149](#)  
 material balance in, [281](#), [287](#)  
 model compounds in, [286f](#)  
 oxygen requirements, [102](#), [196 n.1](#)  
 process, [146-148](#), [147f](#)  
 properties of water in, [146](#), [149](#)  
 reaction rate, [149](#), [152](#)  
 reactor design, [150](#), [152](#)  
 reactor plugging in, [148](#)  
 research needs, [152](#)  
 salt precipitation in, [149-150](#), [151](#), [152](#)  
 waste streams in, [151](#)  
 Superfund Innovative Technology Evaluation Program, [35](#)  
 Surface interface, [10](#)  
 in liquid-phase detoxification of HD, [119-120](#), [186](#)  
 Synthetica Steam Detoxifier  
 advantages, [168](#)  
 applications, [166-167](#)  
 corrosion control in, [167](#)  
 disadvantages, [168](#)  
 energetics in, [166-167](#), [169](#), [291](#)  
 energy use in, [168](#), [290](#)  
 GB in, [287-291](#)  
 heat/material balances in, [287-291](#)  
 moving bed evaporator in, [163-164](#), [166](#), [169](#)  
 operational status, [166](#)  
 process, [163-166](#), [164t](#)  
 product gas in, [165-166](#)  
 research needs, [168-169](#)  
 test results, [166](#)  
 waste streams, [167](#)  
 Synthetica Technologies, Inc., [164](#)
- T**  
 Tabun. [See](#) GA  
 Tetrachloride, [271](#)  
 Tetraethyl lead, [178](#)  
 Texas A & M University, [135](#)  
 Thiodiethanol  
 HD converted to, [119](#)  
 peracid in detoxification of, [120](#)  
 Thiodiglycol, biological detoxification of, [127](#), [132](#)  
 Titanium, [143](#)  
 TMU-28/B spray tanks, [42 n.6](#), [47t](#)  
 TNT, [114](#), [169-170](#)  
 Tooele Army Depot, [24](#), [26](#), [27t](#), [42](#), [49](#), [50f](#), [51t](#), [52t](#), [54](#),  
[56t](#), [57 t](#), [59t](#)  
 disposal schedule, [80](#)  
 Toxic, definition of, [37 n.2](#)  
 Toxic Substances Control Act, [26](#), [81](#)  
 Transportation, [31](#)  
 in assessing alternative technologies, [35](#)  
 in baseline approach, [24](#)  
 of by-product 3X salts, [100-101](#)  
 in demilitarization strategy options, [15-16](#), [32](#), [33](#), [197](#)  
 from Johnston Atoll Chemical Agent Disposal System,  
[235-236](#)  
 Treaties, [3-4](#), [22-23](#)  
 Tributylamine, [41 n.4](#)  
 Trichloroethylene, [175](#), [176 n.9](#), [178](#), [271](#)  
 1,3,5-trimethyl benzene, [148](#)  
 Tris(trimethylsilyl) silane, [122](#)
- U**  
 Ultraviolet light, [10](#), [123](#), [124](#), [125-126](#), [190](#)  
 Umatilla Depot Activity, [27t](#), [50f](#), [51t](#), [52t](#)  
 Underground combustion, [29](#)  
 Unitary chemical weapons, [1 n.1](#), [22 n.1](#)  
 United Kingdom, [69t](#), [70t](#), [71t](#), [113](#), [119](#)  
 United Nations, [72t](#), [73t](#)  
 University of Pittsburgh, [180](#)  
 University of Washington (Seattle), [135](#)  
 UOP HyChlor conversion process, [177f](#), [178](#)
- V**  
 VX, [1](#), [23](#)  
 biodegradation of reaction products from, [131-132](#)  
 chemical detoxification of, [21](#), [65t](#), [67t](#), [74](#)

chemical structure, 37, 37n.1, 38f  
 direct biological destruction of, 128-130, 133-134  
 lethal doses of, 82t  
 level 5X decontamination of, 263-264, 265, 266  
 low-temperature, low-pressure, liquid-phase detoxification of, 6, 10, 109, 186  
 minimum detection limits, 233-234  
 moderate-temperature, high-pressure oxidation of, 11  
 nitrogen compounds in, 101  
 organic synthesis agents and, 121-122  
 oxidation agents for, in acid, 117  
 past disposal experiences, 59t, 60t, 62  
 permissible air concentrations, 82t  
 properties, 38, 39-40t  
 reaction with sodium hydroxide, 113-114, 116, 186  
 reactions in low pH solutions, 186  
 storage of, 42  
 toxicity of, 41, 41n.5

## W

Waste streams/management, 1, 4, 13-15  
 in Adams process, 180, 183  
 assessment of, 93  
 in baseline technology, 2, 24  
 biological detoxification of, 126-127, 131, 134-135  
 in catalytic fluidized-bed oxidation, 170  
 in catalytic oxidation, 175  
 chemical breakdown products, 76-77  
 in coal gasification, 163  
 demilitarization strategies for, 15-19, 32-33  
 drying wet wastes, 4, 100  
 in electrochemical oxidation, 278  
 heteroatoms in, 30  
 high-temperature, low-pressure oxidation treatment for, 12-13  
 in hydrogenation processes, 178-179  
 in ionizing radiation process, 272  
 in low-temperature, liquid-phase processes, 10, 109, 110, 111, 190  
 metal wastes in, 193  
 in molten metal pyrolysis, 153, 156  
 in molten salt oxidation, 173, 174  
 in munitions destruction, 77-78  
 nitrogen oxides in, 101  
 in peroxydisulfate salt oxidation, 10, 124  
 in plasma arc processes, 157-159  
 solid wastes, 4, 78, 82-83, 98-99, 193-194  
 in supercritical water oxidation, 151  
 in Synthetica Steam Detoxifier, 167  
 water, 101-102  
 in wet air oxidation, 139, 144  
See also Gas wastes;  
 Liquid wastes;  
 Metal parts;  
 Salt wastes;  
 Storage and certification  
 Water wastes, 101-102  
 Westinghouse plasma system, 158f  
 Wet air oxidation, 11, 16, 17-18, 21, 102, 190-191  
 addition of caustic in, 142-143  
 advantages of, 144  
 application of, 139-141  
 corrosion concerns in, 142-143

development status, 139  
 development time, 146  
 disadvantages of, 145  
 experience with, 139  
 of GB, 141-142, 143, 144  
 material balance in, 279-281  
 operating temperatures, 141, 142t, 143  
 process, 138-139, 140f  
 pure oxygen in, 143-144  
 reaction rate in, 141  
 reactor design, 141  
 research needs, 145-146  
 waste streams, 139, 144, 145t  
 Work environment, 78, 81  
 Worker protection, 81