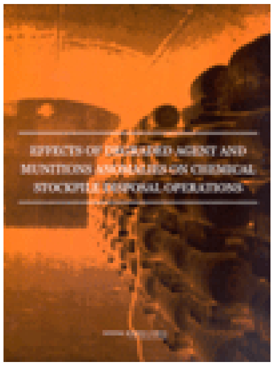

Effects of Degraded Agent and Munitions Anomalies on Chemical Stockpile Disposal Operations

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

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EFFECTS OF DEGRADED AGENT AND MUNITIONS ANOMALIES ON CHEMICAL STOCKPILE DISPOSAL OPERATIONS

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

Board on Army Science and Technology

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In memory of

Dr. John L. Margrave, National Academy of Sciences

1931-2004

and

Dr. Frederick G. Pohland, National Academy of Engineering

1924-2003

Preface

The purpose of this report is to examine the effects of leakers and other anomalies in stored munitions on the operation of chemical agent disposal facilities. To do this, the Committee on Review and Evaluation of the Army Chemical Stockpile Disposal Program evaluated the munitions' history, reviewed and evaluated leaker detection and reduction activities, reviewed unusual occurrences resulting from the delivery of atypical (i.e., anomalous) munitions and containers to disposal facilities, reviewed and evaluated the implications of atypical agents and munitions for risks to workers, and assessed the impacts of these atypical munitions on the Army's Chemical Stockpile Disposal Program (CSDP).

The United States has maintained the current stockpile of chemical warfare agents and munitions since World War II. In 1985, Public Law 99-145 mandated the expeditious destruction of M55 rockets containing chemical agents because of the chance that they might self-ignite. The program was soon expanded into the CSDP, which was given the mission of disposing of the entire 31,496 tons of nerve and mustard agents in the chemical stockpile. The stockpile of munitions has already been destroyed at one site, Johnston Island (part of Johnston Atoll), in the Pacific Ocean southwest of Hawaii. The remainder of the stockpile is dispersed among eight storage sites in the continental United States. The United States is a signatory to the Chemical Weapons Convention treaty, which requires that the entire stockpile be destroyed by April 29, 2007, with the possibility of a 5-year extension. Recently, the Army indicated that this extension would be necessary to complete disposal operations.

Congress mandated that the Army seek outside, unbiased advice on how best to dispose of the stockpile. In 1987, at the request of the Under Secretary of the Army, the National Research Council (NRC) established the Committee on Review and Evaluation of the Army Chemical Stockpile Disposal Program (the Stockpile Committee) to provide scientific and technical advice and counsel on the CSDP. The committee has since produced 30 full-length and letter reports covering the evolution of the CSDP from the design and construction of the first incineration-based chemical agent disposal facility on Johnston Island in 1990 to the present. The Johnston Island facility is now being closed. A second incineration-based facility has been operating for more than 7 years at Tooele, Utah, adjacent to the largest stockpile site. The third incineration facility, at Anniston, Alabama, has just begun operations. Similar incineration facilities are being constructed at Pine Bluff, Arkansas, and Umatilla, Oregon. Although details differ at the five sites, the basic technology is the baseline incineration system. At the four other sites—Aberdeen, Maryland; Newport, Indiana; Pueblo, Colorado; and Blue Grass, Kentucky—technologies other than incineration are being implemented.

STATEMENT OF TASK

This report has been prepared by the National Research Council (NRC) in response to a request from the Program Manager for Chemical Demilitarization (PMCD) suggesting that a better understanding of the condition of the stockpile in storage might enable improvements in operational efficiency and reduce risk to the public and plant employees. The statement of task is as follows:

> The NRC study will accomplish the following:
>
> - Evaluate the history of munitions and containers delivered to operating and closing chemical disposal facilities.
> - Review storage leaker detection and leak reduction activities currently in place at chemical agent storage facilities.
> - Review unusual occurrences resulting from the delivery of atypical agents, munitions, or containers to disposal facilities for destruction. Review resulting corrective actions and effects on disposal operations.
> - Review worker risk implications of atypical agent and munitions delivered to disposal facilities.
> - Assess programmatic impacts, including stakeholder perceptions.

Among the issues addressed are the state of the stockpile munitions and containers as delivered to disposal facilities and the effects that any atypical munitions and containers have had, are having, or might have on processing, handling, and monitoring during disposal operations. Atypical conditions include corrosion, leakage, agent deterioration, agent solidification, explosives deterioration, environmental exposure, and overpack operations. The report also addresses considerations pertaining to public and worker risks.

COMMITTEE MEMBERSHIP AND ACTIVITIES

The Stockpile Committee consists of members with expertise in the following areas: analytical chemistry; biochemical engineering; chemistry; chemical engineering; chemical industry management; chemical technology and manufacturing; civil and environmental engineering; combustion technology; engineering design and management; environmental planning and management; environmental restoration; facility closure; hazardous waste management; health risk assessment; incineration; industrial hygiene; materials science; mechanical engineering, monitoring and instrumentation; occupational medicine; risk assessment, management, and communication; safety; toxicology; urban planning; and waste treatment and minimization.

The committee met with selected personnel from PMCD and the Soldier Biological and Chemical Command (SBCCOM) throughout the development of this report. Members were provided with numerous documents containing data on stockpile surveillance activities and on the occurrence of leakers and other anomalies. Site visits were conducted. The report developed by the committee was peer reviewed by several experts in accordance with NRC procedures prior to publication.

The Stockpile Committee would like to recognize the assistance given by Army staff and contractors in providing information and answering questions from the committee. It is likewise grateful for the assistance of NRC staff members Donald L. Siebenaler, Harrison T. Pannella, Carter W. Ford, James C. Myska, William E. Campbell, Richard E. Rowberg, and Elizabeth Fikre in producing this report. The committee is also grateful for the assistance provided by Stephen P. Bailey of DuPont Engineering Technology.

Peter B. Lederman, *Chair*
Charles I. McGinnis, *Vice-Chair*
Committee on Review and Evaluation of the
Army Chemical Stockpile Disposal Program

Acknowledgment of Reviewers

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

Dennis C. Bley, Buttonwood Consulting Inc.,
Jere H. Brophy, Independent Consultant,
B. John Garrick, Independent Consultant,
Robert L. Mason, Southwest Research Institute,
George W. Parshall, Independent Consultant,
James P. Pastorick, GEOPHEX UXO, Ltd., and
Peter S. Spencer, Oregon Health and Science University.

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

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List of Acronyms

AMC	Army Materiel Command
ANCA	Anniston Chemical Activity
ANOVA	analysis of variance
AQS	agent quantification system
BGCA	Blue Grass Chemical Activity
BRA	brine reduction area
CAMDS	Chemical Agent Munition Disposal System
CDC	Centers for Disease Control and Prevention
CRDEC	Chemical Research, Development, and Engineering Center
CSDP	Chemical Stockpile Disposal Program
DA	Department of the Army
DAC	Defense Ammunition Center
DCD	Deseret Chemical Depot
DFS	deactivation furnace system
DICDI	diisopropyl carbodiimide
DIMP	diisopropyl methyl phosphonate
DOD	Department of Defense
DODIC	Department of Defense Identification Code
DPE	demilitarization protective ensemble
ECR	explosion containment room
EMPA	ethyl methylphosphonic acid
FOIA	Freedom of Information Act
FPEIS	Final Programmatic Environmental Impact Statement
GA	tabun, a nerve agent (ethyl-N,N-dimethylphosphoramidocyanidate)
GAO	Government Accounting Office
GB	sarin, a nerve agent (methylphosphonofluoridate, isopropyl ester)
H	sulfur mustard, bis(2-chloroethyl) sulfide
HD	sulfur mustard, distilled H
HDC	heated discharge conveyor
HT	sulfur mustard, 60 percent HD and 40 percent T, which is bis[2(2-chloroethylthio)ethyl] ether
IMPA	isopropyl methyl phosphonic acid
JACADS	Johnston Atoll Chemical Agent Disposal System
JI	Johnston Island
LIC	liquid incinerator
MDM	multipurpose demilitarization machine
MPA	methyl phosphonic acid
MPF	metal parts furnace

MPFA	methyl phosphonofluoridic acid
MSN	manufacturer stock number
NC	nitrocellulose
NCRS	nose closure removal system
NDPA	2-nitrodiphenylamine
NG	nitroglycerine
NRC	National Research Council
PAS	Pollution Abatement System
PBCA	Pine Bluff Chemical Activity
PCB	polychlorinated biphenyl
PCD	Pueblo Chemical Depot
PFS	pollution abatement system filter system
PMCD	Program Manager for Chemical Demilitarization
PMD	projectile/mortar disassembly
PRO	preroundout agent
PR-RS	restabilized preroundout
PUCDF	Pueblo Chemical Agent Disposal Facility
QASAS	quality assurance specialist ammunition surveillance
QRA	quantitative risk assessment
RCRA	Resource Conservation and Recovery Act
RD	redistilled agent
RMA	Rocky Mountain Arsenal
RO	roundout agent
RS	restabilized agent
RSM	rocket shear machine
SAIC	Science Applications International Corporation
SBCCOM	Soldier and Biological Chemical Command
SFT	shipping and firing tube
SMI	Storage Monitoring and Inspection
SRC	single round container
STS	Stockpile Tracking System
SUPLECAM	Surveillance Program for Lethal Chemical Agents and Munitions
TBA	tributylamine
TC	ton container
TOCDF	Tooele Chemical Agent Disposal Facility
TWA	time-weighted average
UMCD	Umatilla Chemical Depot
VX	a nerve agent, O-ethyl S-(2-diisopropylaminoethyl) methylphosphonothiolate

Executive Summary

For over 50 years, the United States has maintained a stockpile of chemical agents and munitions at eight military depots in the continental United States.[1] Under a congressional mandate in 1985, the Army instituted a program to destroy M55 chemical rockets. It extended this program in 1992 to destroy the entire chemical munitions stockpile.

The chemical weapons stockpile contains two types of chemical agents: (1) cholinesterase-inhibiting nerve agents (GB and VX) and (2) blister agents, primarily various forms of mustard agent (H, HD, and HT).

The purpose of this report is to examine the effects of leakers and other anomalies in the stored munitions on the operation of chemical agent disposal facilities. The Stockpile Committee evaluated the munitions' history, reviewed and evaluated leaker detection and reduction activities, reviewed unusual occurrences resulting from the delivery of atypical (i.e., anomalous) munitions and containers to disposal facilities, reviewed and evaluated the implications of atypical agent and munitions for risks to workers, and assessed programmatic impacts of these atypical munitions.

The report presents the Army's experience in tracking and handling anomalous munitions. It also describes data collection and data analyses by the Army and the committee.

The report also provides a fairly detailed description of the degradation processes affecting chemical agents and (to a lesser degree) propellants in stored munitions. Stabilizers were added to the nerve agents at the time of manufacture to retard decomposition, but these stabilizers have degraded over time. The resulting acidic decomposition products may corrode metal containment vessels, leading to agent leakage (particularly for GB). The decomposition mechanism is such that agent degradation may be expected to accelerate at elevated temperatures and over longer storage times.

The Stockpile Committee considered the chemical stockpile as a whole, and the Anniston chemical stockpile in particular, to determine what evidence might exist that the leaker rate is increasing with time. No statistical evidence for this was apparent. A relatively small number of munition types contain the bulk of the leakers. Most of the leakers are found among GB-filled munitions, the bulk of which are M55 rockets. The time in years to the first leak detection is different for different GB agent subtypes. Munitions filled with one GB subtype, PR-RS, appear to leak earlier in their life cycle than those filled with other GB agent subtypes. It is possible that the VX munitions are leaking within their

---

[1] The agent and munitions at a ninth site, Johnston Island, which is located in the Pacific Ocean about 800 miles southwest of Hawaii, were destroyed during a decade of disposal operations that concluded in November 2000.

casings, but the externally detected VX leakage so far has been minimal.

The discovery of anomalous munitions in the course of destroying the chemical stockpile is well documented. Such munitions increase risk to the general public, the environment, and especially to workers. By their nature, they are not predictable, and in several cases they have necessitated substantial process and permit modification. The fact is that stockpile degradation and the discovery of anomalies could well continue throughout the remaining life of the stockpile. This will call for regular testing, monitoring, and data recording in a standardized mode; improved statistical analysis of better databases to discover possible trends at the earliest possible time; and public comprehension of demilitarization operations, with as much information disclosure as can be permitted consistent with security concerns. Suitable coordination between Army personnel and emergency preparedness officials to mitigate the effects of any storage mishaps on surrounding communities is also warranted. As a whole, the effects of leakers and other anomalies can best be minimized by the earliest possible destruction of all agents at all sites.

Detailed findings and recommendations are presented in Chapter 5.

1

Introduction

OVERVIEW OF THE CHEMICAL STOCKPILE DISPOSAL PROGRAM

For over 50 years, the United States has maintained a stockpile of chemical agents and munitions at eight military depots in the continental United States.[1] Most of the chemical agents and associated munitions were manufactured over 40 years ago. Under a congressional mandate in 1985 (Public Law 99-145), the Army instituted a program to destroy M55 rockets. This original program was extended in 1992 and became the Chemical Stockpile Disposal Program (CSDP) when Congress enacted Public Law 102-484, which required destruction of the entire stockpile.

The Army, through its office of the Program Manager for Chemical Demilitarization (PMCD), is responsible for the design, construction, operation, and closure of the disposal facilities constructed at each storage site. Separately, the U.S. Army Soldier and Biological Chemical Command (SBCCOM) is responsible for the security and monitoring of the agents and munitions while they are in storage and until they are delivered to the disposal facilities.[2]

PMCD has over 17 years of operating experience with disposal facilities at two locations, the Johnston Atoll Chemical Agent Disposal System (JACADS) on Johnston Island and the Tooele Chemical Agent Disposal Facility (TOCDF) at Deseret Chemical Depot (DCD) in Tooele, Utah.[3] By the beginning of 2003, TOCDF had destroyed approximately 45 percent of the agent stored at DCD, including, by March 2002, all the munitions and containers filled with sarin (GB). The incineration facility at Anniston, Alabama, has just begun disposal operations. Disposal facilities are being constructed at four other sites: Aberdeen, Maryland; Newport, Indiana; Pine Bluff, Arkansas; and Umatilla, Oregon. Facilities are in the planning stage for the remaining two sites: Blue Grass, Kentucky, and Pueblo, Colorado.

The chemical weapons stockpile contains two types of chemical agents: (1) cholinesterase-inhibiting nerve agents (GB and VX) and (2) blister agents, primarily various forms of mustard agent (H, HD, and HT). Both mustard and nerve agents are frequently, but erroneously, referred to as gases, although they are liquids at room temperatures and at normal pressures. The stockpile contains bulk (ton) containers of nerve and mustard agents; agent-filled munitions, including rockets, mines, bombs, and projectiles; and spray tanks. Many

---

[1] The agent and munitions at a ninth site, Johnston Island, which is in the Pacific Ocean about 800 miles southwest of Hawaii, were destroyed during a decade of disposal operations that concluded in November 2000.

[2] As this report was being prepared, the functions of SBCCOM and PMCD pertaining to storage and disposal of the stockpile, respectively, were being integrated into a new Army organization known as the Chemical Materials Agency.

[3] The database of leaking munitions discussed in detail in Chapter 3 uses the acronym DCD interchangeably with TOCDF.

munitions contain both agent and energetic materials (propellants and/or explosives).

PMCD is responsible for operations of chemical agent disposal facilities but, as noted previously, it does not have responsibility for the chemical munitions or containers until they are delivered to a disposal facility. The munitions and containers are stored in igloos (concrete bunkers covered with earth) and at other locations on the depots and are under the control of SBCCOM. The age of the munitions and containers, as well as other factors, has contributed to the development of leaks and other anomalies, which are described in Chapter 2. Leakers (containers or munitions that leak) can result from manufacturing defects such as improper welds or construction materials. Chemical attack on the containment material is also a factor, the details of which are presented in Chapter 2.

The energetics in chemical munitions are standard, stable materials that do not degrade over the anticipated time period of storage. In some cases, particularly in M55 rockets, energetics can react with agent to form sensitive compounds. Only propellants have the potential to become more hazardous (less stable) with age even if there is no agent leaking into the propellant. Thus, tests are routinely performed to track propellant stability. Three types of chemical agent munitions that include propellants are 105-mm projectiles, 4.2-inch mortar rounds, and M55 rockets (U.S. Army, 1991). In 1996, the Army reported that energetics are stable under storage conditions and that the risk of munitions exploding in a storage igloo is less than 10^{-8} (one in 100 million) (U.S. Army, 1996a).

PURPOSE OF THE REPORT

The purpose of this report is to examine the effects of leaks and other anomalies on the operation of chemical agent disposal facilities. The Stockpile Committee (1) evaluated the history of munitions and containers that were or will be delivered to chemical agent disposal facilities; (2) reviewed and evaluated leak detection and reduction activities at the storage facilities; (3) reviewed and evaluated unusual occurrences resulting from the delivery of atypical (i.e., anomalous) munitions and containers to disposal facilities, including a review of corrective actions taken and effects on disposal operations; (4) evaluated and reviewed the implications of atypical agents and munitions on risks to workers at the disposal facilities; and (5) assessed programmatic impacts of these atypical munitions, including the perceptions of stakeholders (see statement of task, in the Preface).

Over the years and using a variety of protocols, the Army has accumulated quantitative data on the leaking munitions in storage at each site. These data are the best quantitative indicator of one type of challenge, leakers, faced by disposal facilities. They have been analyzed for munitions management purposes by two organizations within the Army and were further analyzed by the Stockpile Committee for this report. The committee also recognizes that besides leaking munitions, other types of anomalous munitions are being delivered to disposal facilities (e.g., overpacked leakers and gelled mustard munitions). However, only anecdotal information is available on the effects of these other anomalous munitions on disposal operations. While such anecdotal information is extensive, it is not amenable to either historical evaluation or quantitative analysis. Anomalies other than leakers are also discussed later in the report, primarily in Chapter 4.

This report presents a historical perspective of the Army's experience in tracking and handling anomalous munitions. Data collection and data analyses by the Army and the Stockpile Committee are described, followed by a discussion of what the analyses show and which kinds of further analysis could prove useful.

In Chapter 2, the various causes of degradation leading to the presence of anomalous munitions are discussed. Particular attention is paid to the chemical degradation of nerve agent GB. The munitions most prone to leakage are M55 rockets containing GB. Of particular concern are the chemical reactions and kinetics that lead to by-products that corrode the rockets, causing leaks.

Data on leakers are presented and summarized in Chapter 3; they may be different, depending on the protocols used for monitoring. These protocols varied over time, depending on the needs of the Army. The chapter discusses modifications and additions to the database to make it more amenable to statistical analysis. The statistical analysis program and the results of the analyses are also presented in Chapter 3.

The analysis of the data presented in Chapter 3 provides a basis for discussing the effects of processing leaking munitions. The effect of other anomalies, together with an analysis of the risks associated with them, is presented in Chapter 4.

Finally, the report presents the committee's findings and recommendations in Chapter 5.

2

Occurrences and Origins of Anomalies

OVERVIEW OF ORIGINS OF ANOMALIES

The Army is progressing with CSDP demilitarization activities with the goal of completing disposal activities by 2012 in accordance with an extended deadline provided for by the Chemical Weapons Convention. The U.S. unitary chemical agent and munitions stockpile contains a variety of agent storage containers and weapons types, some of which are configured with bursters, fuzes, and/or propellant charges. Figure 2-1 shows the locations of the eight stockpile storage sites in the continental United States.[1]

Munitions in the stockpile were last manufactured in 1968, and some are now almost 60 years old. Concerns about the potential consequences of leakages and accidents involving degrading stockpile munitions and containers pending their disposal have been reinforced by continuing observations of deterioration, corrosion, and, occasionally, leaks. Leakages have been most frequently encountered in GB M55 rockets, as noted in a report issued by the Government Accounting Office (GAO) in December 1994 (see Box 2-1 for the relevant excerpt). Leaks have continued to occur, with a total of 4,789 leakers reported from 1973 through June 2002 out of more than 3 million munitions (Studdert, 2002).

A number of chemical and mechanical anomalies have frequently led to leaks or have otherwise presented difficulties during operations at baseline incineration system disposal facilities (Denison et al., 2002; Thomas, 2002a):

- gelled agent (GB)
- crystallized agent (GB)
- sludged agent (HD)
- randomly occurring heavy metals, which create problems in meeting stack emission limits during processing
- foaming mustard agent
- internal pressurization of munitions from hydrogen gas generation
- various mechanical anomalies such as fabrication discontinuities (cracks and scratches) and unexpected obstacles to disassembly (such as difficulty in loosening screw threads)

A promising approach for developing a predictive method to help assess the formation and future frequency of leaks is to combine an understanding of the chemistry of agent manufacture and degradation processes (including those associated with stabilizers added to the agents) with a statistical analysis of data accumulated to date on stockpile leaks. This chapter discusses the stockpile in terms of what is known about the original manufacturing processes,

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[1] The small portion of the stockpile that originally existed at Johnston Atoll in the Pacific Ocean has been destroyed, and JACADS is undergoing final closure operations.

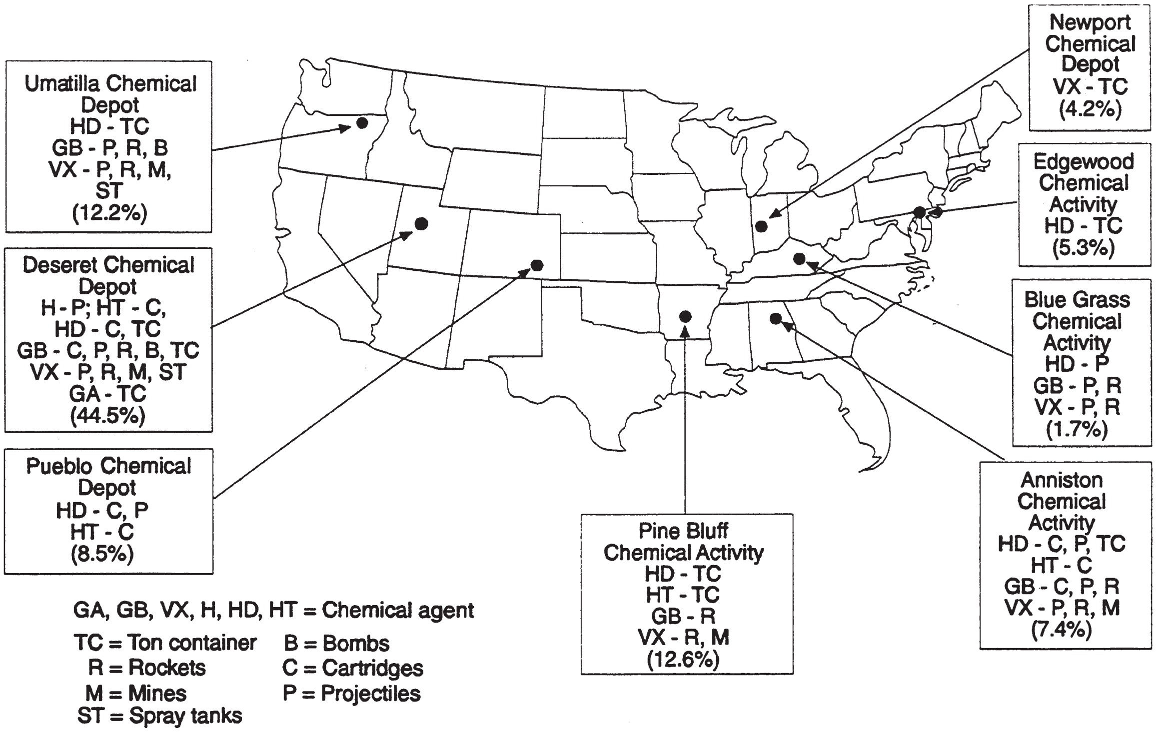

FIGURE 2-1 Location and size (percentage of original stockpile) of eight continental U.S. storage sites. Source: OTA (1992).

the chemistry of the agents, the configurations of munitions containing agents, and applicable corrosion mechanisms.

DESCRIPTION OF MUNITIONS AND CONTAINERS

A detailed description of the original stockpile is given in *Chemical Stockpile Disposal Program Final Programmatic Environmental Impact Statement* (FPEIS) (U.S. Army, 1988a) and can also be found in the NRC report *Disposal of Chemical Munitions and Agents* (NRC, 1984). Both reports and a later NRC report, *Recommendations for the Disposal of Chemical Agents and Munitions*, address earlier expressions of concern about the potential impacts of a degrading stockpile on disposal operations (NRC, 1994a).

As noted in Chapter 1, the stockpile contains three main agent types:

- GB (sarin),[2] a fairly volatile (2.9 mm Hg at 25°C), highly toxic (LD_{50} = 24 mg/kg) nerve agent (NRC, 1993, 1997a)
- VX,[3] a much less volatile (0.001 mm Hg at 25°C) but more toxic (LD_{50} = 0.14 mg/kg) nerve agent (NRC, 1993, 1997a)
- H,[4] HD,[5] and HT[6] (sulfur mustards), blister agents with moderate volatility (vapor pressures 0.08 to 0.11 mm Hg at 25°C) and moderate toxicity (LD_{50} = 100 mg/kg) (Munro et al., 1994; NRC, 1997a).

The stockpile also included some nerve agent GA (tabun),[7] which is similar to GB. However, all GA was stored at DCD in Utah and has been destroyed along with all of the GB that was stored there. A small amount

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[2] Methylphosphonofluoridate isopropyl ester.

[3] a nerve agent, O-ethyl S-(2-diisopropylaminoethyl) methylphosphonothiolate.

[4] Bis(2-chloroethyl) sulfide.

[5] Distilled H.

[6] 60 percent HD and 40 percent T, which is bis[2(2-chloroethylthio)ethyl] ether.

[7] Ethyl-N,N-dimethylphosphoramidocyanidate.

of lewisite,[8] an organic arsenical blister agent, remains in the stockpile.

Box 2-1

Excerpt from a Report on the Stability of the Stockpile of Chemical Weapons

Over time, nerve agents—particularly the nerve agent GB—become acidic and can corrode the metal warheads of rockets, mortars, and projectiles. In some cases, the corrosion can eat small holes in the metal warheads that allow the agent or agent vapors to escape. These leaks can be either external or internal to the munition.

External leaks allow an agent to escape outside the weapon or storage container and are quickly detected by monitoring. When detected, such leaks are controlled by placing the leaking munition in a special airtight container and segregating it. Army reports showed that from 1983 through 1993, 1,824 chemical munitions, mostly nerve agent-filled (GB) M55 rockets, developed external leaks. Leaking munitions have been found at all 6 storage sites that store munitions. In 1992, the last year data were available, 0.25% of M55 rockets in the total stockpile had external leaks and 0.02% of other munitions in the total stockpile had external leaks.

Internal agent leaks cannot be detected without disassembling the munition. When a munition leaks internally, an agent can come in contact with its explosive components. Such contact, according to Army reports, could increase the risk of unanticipated ignitions or explosions during handling, movement, and disassembling prior to final destruction. Possible problems that could result from internal leaks include accelerated aging of the propellant stabilizer, formation of sensitive explosive metal salts from reaction of the agent on burster explosives, corrosion of metallic parts in fuses, and formation of hazardous metallic salts in the fuse assembly. Again, internal agent leaks are most acute with M55 rockets. In a 1985 assessment of M55 rockets, the Army estimated that 1 to 3 percent had internal leaks. However, the limited sample size makes this estimate uncertain.

The extent of the hazard posed by internal leaks is unknown….Army officials report that the probability of an agent reaching a propellant is considered low.

Source: GAO (1994).

A variety of containers and munitions compose the chemical stockpile, some of which are depicted in Figure 2-2. Containers include bombs that are stored without explosives, aerial spray tanks, and bulk storage tanks known as ton containers. Munitions include land mines, M55 rockets, artillery projectiles, and mortar projectiles. Munitions typically contain some combination of fuze, booster, burster, and propellant—collectively referred to as "energetics."

Table 2-1 indicates which munitions incorporate energetics. The fuze is a small, highly sensitive explosive charge that initiates an explosive chain by detonating a booster. The booster is a medium-size charge that can be detonated by the fuze and is large enough to detonate a much larger burster charge. The burster charge is large enough to rupture the munition and to disperse the agent contained within. The M55 rocket also incorporates a section of solid rocket propellant. Dunnage refers to munition packing materials, which also may be destroyed by combustion.

Most of the munitions in the stockpile have been stored inside igloos that provide protection from the elements. The enclosed space of the igloo facilitates the monitoring performed to detect leaks and limits the quantities of agents and energetics that are likely to be involved in any single accident. Some bulk ton containers had been stored outdoors but were more recently moved into enclosed shelters to enhance their security. When leaking items are found, they are overpacked (placed inside another container and sealed) and returned to storage. Some leakers have been overpacked several times.

Problems with degraded items in the stockpile affect the safety of workers engaged in the maintenance of the stockpile and the transport of stockpile items from storage areas as well as that of workers involved in disposal operations. For example, workers in protective clothing perform the overpacking procedure and also decontaminate any area that has been affected by a leak. In general, hazards to workers may arise from conditions such as the following:

- agent leakage
- potential ignition of energetics by a spurious electric discharge
- instabilities of stabilizers used in energetics—especially the stabilizer in the M55 rocket propellant
- interactions between agent, energetics, and/or structural materials
- undetected manufacturing flaws

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[8] Dichloro(2-chlorovinyl)arsine.

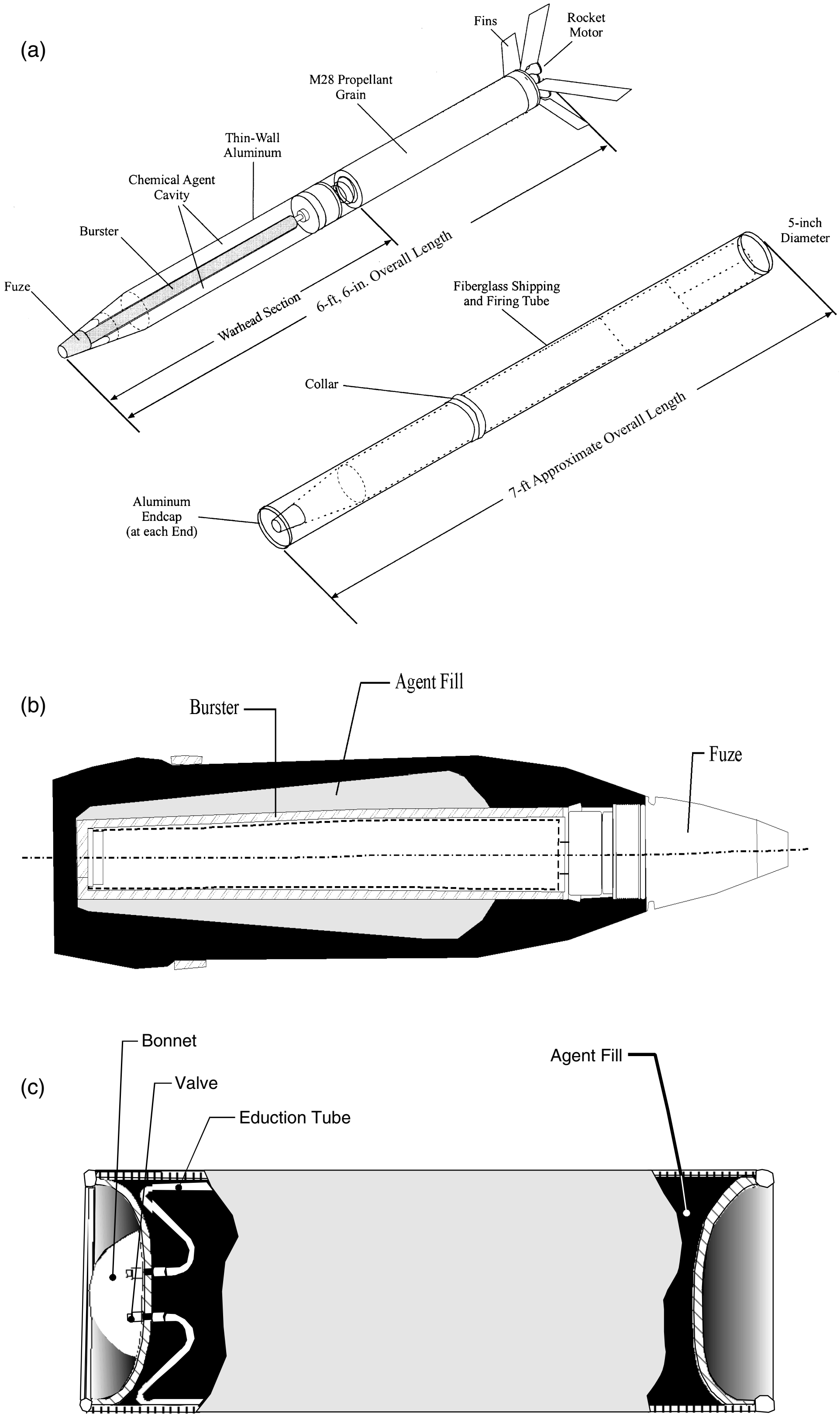

FIGURE 2-2 (a) M55 rocket; (b) 105-mm projectile; (c) ton container. Source: U.S. Army (2002a).

TABLE 2-1 Composition of Munitions in the U.S. Chemical Stockpile

Munition Type	Agent	Fuze	Burster	Propellant	Dunnage
M55 115-mm rockets[a]	GB, VX	Yes	Yes	Yes	Yes
M23 land mines	VX	Yes[b]	Yes	No	Yes
4.2-inch mortars	Mustard	Yes	Yes	Yes	Yes
105-mm projectiles	GB, mustard	Yes[c]	Yes[c]	No	Yes
155-mm projectiles	GB, VX, mustard	No	Yes[c]	No	Yes
8-inch projectiles	GB, VX	No	Yes	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,[d] mustard, lewisite[e]	No	No	No	No

[a] M55 rockets are processed in individual fiberglass shipping containers.
[b] Fuzes and land mines are stored together but not assembled.
[c] Some projectiles have not been put into explosive configuration.
[d] GA (tabun), or ethyl-N,N-dimethyl phosphoramidocyanidate, is a nerve agent.
[e] Lewisite, or dichloro(2-chlorovinyl) arsine, is a volatile arsenic-based blister agent.
Source: U.S. Army (1988a).

Chapter 4 describes some specific risks to workers that have been encountered during disposal operations.

MANUFACTURING PROCESS ORIGINS OF ANOMALIES

The manufacture of the agents in the stockpile and munition components took place at several locations over a long period of time. This section provides a brief overview of how manufacturing processes and specifications have contributed to anomalous items in the stockpile.

Agent Characteristics

GB

GB was manufactured at Rocky Mountain Arsenal (RMA) from 1953 to 1957 and stored by manufacturing lot in bulk tanks before being loaded into munitions or, in the 1960s, into the current storage containers. The purity of GB agent was originally specified at 92 percent, and tributylamine [TBA, $(C_4H_9)_3N$] was used as the stabilizer (U.S. Army, 1986a). During the first 2 years of GB production, between 1953 and 1955, the Army produced GB by a two-step distillation process that met the 92 percent purity specification. However, from 1955 to 1957, the Army eliminated the second distillation step, which reduced agent purity to about 88 percent.

Each batch of GB manufactured in 1953-1957 at the RMA was assigned an agent lot number. Differences in the production methods and the subsequent treatment of these lots are documented in Army records. In the 1960s, the bulk agent was loaded into a variety of containers and munitions that are identified by a munitions lot number. Thus, each item in the stockpile is identified by both an agent lot number and a munitions lot number. Since the decomposition products of GB were known to be acidic, stabilizers were added to scavenge acidic decomposition products and water as they formed.

There are currently four main subtypes of GB agent: PRO, PR-RS, RO-RS, and RD-RS. These subtypes arise from combinations of the following designations, because agents of different initial purity were treated in different ways:

- PRO (preroundout agent) was manufactured from 1953 to 1955 to meet a 92 percent purity specification. TBA was added as a stabilizer. Subsequent testing of these stored agent lots showed purities ranging from 81 to 94 percent, indicating a widely varying degree of decomposition (U.S. Army, 1985). The TBA was mostly in the form of $(C_4H_9)_3NH^+F^-$, possibly indicating the formation of HF. Varying amounts of diisopropyl methyl phosphonate (DIMP) and methylphosphonofluoridic acid (MPFA) were also found in the agent: 2 to 6 percent by weight DIMP and 2.7 to 10 percent by weight MPFA.

- RO (roundout agent) was manufactured from 1955 to 1957 to meet a modified purity goal of 88 percent. The Army continued to test the agent lots over the next few years and found that the RO lots were showing significant acidity. Since some of the agent was intended for use in aluminum M55 rockets, there was concern that acidity would cause corrosion problems. For this reason, over the next 6 years, some RO lots were redistilled to improve purity.
- RD (redistilled RO). In addition to the redistillation of some RO lots, the TBA stabilizer was replaced by DICDI (diisopropylcarbodiimide) to reduce the acidity problems and allow the placement of GB into aluminum casings.
- RS. Lots restabilized with DICDI were designated by the addition of RS to the basic agent category. M55 rockets were loaded with GB from various agent lots during the 1960s.

VX Nerve Agent

VX was originally manufactured from 1961 to 1968 at Newport, Indiana. It was 92 to 95 percent pure and had approximately 2 percent added stabilizer (usually DICDI, less frequently dicyclohexyl carbodiimide). When the agent fills were sampled in 1975, the VX content had decreased by 2 to 7 percent, and in some of the lots, about half the DICDI stabilizer had decomposed (U.S. Army, 1995a). Unlike GB, the VX was never redistilled or restabilized. The fact that a large fraction of the stabilizer had decomposed within 15 years of manufacture and that the VX has not been redistilled or restabilized suggests that little stabilizer may remain after the 28 additional years that have elapsed since 1975.

Mustard Agent

Mustard agent was produced at RMA from 1942 to 1945 by the Levinstein process. This produced the form of mustard that is designated H along with sulfur, which was removed by washing. From 1945 to 1946, most of this product was then vacuum-distilled at RMA to produce HD. HD was also manufactured at Aberdeen Proving Ground, in Maryland, using a 500-gallon vacuum distillation still and five vertical reflux condensers. The initial HD content of mustard agent manufactured circa 1945 was reported to be 94 percent, with less than 0.005 percent (50 ppm) HCl content. When sampled in 1982, the HD content had decreased to between 50 and 89 percent, with most analyses indicating less than 85 percent. The agent fills also contained approximately 0.2 percent Fe^{++} ion, indicating partial dissolution of the steel container material by acidic impurities or by HCl that came from hydrolysis of the agent (U.S. Army, 1995a).

Munition Assembly, Quality Control, and Component Compatibility

In the 1960s, when the bulk agents were introduced into the various stockpile munitions and containers, the specification and manufacturing procedures for the assembly of munitions was controlled to a level of quality that ensured the requisite functionality and a reasonably stable storage life. These specifications covered agent purity, energetics type and configuration, and component metal parts, along with assembly sequences and joining and sealing procedures. Ranges of acceptable variability in properties were also provided. Agent and munitions lots were systematically identified by type and numbered to allow future traceability. However, the possibility that disassembly and deactivation might be necessary at a future date was not considered in the design of the munitions. Moreover, when these munitions were manufactured 30 to 60 years ago, chemical analysis and mechanical assembly techniques were less sophisticated than they are now, making it possible for anomalies to have been introduced into the munitions during the initial manufacturing.

Some anomalies were discovered early in the disposal program—for example, the brass valves and plugs that were used on GB ton containers were found to have been attacked by the acidic products of GB decomposition, which leached the zinc from the brass alloy in the plug material. These fittings were subsequently replaced with steel fittings on all the ton containers.

One common type of anomaly—munitions containing either GB or mustard agent that has gelled—has consequences for the conduct of disposal operations. This phenomenon occurs with age. In the case of GB, gelling is probably related to reactions between GB degradation products and aluminum. For mustard agent, sludging is associated with the formation of dithianium ion. Another anomaly that became apparent during the disposal of mustard munitions, specifically projectiles, has been attributed to impurities that may lead to a slow, gas-producing reaction. During demilitarization operations at JACADS, some projectiles with mustard agent foamed when the burster well was extracted; this was due to the buildup of internal pressure.

A more pressing concern in terms of the risks associated with continued storage of the stockpile is the stability of the M28 propellant used in M55 rockets. This propellant includes nitrocellulose, which is unstable, decays exothermically, and is autocatalyzed by its own acidic nitrate products. During manufacture, a stabilizer that reacts with the acidic nitrate products to prevent autocatalysis was added, although nitrocellulose decay itself is not inhibited. M55 rockets were manufactured from 1959 to 1965, with stabilizer content averaging about 1.8 percent (U.S. Army, 1985). Initial stabilizer decays continuously over time. The Army has set a level of 0.5 percent stabilizer as the "increased surveillance threshold" and has observed autoignition at levels of 0.2 percent under controlled conditions (NRC, 1994a). Sampling of stabilizer levels over time has not shown variability beyond what might be expected from degradation alone. In 1985, 393 M55 rockets were randomly selected from 478,000 rockets in the stockpile, and stabilizer levels were found to be between 1.6 and 2.2 percent. Since the precise starting concentrations for individual lots were unknown (there was considerable variability around the 1.8 percent initial nominal concentration),[9] rates of degradation could not be inferred (OTA, 1992). Similarly, too little stabilizer might have been added during manufacture in some cases. The degradation of M28 propellant is discussed in more detail later in this chapter.

Another problem is the corrosive effect of GB agent degradation products on the aluminum of which M55 rockets are constructed. This corrosion has been responsible for the majority of leakage problems with these rockets. Aluminum was used in these rockets to achieve certain aerodynamic characteristics.

Among the manufacturing flaws that might accelerate corrosion in chemical munitions and containers are (1) the use of dissimilar metals for junctions, leading to electrochemical reactions, and (2) the improper cleaning of welded parts. However, subsequent observations of leakage sources suggest that these are not important causes of corrosion problems.

While anomalies that arose during manufacturing and initial filling can present unique operational issues during disposal, the long history of storage to date suggests that most manufacturing causes have already been identified from an examination of stockpile items that have leaked. For example, lead, cadmium, and mercury are occasionally identified in ton containers that were reused by the Army, and it is possible that these heavy metals were residual contaminants, even though the containers were presumably cleaned before refilling. In munitions, the presence of lead may have come from lead-based solder, lead compounds in energetic materials, or lead components in fuze assemblies. The presence of mercury, which has been found in ton containers, may be the result of pressure gauge breakage and splashback during filling operations or residual contamination.

DETERIORATION PROCESSES FOR AGENTS

Surveillance of Agent Deterioration

As noted above, the chemical agents stored in the U.S. stockpile were originally manufactured 30 to 60 years ago. The purity of the agent contained in various munitions and bulk containers was sporadically checked during the 1960s and 1970s (U.S. Army, 1985, 1995a). Following recommendations from a blue ribbon panel convened in March 1983 to review the chemical retaliatory surveillance and sampling program, the Surveillance Program for Lethal Chemical Agents and Munitions (SUPLECAM) was established for purposes that included the following (U.S. Army, 1988b):

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[9] According to the 1985 study by the Army Materiel Systems Analysis Activity, the first evaluation of M28 propellant stockpiled since production, the original stabilizer content at the time of manufacture ranged from 1.57 to 2.17 percent of total weight (U.S. Army, 1985). In that study, lots stored at Johnston Island had an average stabilizer content of 1.63 percent (95 percent confidence interval of 1.60 to 1.66 percent). These lots exhibited the largest stabilizer loss of all locations. Four lots produced in 1960 and stored at Pine Bluff had low original stabilizer content (1.62 percent), and the report noted the current assay average was 1.45 percent (95 percent confidence interval of 1.45 to 1.53 percent) [*sic*]. The remaining lot segments for all locations (except Johnston Island) were found to be homogeneous. The average stabilizer for these lots was 1.76 percent (95 percent confidence interval of 1.75 to 1.77 percent).

- determining the rate of agent decomposition
- gaining an improved understanding of the mechanisms of decomposition and stabilization of agents, specifically GB and VX.

The SUPLECAM studies, carried out by the U.S. Army Chemical Research, Development, and Engineering Center (CRDEC), developed a substantial quantity of data on degradation kinetics and mechanisms for GB and VX. This blue ribbon panel offered recommendations on seven items:

1. Are surveillance plans and procedures good enough to determine the current condition of the stockpile?
2. How can the surveillance plans be improved?
3. What further tests or analyses can be performed to provide useful information?
4. Is field testing necessary or desirable?
5. What will be the condition of the munitions by 1990? (The assumption then was that binary munitions would be available and the existing stockpile would be available for demilitarization.)
6. What additional data analysis or studies are needed to improve predictions about the condition of these munitions?
7. Can anything be done to prolong the life of the stockpile?

The panel recommended the immediate funding of SUPLECAM "to study VX decomposition as a function of time, temperature, inhibitors, and impurities" (U.S. Army, 1988b). Accelerated aging tests were conducted with and without inhibitors. Also, viscosity measurements were taken on pure and partially decomposed agent to determine if thickening or precipitation of the agent had occurred (U.S. Army, 1988b). This work led to intrusive sampling to obtain the necessary VX samples from the stockpile. The samples were stored in glass containers and sent back to the Army's Edgewood, Maryland, facilities for kinetic and mechanistic studies. An important finding was that the DICDI inhibitor decomposes in the presence of water to form urea crystals but does not readily decompose in the absence of water. The SUPLECAM program extended through the 1980s, but similar sampling efforts have not been conducted since that time.

Mechanisms and Products of Agent Deterioration

Over time, mustard and nerve agents can undergo chemical decomposition. In this section, the mechanisms and products of such decomposition are discussed in greater detail. Table 2-2 shows the products resulting from the degradation of nerve and mustard agents. Details of the decomposition pathways for individual agents have been discussed extensively (Munro et al., 1999; NRC, 2001a) and are summarized below.

GB

Three pathways, shown below, have been identified for the degradation of GB in storage (U.S Army, 1986b, 1988c, 1999a). GB can reversibly form DIMP and DF (Pathway I). The P—CH_3 bond is the most resistant to

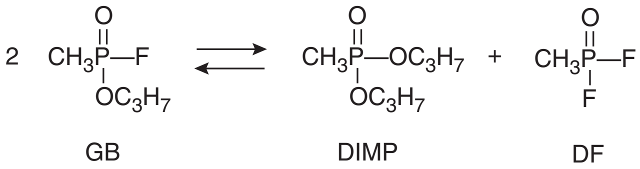
TABLE 2-2 Expected Products from Chemical Agent Decomposition Due to Age

Agent	Decomposition Products
VX	Thiolamine; ethylmethylphosphonic acid; ethanol; bis(2-diisopropylaminoethyl) thioether; bis(2-diisopropylaminoethyl) disulfide; *o,o*'-diethylmethyl phosphonolate; *o,o*'-diethylmethyl phosphonothiolate; diisopropylaminoethyl mercaptan; *o,*S-diethyl methyl phosphonothiolate; diisopropylaminoethylethyl sulfide; *o,*S-diethyl methyl phosphonate; N,N'-diisopropylamino ethyl methyl phosphonate; S-ethyl, S-diisopropyl amino ethyl methyl phosphonothiolate; *o*-ethyl, S-diisopropyl amino ethyl methyl phosphonothiolate; S'-diisopropyl amino ethyl methyl phosphonothiolate; diisopropylamine
GB	HF; isopropyl methylphosphonic acid (IMP); isopropanol; propene; methyl phosphono fluoridate; diisopropyl methyl phosphonate (DIMP); methylphosphonic acid (MPA)
Mustard (HD)	HCl; H_2S; ethylene; ethylene dichloride; vinyl chloride; 2,2'-dichlorodiethyl disulfide

Source: U.S. Army (1988a).

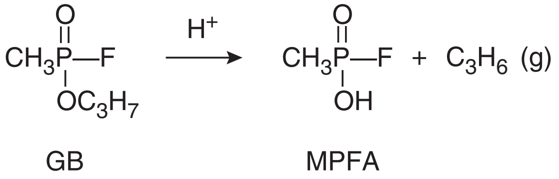
hydrolysis. The P—F bond is hydrolyzed (Pathway III) more rapidly than the P—OC_3H_7 bond (Pathway II).

(I) Reversible disproportionation of GB to form diisopropyl methyl phosphonate (DIMP):



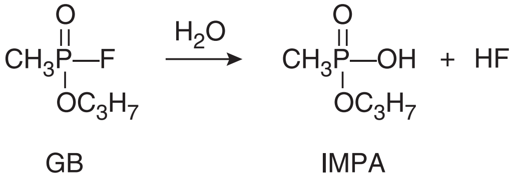
$$2\ CH_3P(=O)(F)(OC_3H_7) \rightleftharpoons CH_3P(=O)(OC_3H_7)(OC_3H_7) + CH_3P(=O)(F)(F)$$

(II) Acid-catalyzed hydrolysis to form methyl phosphonofluoridic acid (MPFA):



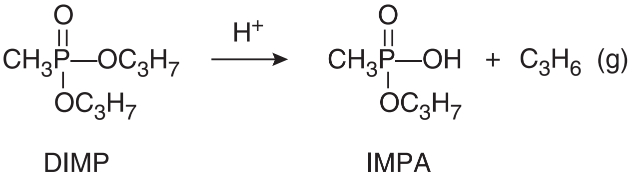
$$CH_3P(=O)(F)(OC_3H_7) \xrightarrow{H^+} CH_3P(=O)(F)(OH) + C_3H_6\ (g)$$

(III) Neutral hydrolysis to form isopropyl methyl phosphonic acid (IMPA):

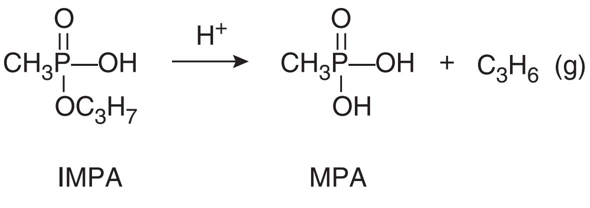


$$CH_3P(=O)(F)(OC_3H_7) \xrightarrow{H_2O} CH_3P(=O)(OH)(OC_3H_7) + HF$$

The DIMP product of the disproportionation reaction can be further hydrolyzed to form IMPA, which can undergo a slow further hydrolysis to form methyl phosphonic acid (MPA):



$$CH_3P(=O)(OC_3H_7)(OC_3H_7) \xrightarrow{H^+} CH_3P(=O)(OH)(OC_3H_7) + C_3H_6\ (g)$$



$$CH_3P(=O)(OH)(OC_3H_7) \xrightarrow{H^+} CH_3P(=O)(OH)(OH) + C_3H_6\ (g)$$

MPFA, IMPA, and MPA are all acidic and thus may be expected to further accelerate GB decomposition by the autocatalytic process described below. In experiments in which small amounts of these compounds were added to GB, the acceleration effect was in the order MPA > IMP ~ MPFA ~ water. In the presence of ferrous metals such as those used in many munitions, and if not inactivated by a stabilizer compound, these acidic compounds would be expected to react at the inner metal surface of the munition to liberate hydrogen:

$$\text{Steel} + 2\ HA \longrightarrow Fe^{++} + 2\ A^- + H_2\ (g)$$

where HA is an acidic compound. Aluminum will react with the HF produced in Pathway III (above) to form AlF_3 and liberate hydrogen gas:

$$\text{Aluminum} + 3\ HF \rightarrow AlF_3 + 3/2\ H_2$$

The AlF_3 can complex with additional fluoride ion to form AlF_4^- or the highly stable AlF_6^{3-} anion.

Two factors that could affect GB decomposition rates need to be considered: autocatalytic processes and rate acceleration at higher temperatures. Since the products of GB decomposition are themselves acidic and several of the decomposition pathways noted above are acid-catalyzed, it is possible that the decomposition process could proceed by an autocatalytic mechanism once the added stabilizer has been exhausted (Munro et al., 1999). One characteristic of an autocatalytic process is a lengthy induction period during which little or no reaction occurs, followed by a sudden rapid increase in the overall reaction rate (Steinfeld et al., 1999) (see Figure 2-3). An autocatalysis rate law for GB decomposition has been suggested:

$$[GB]_t = \frac{[GB]_{initial}\left(k_s + k_u[GB]_{initial}\right)}{k_u[GB]_{initial} + k_s \exp\left\{\left(k_s + k_u[GB]_{initial}\right)\left(t - t_{\mathrm{I}}\right)\right\}}$$

where $[GB]_{initial}$ is the concentration at time t_{I}, when all of the stabilizer is consumed, and $[GB]_t$ is the concentration of GB remaining at time t. The GB loss rate coefficients are k_s and k_u, in the presence and absence of stabilizer, respectively (U.S. Army, 1985, 1986a). On the basis of very limited data, it has been suggested that loss of GB could begin to accelerate at $t \geq 30$ years (U.S Army, 1986a).

Many reaction rates increase at higher temperatures according to the Arrhenius rate law (Steinfeld et al., 1999):

$$k(T) = A \exp\left(-E_{act}/RT\right)$$

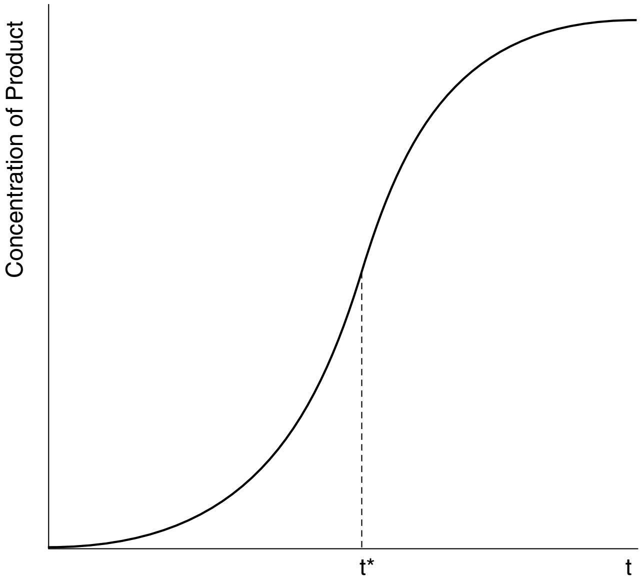
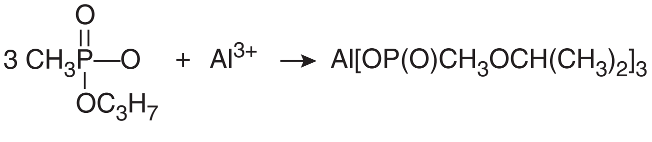


FIGURE 2-3 Autocatalysis rate profile, product concentration versus time; t* is the inflection time, i.e., the time at which product formation occurs most rapidly. Source: Adapted from Steinfeld et al. (1999).

where A is a preexponential factor, E_{act} is the activation energy, R is the gas constant, and T is the temperature in kelvins (°C + 273.16). Measurements at elevated temperatures give Arrhenius activation energies for Pathways I and II above as 28.3 kcal/mole and 25.4 kcal/mole, respectively (U.S. Army, 1999a). Analysis of SUPLECAM results on overall decomposition rates suggests an effective activation energy of 31 kcal/mole, which is within 20 percent of an earlier result reported in the United Kingdom (U.S. Army, 1999a) but based on only two data points. While Arrhenius behavior would suggest an accelerated decomposition rate for GB at higher temperatures, the data presented in Chapter 3 do not show any clear dependence of munition leak rate on ambient temperature.

As previously noted, all of the GB that was stored on Johnston Island and at DCD has been destroyed at JACADS and TOCDF, respectively. Gelling of the agent was encountered in about 12 percent of the GB munitions in the DCD stockpile (EG&G, 2002). GB gelling had previously been encountered in only a few 155-mm GB-filled projectiles during processing at JACADS. The degree of gelling ranges from increased viscosity that slows the draining process to a semisolid state or to a crystallized state, either of which makes it impossible to drain agent after the agent cavity of the rocket has been punched open.

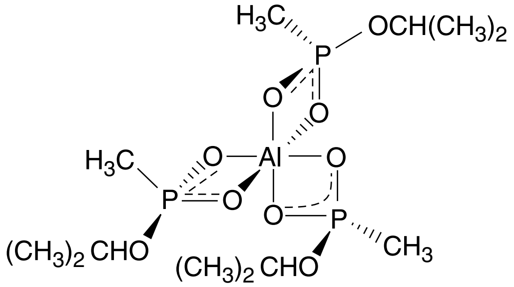
Gel formation has been attributed to the formation of aluminum phosphonate complexes.[10] The Al^{3+} ions, formed during the acidic corrosion of aluminum munition parts, can react with the $IMPA^-$ ions formed in Pathway III to form a tris-isopropyl methyl phosphonatoaluminate complex:



$$3\ CH_3\underset{OC_3H_7}{\overset{O}{\overset{\|}{P}}}—O + Al^{3+} \rightarrow Al[OP(O)CH_3OCH(CH_3)_2]_3$$

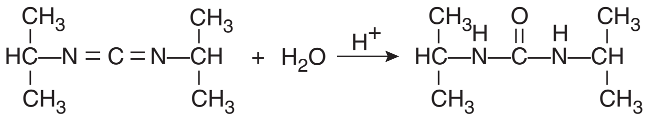
GB

which has the following suggested structure:[11]



The complexes, which are mostly viscous liquids, can form either a solid that is sparingly soluble in GB or oligomeric or polymeric phosphorus compounds.[12] Complexes can also form as a result of reaction with nickel or copper ions produced from the corrosion of other metal parts, such as brass fittings.

Another mechanism that has been suggested for the formation of crystalline solids in stored GB is the formation of 1,3-diisopropyl urea when DICDI (the stabilizer added to –RS lots) reacts with water in the presence of acid.[13]



$$\underset{CH_3}{\overset{CH_3}{HC}}—N=C=N—\underset{CH_3}{\overset{CH_3}{CH}} + H_2O \xrightarrow{H^+} \underset{CH_3}{\overset{CH_3}{HC}}—\overset{H}{N}—\overset{O}{\overset{\|}{C}}—\overset{H}{N}—\underset{CH_3}{\overset{CH_3}{CH}}$$

diisopropyl carbodiimide (DICDI) 1,3-diisopropyl urea

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[10] Yu-Chu Yang, Chief Scientist PMACWA, personal communication to the committee on June 27, 2003. Also see Wagner et al. (2001).

[11] Yu-Chu Yang, Chief Scientist PMACWA, personal communication to the committee on June 27, 2003. Also see Wagner et al. (2001).

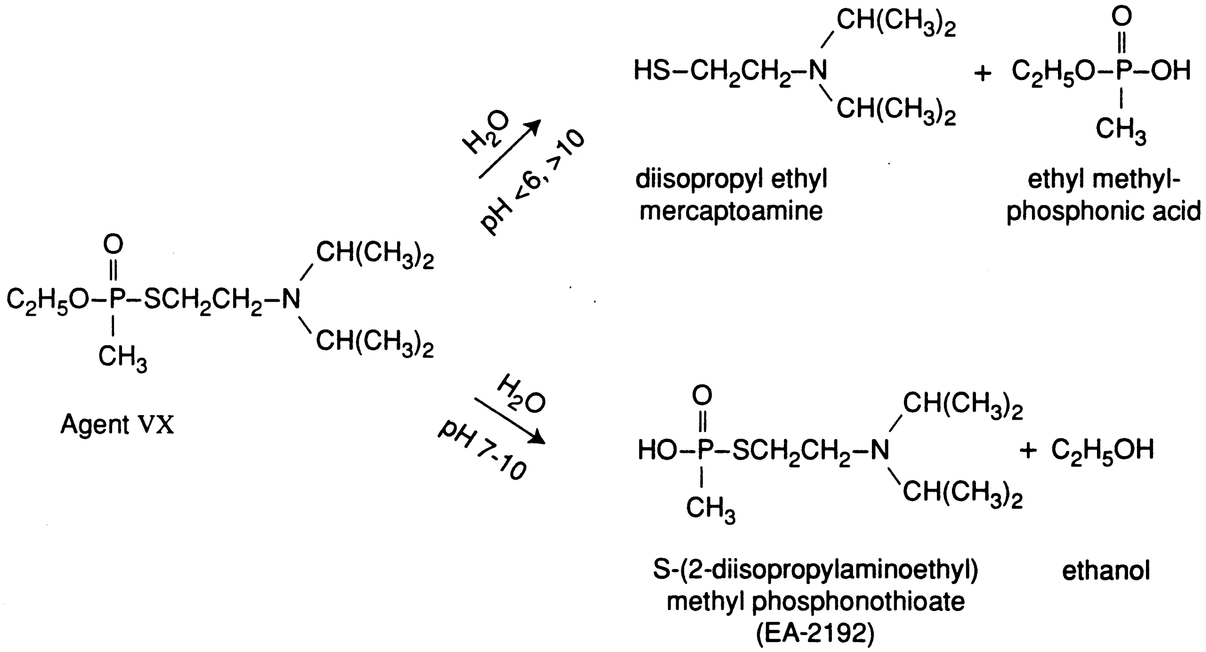
[12] Yu-Chu Yang, Chief Scientist PMACWA, personal communication to the committee on June 27, 2003.

[13] Yu-Chu Yang, Chief Scientist PMACWA, personal communication to the committee June 27, 2003. See also U.S. Army (2002b).

This hypothesis is supported by the fact that urea crystals were observed during the filling of rockets and projectiles when GB agent RS lots were used (U.S. Army, 2002b).

VX Nerve Agent

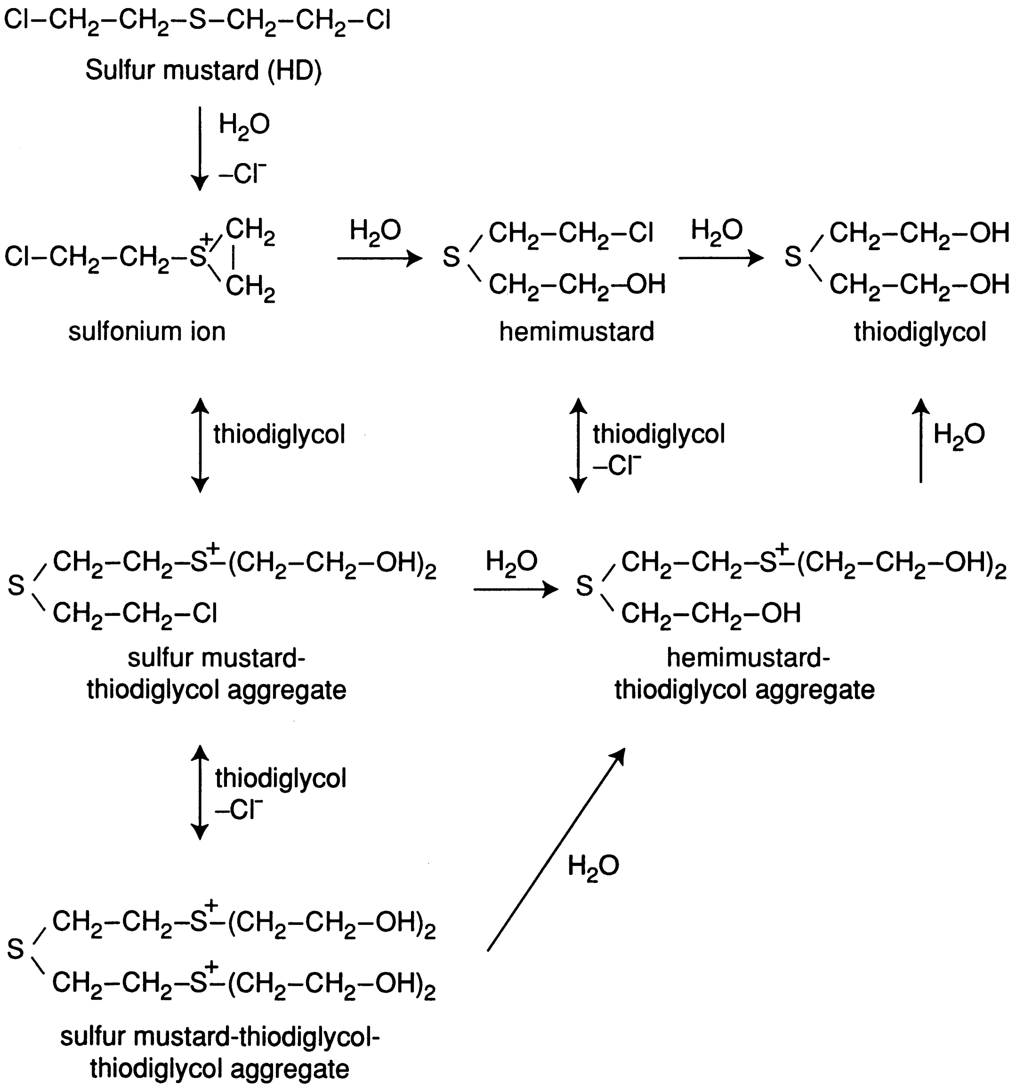
Hydrolysis of VX agent occurs by cleavage of the P—S bond under acidic or alkaline conditions or by cleavage of the P—ethoxy bond under near-neutral conditions (Munro et al., 1999; NRC, 2001a):



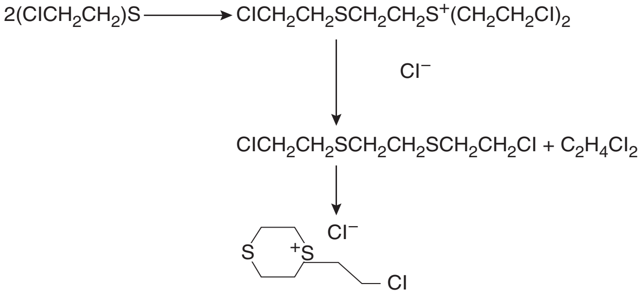
The latter pathway yields the toxic degradation product EA-2192. Other reaction products are listed in Table 2-2. Since the electron-donating tertiary amine group present in VX makes this agent a Lewis base, the hydrolysis rates are slow (Wojciechowski and Goetz, 2002). As a consequence, VX is expected to have a long storage lifetime, with little or no acidic attack on steel containers and little or no bimetallic electrochemical reaction at metal junctions. But since VX is a highly toxic material, these assumptions may need to be verified, as a precaution. Note that at least one of the decomposition products above (ethyl methylphosphonic acid) is acidic. An Arrhenius activation energy of 23 kcal/mole has been estimated for VX decomposition (Evans, 1999).

Mustard Agent

Mustard agent H (bis-2-chloroethyl sulfide) undergoes the complex sequence of hydrolysis reactions shown below (Bizzigotti et al., 1998; Munro et al., 1994; NRC, 2001a).



A further degradation mechanism is responsible for the formation of the solid or semisolid residues ("heels") that are present at 20-30 percent of the total volume of HD in stored ton containers. Recent tests on mustard-filled projectiles stored at DCD found that up to 70 percent of the agent fill was present as heels (Novad, 2003). The main constituents of these heels have been identified as a cyclic six-membered ring sulfonium ion, S-(2-chloroethyl)-1,4-dithianium chloride, entrained HD, and dissolved iron (Yang et al., 1997). The mechanism responsible for the formation of the dithianium ion is as follows:



The dithianium ion has been identified and characterized by ^{13}C cross polarization magic angle spinning nuclear magnetic resonance and by liquid chromatography/electrospray mass spectrometry (Rohrbaugh and Yang, 1997; Wagner and Yang, 1999). Both the hydrolysis and heel-forming reactions can lead to corrosion of the steel container materials as well as the brass valves and fittings that were used originally in the bulk (ton) containers. Hydrochloric acid reacts with iron to produce ferrous chloride and liberate hydrogen gas; the latter is responsible for the frothing[14] ("champagning") encountered when some mustard rounds are opened. Thiouronium salts absorbed on steel surfaces can also lead to corrosion via a dehydrohalogenation-like mechanism, giving Fe^{++} ion, vinyl chloride, dithiane, and hydrogen. All of these products of mustard decomposition have been observed during sampling and analysis programs conducted by the Army, including SUPLECAM.

In recent tests, mustard-filled projectiles stored at DCD were opened and drained at CAMDS in preparation for agent destruction at PUCDF. It was found that in many cases only 3 to 4 lb of the 11 lb of agent fill could be drained; the rest of the material remained solidified in the munition casing (Novad, 2003).

DETERIORATION PROCESSES FOR ENERGETIC MATERIALS

At the time this report was prepared, the chemical stockpile included 367,000 M55 rockets (276,000 GB; 91,000 VX), each filled with 10.7 lb of GB or 10.1 lb of VX, respectively. To date, more than 80,000 M55 rockets have been destroyed in the campaigns at JACADS and TOCDF. Since these rockets were manufactured in the early to mid-1960s, the average age of the remaining rockets is now about 40 years. Deterioration of energetic materials has been recognized as a potential source of autoignition in these rockets. A series of studies and reports has investigated this issue (e.g., GAO, 1994; NRC, 1994b; U.S. Army, 1988d, 1994). More recently, a comprehensive and substantive evaluation of the autoignition potential, drawing on past theoretical and empirical studies, concluded that risk of autoignition is small compared with risk of ignition from external sources such as lightning strikes (U.S. Army, 2002c). See Table 4-3 for details.

Nevertheless, because GB M55 rockets have been identified as posing increased risk and because of the uncertainties inherent in the risk estimates, the Army's decision to expedite their destruction early in the disposal schedule for each site is certainly prudent. Although M55 rockets containing VX are less likely to autoignite than those containing GB, the disposal of rockets in general remains a priority.

OBSERVED LEAK FACTORS AND OCCURRENCES BY MUNITION TYPE

A memorandum dated April 10, 1996, from Donald E. Brooke summarizing postmortem investigations conducted on chemical munitions was used as a framework for the information on leakers and factors contributing to such occurrences that is presented in Appendix B (U.S. Army, 1996b).

SUMMARY

This chapter, with Appendixes A and B, provides a fairly detailed description of the degradation processes affecting chemical agents and (to a lesser degree) pro-

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[14] "Champagning" is sometimes used by the Army to describe this reaction and its manifestation during projectile opening operations.

pellants in stored munitions. While stabilizers were added to GB and VX at the time of manufacture to retard decomposition, these stabilizers have degraded over time. The resulting acidic decomposition products may corrode metal containment vessels, leading to agent leakage (particularly for GB). The decomposition mechanism is such that agent degradation may be expected to accelerate at elevated temperatures and longer storage times; these hypotheses are explored in Chapter 3.

Additional anomalies were identified that may affect subsequent processing of munitions in demilitarization activities. These include mechanical defects, improperly assembled munitions, gelling or solidification of agent fills, pressurization, and contamination by substances such as lead or mercury. The processing consequences of these anomalies are explored further in Chapter 4.

3

Tracking and Analysis of Stockpile Leakers

Leaking munitions or containers (leakers) represent a unique class of stockpile anomaly that affects both storage and disposal operations. For this reason, the occurrence of leakers in storage igloos containing stockpiled chemical munitions and containers has long been subject to attention and tracking. The Army has had programs in place to monitor and inspect stored chemical munitions and containers for leakers since their manufacture. The original intent of the program was to identify problems that would affect the battlefield readiness of the munitions. Both the U.S. Army Soldier and Biological Chemical Command (SBCCOM) at Aberdeen Proving Ground, Maryland, and the U.S. Army Technical Center for Explosives Safety of the Defense Ammunition Center in McAlester, Oklahoma, have been responsible for monitoring and inspecting the stockpile and maintaining databases.

Members of the Stockpile Committee visited both of the above organizations to review and gather information on these databases.[1] This chapter discusses the occurrence and measurement of leaking munitions in the chemical stockpile. The committee primarily considered the database provided by SBCCOM but also referred to the Defense Ammunition Center data as needed. The committee also developed several new data fields to facilitate its analyses. It used a commercial statistics software program (Minitab) to analyze the leaker data and to determine if any significant trends were discernible.

In a briefing to committee members in July 2002, SBCCOM explained how data had been obtained and how the Stockpile Tracking System (STS) database has been used. Since 1973, there have been three distinct periods when different inspection protocols were used. Until 1984 (Period I), the primary focus of Army monitoring was to obtain data on the frequency of leakers, with the goal of ascertaining the combat readiness of the munitions rather than identifying the leakers per se or their sources.[2] In 1984, when the Resource Conservation and Recovery Act (RCRA) became applicable to the stockpile, new regulations required more information to be gathered and maintained at facilities where

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[1] Destruction of the chemical agent and munitions stockpile on Johnston Island was completed at Johnston Atoll Chemical Agent Disposal System (JACADS) in November 2000. By March 2002, destruction of all GB munitions stored at Deseret Chemical Depot (DCD) was completed at Tooele Chemical Agent Disposal Facility (TOCDF). Leaker data from these destroyed munitions were included in the database used for the statistical analyses in this report.

[2] Identification of a leaker required the parent ammunition lot to be declared unserviceable, adversely impacting the Army's readiness posture. Currently, the Army monitors for leakers and mitigates the consequences associated with their occurrence because such efforts are directly linked to safe storage of the stockpile.

chemicals and various classes of chemical wastes were stored.[3] At stockpile sites, the implementation of the RCRA regulations coincided with the replacement of relatively unsophisticated techniques, such as paper tape (which was able to detect only relatively high levels of liquid agent), by much more sensitive means.

From 1984 to 1991 (Period II), the Army also conducted a program of limited intrusive sampling for detection of internal munition leakers (the program was called SUPLECAM). Approximately 0.0145 percent of stockpiled munitions were tested in this manner (see Chapter 2).[4] At the same time, the Army continued to monitor the overall stockpile externally using the more sensitive instruments that were becoming available. During this period, leakers were recorded in the STS database in one of two ways: SUPLECAM or "standard."

After 1991 (Period III), the Army developed new inspection protocols under its storage monitoring and inspection (SMI) program, in accordance with procedures detailed in Army Supply Bulletin SB 742-1 (U.S. Army, 1998a). These protocols have been used ever since for monitoring the chemical stockpile for the presence of leakers. Thus, monitoring and inspection protocols changed during three distinct periods. In each period, the motivation for the protocols used was different. As discussed below, the committee primarily used data developed during Period III, although some analyses were performed using data from Periods I and II to help provide a historical context.

The committee performed various analyses that encompassed all types of munitions, even as it recognized that the Army has placed appropriate emphasis on monitoring and inspecting GB M55 rockets for leakers in recent years (U.S. Army, 1997; SAIC, 2002). It should be noted that the Army continued to monitor all munitions for leaks while performing more comprehensive inspections of GB M55 rockets.[5] This emphasis on inspecting GB rockets is a prominent feature of some of the data presented later in the chapter. In addition, the committee focused on the leaker data for stockpile munitions at one storage site, the Anniston Chemical Activity (ANCA), near Anniston, Alabama. This site, which has 661,529 stockpile items containing 2,254 tons of agent, or 7.4 percent of the original stockpile tonnage, has experienced the second highest incidence of leakers since 1991 (Period III) (U.S. Army, 1995b). (The largest number of leakers occurred at the Deseret Chemical Depot (DCD) near Tooele, Utah, which originally had 1,138,488 items containing 13,616 tons of agent, or 44.5 percent of the original stockpile tonnage. All GB munitions at DCD have been destroyed.)

THE ARMY'S STORAGE MONITORING AND INSPECTION PROGRAM

The SBCCOM Stockpile Tracking System (STS) database is the primary source of agent and munition information (Studdert, 2002). It has been used by the Army as a basis for analyses of the stockpile to generate data reports and to maintain specific information on the stockpile. The parameters included in the database (before any additions by the committee) are chemical activities (storage locations of the munitions), munition models (M104, M110, etc.), munition types (rocket, bomb, cartridge, mine, etc.), munition classes (105-mm, 155-mm, etc.), component types with associated component models (burster casings, burster charge, etc.), munition names, and numerical identifiers.

Another source of data is the STS Lot Book (U.S. Army, 2001a), which provides complementary munition and agent information pertinent to the STS database and which is periodically updated by the Army. The STS Lot Book provides information on leakers and other suspected munition anomalies based on processing experience at JACADS and TOCDF. The information is largely (but not exclusively) lot-specific and includes some one-of-a-kind occurrences.

The STS database covers the geographic distribution of munitions (eight sites in the continental United States and one on Johnston Island in the Pacific Ocean). In concert with the STS Lot Book, it describes the anomalies that have been observed in the chemical stockpile over time. Not all data are directly comparable because of the differences in monitoring protocols during the three periods noted previously: Period I, before 1984; Period II, 1984 to 1991; and Period III, after 1991.

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[3] In 1982, M55 chemical rockets were declared obsolete and of no military value. These rockets were declared hazardous waste in August 1984 (SAIC, 2002).

[4] Kevin Dolan, U.S. SBCCOM, e-mail to the committee, February 20, 2003.

[5] In this discussion, monitoring refers to examination of the munitions stockpile with leak detection instruments to determine whether a leak occurs. Inspection refers to visual examination of leaking munitions once they are detected during monitoring operations.

The committee concluded that Period III data for the 10-year period from 1992 through 2001 are the most reliable for a number of reasons:

- In Period I, some rocket lots were designated as leaker lots if only one or a few leaking munitions were found. This designation did not result in an overcount of leakers. It did, however, result in closer monitoring of those lots because they were considered more likely to harbor future leakers.
- Since 1991, improved detection methods and more sensitive equipment have contributed to better detection.
- Also, since 1991, no intrusive inspections have been conducted on internal parts of munitions. Prior to 1992, internal (within a munition) and external (exterior to a munition) leakers were not differentiated in the database.

A significant aspect of the database is that the monitoring protocols for both Period II and Period III are more reliable than those for Period I. Early on, much less sensitive monitoring (paper tape) was used that might not have been able to detect leakers that could be detected by more sophisticated inspections. (New monitoring techniques were introduced in 1984 that improved detection sensitivity by a factor of 8,000.) In Period II, there was a strong emphasis on intrusive SUPLECAM sampling. In Period III, there has been a strong emphasis on inspecting GB munitions (particularly M55 rockets), which have been the source of the majority of leakers. The Period III monitoring procedures are more rigorous than those in earlier periods, ensuring that all leakers are identified in the year they begin to leak. In addition, the data do not include information on munitions that were inspected but not found to leak; in this sense, all the data sets are incomplete for other than leakage information.

Table 3-1 provides the Army's current SMI requirements for all munitions and containers. Under the current SMI program (Period III), all structures holding the entire chemical stockpile (including the site holding the limited outdoor stockpile of ton containers at Aberdeen Proving Ground, Maryland) are subject to quarterly monitoring and, if necessary, inspection. If agent is not detected in an igloo, it is assumed that none of the munitions in that igloo leak (if agent is detected, the igloo will be entered by personnel in protective gear). Specific guidance states that each item is to be visually inspected for evidence of leakage, condition of the outer pack, dunnage, or any other condition affecting its suitability for continued safe storage. Items, whether in the original shipping and storage container or in overpacks, are to have the outer pack inspected without opening (U.S. Army, 1998a). Once identified as leaking, a munition is segregated from nonleaking munitions, overpacked, and stored separately. While a new generation of overpacks is now in use, the early overpack containers were "acceptable containers of convenience," and it was not uncommon for the overpacks themselves to leak, sometimes more than once. Even though only the leaking munition in the overpack is the ultimate source of a leak from an overpack, a leaking overpack is always reported as a separate leak. Rocket lots that are identified as "leaker lots" are inspected more often.

TABLE 3-1 SMI Requirements for Toxic Chemical Items

Item	Not Overpacked	Overpacked
Ton containers	Quarterly	N/A
Mines	Annual	Quarterly
Projectiles/cartridges	Annual	Quarterly
Bombs	Annual	Quarterly
Spray tanks	Quarterly	Quarterly
DOT bottles	Quarterly	Quarterly
Rockets	Quarterly	Quarterly
SUPLECAM samples	Quarterly	Quarterly
M56 warheads	N/A	Quarterly
Binary components	Quarterly	N/A

Source: U.S. Army (1998a).

Under the monitoring protocols of Periods I and II, a procedure similar to that described above for Period III was used—namely, igloos were entered to determine if a leak had occurred and if it had, the leaker was identified and moved to an overpack igloo. In principle, these protocols were able to identify all leakers that occurred in a given year. Nevertheless, it is probable that many leakers were not detected during Period I.

During SMI inspections conducted according to the frequencies shown in Table 3-1, the storage structures are monitored to an 8-hour time-weighted average (TWA) exposure limit[6] for the type of agent stored

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[6] The TWA exposure limit represents the mean allowable level to which workers can be exposed for 8 hours over the course of a 40 hour/week working lifetime with no adverse health effects.

therein. The follow-up inspections require that personnel enter the storage structures in appropriate personal protective equipment. Moreover, monitoring to the TWA limit from external inspection ports is conducted once daily for igloos containing leaker lots of nonoverpacked GB M55 rockets. Igloos with nonleaker lots or overpacked leakers are monitored at least once a week (Studdert, 2003).

Figures 3-1, 3-2, and 3-3 were prepared by the Army. As far as the committee knows, no statistical analysis of the data was carried out by the Army.

Figure 3-1 depicts leaker data gathered from monitoring during Periods I, II, and III (see also Table 3-2). The data for overpacks and rockets are presented by year; they include leaking munitions from all sites. The more than 500 leakers detected in 1981 resulted primarily from a 100 percent inspection of one type of munitions at DCD. This inspection was carried out because the Army had reason to believe that there were a large number of leakers among these munitions. While it was suspected at the time that GB M360 105-mm projectiles were the principal source of leaks, M55 rockets were subsequently determined to be of greater concern in this regard. The data for 1981 show, as indicated above, that when the occurrence of leakers was more intensively investigated during Period I (e.g., by inspecting 100 percent of a munition type), more leakers could be found. Figure 3-2 shows data similar to the data in Figure 3-1, but for the Anniston stockpile only. It is probable that many of the leakers detected in 1981 had started leaking earlier but were missed because of the relatively poor sensitivity of the detection equipment and the incomplete monitoring that took place at that time.

Figure 3-3 shows the number of leakers by munition type in the overall stockpile. The data in Figure 3-3 and the summary data in Table 3-3 include all types of leakers (internal, external, and overpack). Figure 3-3 shows that GB M55 rockets have the highest number of leakers, almost equal to the number of leakers from all other munition types combined. The highest number of leakers occurs in GB munitions, as indicated in Table 3-3. H munitions show a higher percentage of leakers than GB munitions, but these H munitions comprise a relatively small number of projectiles, located primarily at DCD. Furthermore, H is much less volatile than GB.

The GB in the stockpile comprises several subtypes

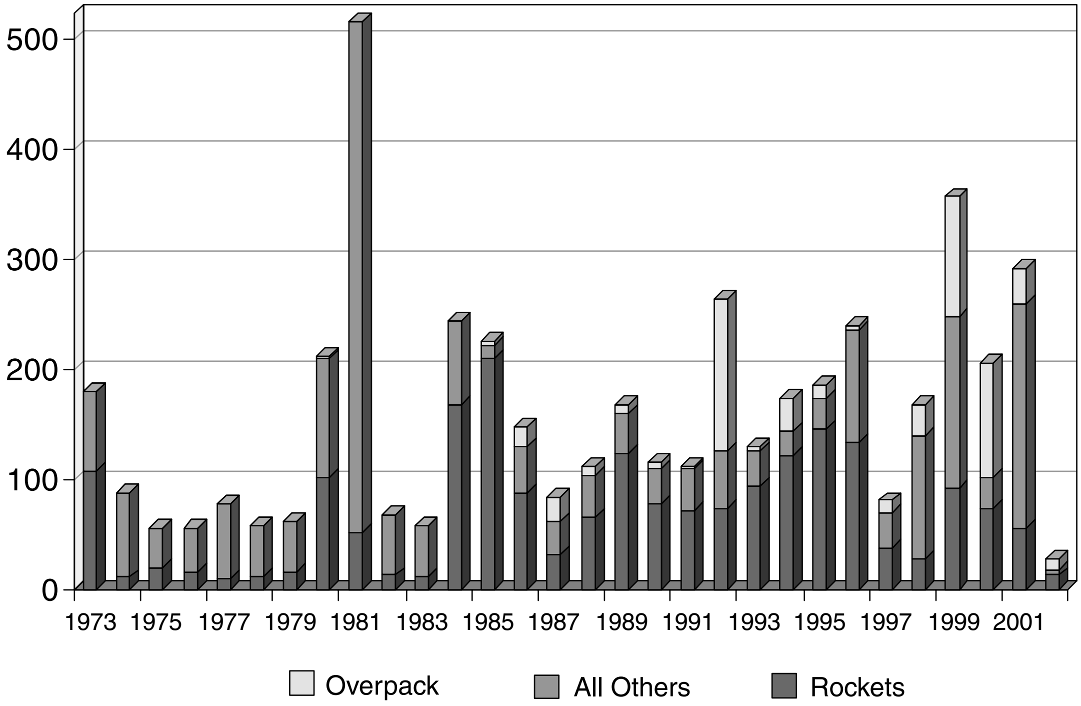

FIGURE 3-1 Distribution of leaking munitions in the U.S. chemical weapons stockpile from 1973 to June 30, 2002. Source: Studdert (2002).

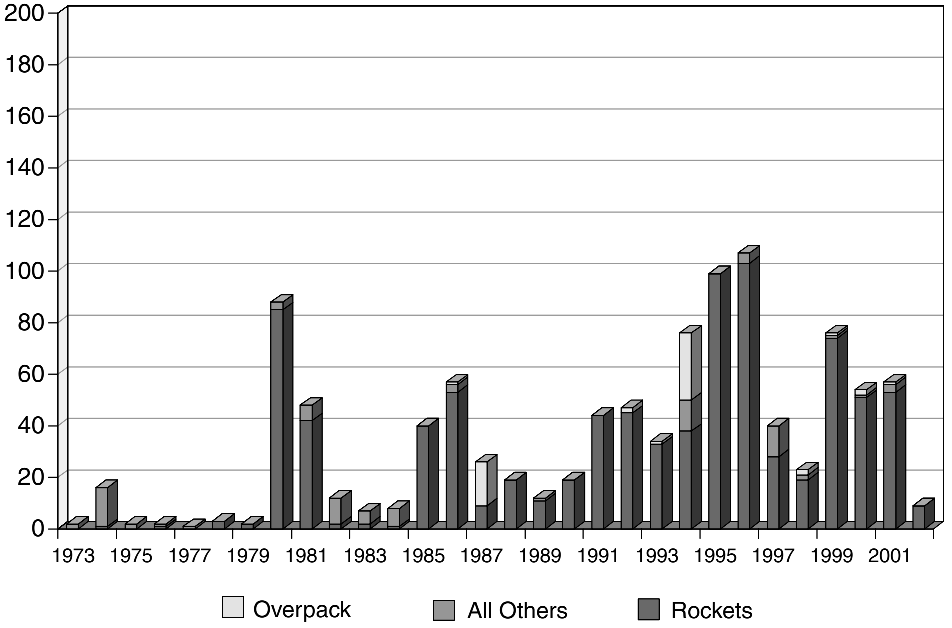

FIGURE 3-2 Distribution of leaking munitions in the Anniston stockpile from 1973 to June 30, 2002. Source: Studdert (2002).

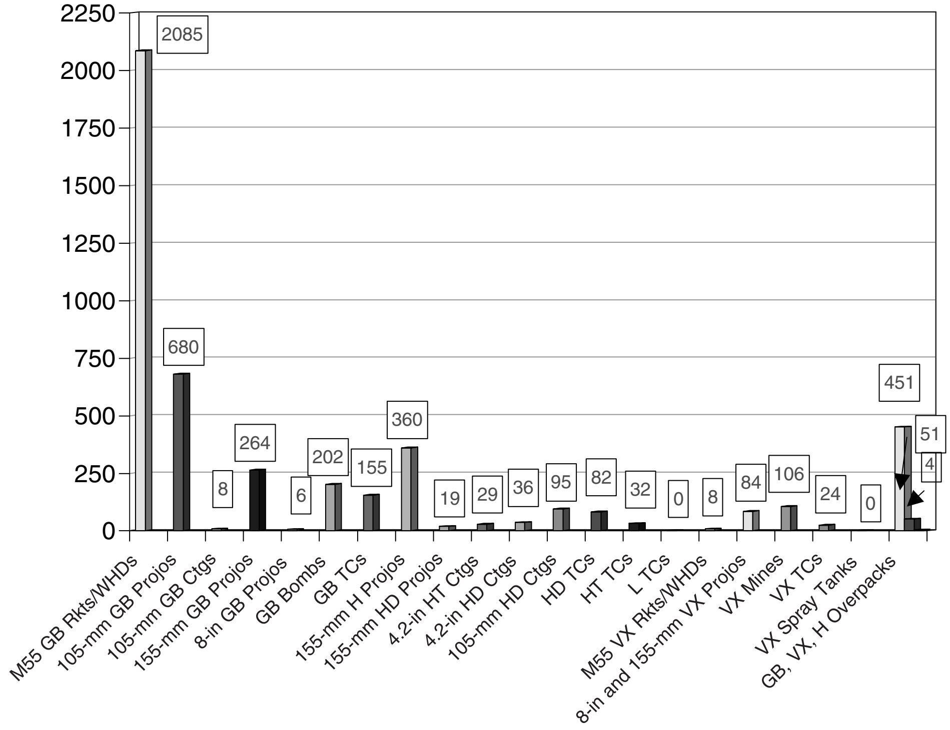

FIGURE 3-3 Number of leaks by munition type, all sites. Key: TC, ton container; WHD, warhead; Projo, projectile; Ctg, cartridge. Source: Studdert (2002). Category Information: GB rockets, M55: includes rockets (H520) and rocket warheads; GB projectiles, 105-mm M360 (C766, formerly 1315-7906); GB cartridges, 105-mm, M360 (C441); GB projectiles, 155-mm: includes 155-mm M122 (D483) and 155-mm M121/M121A1(D542); GB bombs: includes Weteye (E832), 500 lb MK94-0 (E384), and 750 lb MC-1 (E388); VX rockets, M55: includes rockets (H521) and rocket warheads; and overpacks: collated quantity for all overpack failures: 451 GB overpacks, 51 VX overpacks, and 4 each of H/HD/HT overpacks failed.

TABLE 3-2 Total Number of Leakers for All Years, All Sites, and All Categories[a]

Year	Category 1	Category 2	Category 3	Category 4	All
1973	180	0	0	0	180
1974	88	0	0	0	88
1975	56	0	0	0	56
1976	57	0	0	0	57
1977	78	0	0	0	78
1978	58	0	0	0	58
1979	63	0	0	0	63
1980	211	0	2	0	213
1981	516	0	0	0	516
1982	68	0	0	0	68
1983	59	0	0	0	59
1984	244	0	0	0	244
1985	223	0	3	1	227
1986	131	0	15	3	149
1987	63	4	17	1	85
1988	105	1	5	1	112
1989	161	0	2	5	168
1990	111	5	0	0	116
1991	110	0	2	1	113
1992	126	1	0	138	265
1993	127	2	0	1	130
1994	145	2	0	27	174
1995	175	0	0	11	186
1996	237	2	0	1	240
1997	70	5	0	6	81
1998	141	3	1	24	169
1999	249	73	0	36	358
2000	103	87	0	16	206
2001	260	15	0	19	294
2002 (through June)	25	11	0	0	36
All	4,240	211	47	291	4,789

[a] See Box 3-1 for category descriptions. Period I, 1973-1984; Period II, 1984-1991; Period III, 1992 forward.

TABLE 3-3 Munition Leakers by Type of Agent

Agent	GB	H	VX	HD	HT
Stockpile quantity	1,546,387	77,498	497,175	931,945	270,135
Number of leakers	3,859	360	273	236	61
Percent leakers	0.25	0.46	0.05	0.03	0.02

Source: Studdert (2002).

TABLE 3-4 M55 GB Rocket Sampling Plan and M55 GB Rocket Storage Monitoring Inspection[a]

	Quarterly[b] Sample Size by Lot Category[c]		
Lot Size	Category A	Category B	Category C (Leaker Lots)
0-25	8[d]	20[d]	100%
26-150	16[d]	44[d]	25[e]
151-300	6	16	40[e]
301-750	9	23	64
751-3,000	12	30	75
>3,000	15	35	85

[a] Storage inspection entails monitoring the interior of M441 shipping and firing tubes.
[b] Unless otherwise indicated.
[c] Category A – no leaks occurred; Category B – one or more leaks occurred but not considered a leaker lot; Category C – numerous leaks occurred and considered a leaker lot.
[d] Quantity indicated is to be sampled every 3 years. This sampling may be accomplished at one time within the 3 years or in increments as determined by the QASAS-in-Charge.
[e] When total annual sample size exceeds the lot size, the lot will be sampled 100% each year. This 100% sampling may be accomplished at one time within the year or in increments as determined by the QASAS-in-Charge.
Source: Adapted from Studdert (2002).

based on the manufacturing history, the stabilization techniques employed, and the type of stabilizer used (see Chapter 2 for details). The frequency of leaking munitions containing GB is a function of subtype.

In 1984 and 1985 (onset of Period II), the Army increased both the frequency and number of its inspections to detect leaking GB rockets. At that time, the Army was beginning to recognize that the largest number of leakers was occurring in GB munitions. This resulted in more aggressive monitoring using instruments that were more sensitive—that is, the new instruments were able to detect much lower levels of agent than what had been previously used.[7] The increased inspections were undertaken to make certain that the problem of leaking GB munitions was understood. Subsequently, entries became more frequent and more munitions were inspected for possible leaks. Here, the inspection protocol led to an increase in the number of GB rockets inspected from GB lots (batches of munitions) that had a propensity to develop leakers (Studdert, 2002). The SBCCOM-specific SMI protocol for inspecting these rockets, where lots were categorized as A, B, or C on the basis of leaker history, is summarized in Table 3-4. Category A lots are those in which no leakers occurred. Category B lots are those that experienced one or more leakers but were not designated as leaker lots. Category C lots are those that experienced numerous leakers and have been designated as leaker lots. Sampling protocols mentioned in Table 3-4 refer to inspections, not to the basic leaker monitoring that is used to identify leaks in the first place. The sampling covered in Table 3-4 does not relate specifically to the statistical analysis discussed below.

By way of background, the Army uses two types of reports to report leakers. The first is a "chemical event report" (U.S. Army, 2001b), which reports any chemical event that releases agent outside of engineering controls. The second is a "leaker report" (U.S. Army, 1998a), which reports any munition(s) that are leaking upon inspection. The leaker reports contain all the technical information available about each leak. They are the basis for compiling the STS database and for reports derived from that database. The two types of reports serve different purposes and are administered under different regulations by different organizations.

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[7] These actions also produced a substantial increase in the number of leakers detected in 1984 and 1985 relative to 1983 (see Figure 3-1 and Table 3-2). Again, it is probable that many of these leakers occurred before 1984 but went undetected at the time.

Thus, not all leakers reported in the leaker reports are reported as a chemical event and vice versa. Consequently, the leaker reports and the STS database were the primary sources of the information gathered on leakers for this report because they are more specific to the phenomena of interest.

Technical data in leaker reports are used as a management tool to minimize risk associated with the storage of the chemical stockpile (Studdert, 2002). They do this by

- Identifying leakage trends among specific munitions families, manufacturers' lots, and agent populations;
- Establishing or modifying the scope and frequency of surveillance inspections and special studies;
- Prioritizing resources to maximize benefits (e.g., installation of engineering controls on selected magazines or during specific operations);
- Sharing information with PMCD to facilitate lot scheduling within disposal campaigns for specific munition types and for developing site-specific quantitative risk assessments; and
- Providing the basis for response to queries from DOD, DA, and AMC; response to media queries and FOIA requests; response to requests from non-DOD agencies (GAO, CDC, NRC, etc.); negotiation with state environmental agencies; and legal defense during litigation.

STOCKPILE LEAKER DATA

This section describes the STS leaker database for the entire stockpile for the period from 1973 through June 2002, with particular emphasis on the data obtained since 1992 (Period III). The data for Periods I and II are included and addressed in certain instances to assist in placing the Period III materials in appropriate perspective. For reasons that will be discussed below, data from Periods I and II are limited to time-independent analyses, i.e., the Pareto charts. The section also discusses how additional information on the temperature history in storage igloos could make the database more useful for elucidating trends in leaker frequency.

SBCCOM provided the committee with access to the STS database, wherein 4,789 leakers had been documented in 2,792 separate reports from 1973 through June 2002 through its various monitoring programs. These data are shown in Table 3-2, where the leakers are arranged into four categories. Category 1 contains leaks attributable to deterioration of the original item; Category 2 contains leaks from an overpack of an item that leaked in the past; Category 3 contains leaks detected during SUPLECAM or other reliability programs in items that had not previously leaked; and Category 4 contains leaks associated not with deterioration but with, for example, ineffective maintenance and dropped pallets.

The committee, with SBCCOM assistance, added several new fields for additional data. The data were entered into a Microsoft Excel spreadsheet, which was then exported into a statistical software program (Minitab). As discussed previously, statistical analyses were conducted for Period III data obtained during the years 1992 through 2001. As noted above, during that period, the Army recorded 2,103 leakers for all agent and munition types in the stockpile; these leakers generated 1,258 leaker reports.

Twenty-five fields in the STS database as modified by the committee were applicable to the committee's efforts. These fields, with explanatory text given in parentheses where necessary, are listed in Box 3-1.

Various mechanisms for leak formation were discussed in Chapter 2. In general, and especially for GB, leakers can be a result of chemical attack or a result of mechanical failure from bad welds, poor machining, and so forth. The several GB agent subtypes (PRO, PR-RS, RO-RS, RD-RS) in the stockpile have varying purities and stabilizer constituents and concentrations (see Chapter 2). The GB subtype reflects the manufacturing lot and subsequent treatment history of the agent. The composition of the GB agent subtypes affects the degree of acid attack on the metal components of munitions and thus the propensity for leaks to develop.

As discussed in Chapter 2, temperature can affect the rate at which the stabilizer in GB degrades. The rate of agent degradation can also be expected to differ among GB agent subtypes and will also be time and temperature dependent. The time dependence is a function of the concentration of stabilizer. The average ambient temperature at different storage sites is likely to vary. The interior temperatures of storage igloos at each site over time could be a significant variable in the rate of degradation and the extent to which degradation reactions proceed, whatever the GB agent subtype or the type of stabilizer.

The STS database contains reasonably good information on the age of the more than 3 million items recorded.

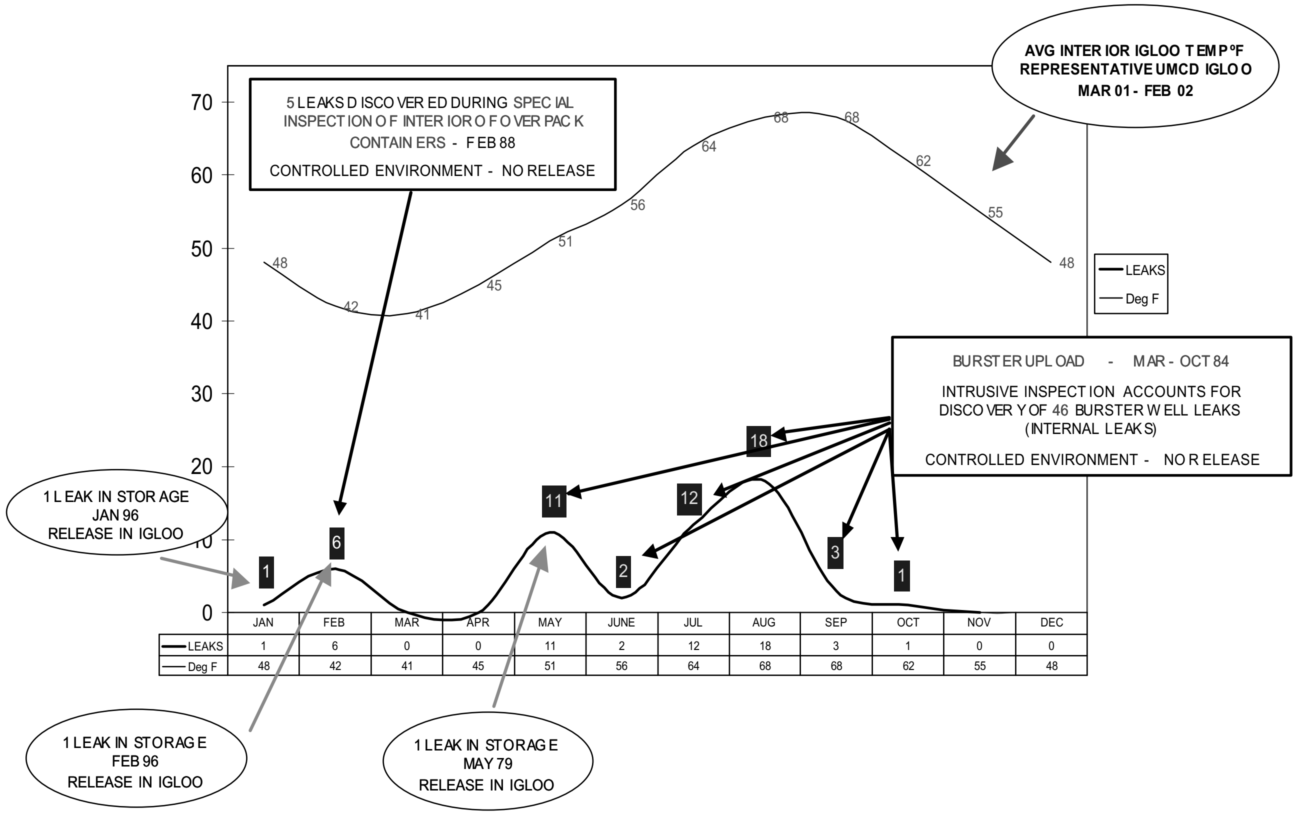
Box 3-1
STS Database Fields Used by the Committee

1. Site (the specific site at which the munition is stored)
2. DODIC (Department of Defense Identification Code), which identifies munitions by a four-position alphanumeric code. (Appendix A describes the various DODIC codes and what munitions they refer to.)
3. MSN (manufacturer stock number)
4. Agent Type (VX, GB, etc.)
5. Lot Number (manufacturing lot number)
6. Quantity at Site (original) (number stored at a site before destruction)
7. Detection Date of Leak (Date at which a particular leak was detected)
8. Year Detected (derived from previous column)
9. Category (Category 1 leaks are those attributable to deterioration of the original item; Category 2 leaks are those from an overpack of an item that leaked in the past and was overpacked to contain leakage; Category 3 leaks are those occurring in items sampled during the SUPLECAM program or other stockpile reliability tests that had not previously leaked, even if the item was overpacked as a precautionary measure; Category 4 leaks are those that explain any leaking item that does not fall clearly into one of the three previously stated categories, e.g., ineffective maintenance (replaced brass valves with steel plugs on ton container, which leaked the following day); dropped pallet while loading onsite container for shipment to disposal facility, initiating leakage (U.S. Army, 1998a)
10. Exudate (a type of leak)
11. Liquid (a type of leak)
12. Vapor (a type of leak)
13. Total Leaks (the sum of columns 10, 11, 12)
14. Leaker Report Number
15. Munition Type (rocket, mine, etc.)
16. Munition Class
17. Munition Model
18. Manufacturing Date
19. Manufacturing Year
20. Manufactured Quantity
21. GB Agent Subtype (characterized by manufacturing criteria and subsequent treatment of specific agent lots)
22. Difference (original number minus destroyed munitions, i.e., remaining munitions at any given time)
23. Demilitarization Date
24. Age at Demilitarization
25. Period (I = pre-1984, II = 1984-1991, III = post-1991)

However, information over time on the interior temperatures of storage igloos is sparse to nonexistent. Figure 3-4 is a representation of the only available data that relate storage igloo temperature to leaker rates; the data are for leakers of one type of munition (155-mm projectiles) at one site. To complicate matters, the degradation rate is related to the temperature of the agent in the munitions, and the igloo temperature may only be a surrogate for that parameter. Based on the very limited data presented in Figure 3-4, it is not possible to infer any correlation between degradation rate or leaker formation and temperature. Having more detailed information on the temperature inside igloos and on a wider range of munitions over a period of several years could be useful for ascertaining if there is a correlation.

STATISTICAL APPROACH OF THE STOCKPILE COMMITTEE

Approximately 3,300,000 munitions were in the original stockpile prior to destruction operations at JACADS and TOCDF. From the monitoring protocols used by the Army from 1973 to June 2002 to inspect the stockpile, 4,789 leakers were reported in the four categories described in the preceding section (see Item 9 in Box 3-1 and Table 3-2). This number includes some



AVG INTERIOR IGLOO TEMP °F
REPRESENTATIVE UMCD IGLOO
MAR 01 - FEB 02

5 LEAKS DISCOVERED DURING SPECIAL INSPECTION OF INTERIOR OF OVERPACK CONTAINERS - FEB 88

CONTROLLED ENVIRONMENT - NO RELEASE

BURSTER UPLOAD - MAR - OCT 84

INTRUSIVE INSPECTION ACCOUNTS FOR DISCOVERY OF 46 BURSTER WELL LEAKS (INTERNAL LEAKS)

CONTROLLED ENVIRONMENT - NO RELEASE

1 LEAK IN STORAGE
JAN 96
RELEASE IN IGLOO

1 LEAK IN STORAGE
FEB 96
RELEASE IN IGLOO

1 LEAK IN STORAGE
MAY 79
RELEASE IN IGLOO

	JAN	FEB	MAR	APR	MAY	JUNE	JUL	AUG	SEP	OCT	NOV	DEC
LEAKS	1	6	0	0	11	2	12	18	3	1	0	0
Deg F	48	42	41	45	51	56	64	68	68	62	55	48

FIGURE 3-4 Seasonal distribution of 155-mm projectiles leaker occurrences at Umatilla by month and igloo temperature. Source: Studdert (2002).

overpack leakers, which in the statistical context of munitions per se would constitute a double count. There are 4,240 leakers in Category 1, which does not include overpacks, SUPLECAM data, or leakers due to mechanisms other than deterioration. For Period III (after 1991), there are 1,633 Category 1 leaks, and these are predominately in munitions containing GB. Of these leakers, 578 are at ANCA and 846 were at DCD (the latter were destroyed). Of the 578 leakers at ANCA, 547 are GB-filled (across all GB subtypes); of these, 543 are M55 rockets. The number of M55 leakers by GB subtype are 101 PRO, 378 PR-RS, and 64 for which the data are incomplete and the identification uncertain.

The committee limited the data used for the analysis to Category 1 leaks to eliminate the double counting that would occur because of leakers in overpacks and to concentrate on leaks resulting from deterioration. Statistical tools included (1) Pareto charts; (2) descriptive statistics packages; (3) a chi-squared test; and (4) analysis of variance.

For statistical analyses of trends and variance by the committee (see below), only Period III data were used. For the Pareto charts, data from all three periods were used in order to gain perspective on the distribution of leaker types over the entire time the stockpile was monitored. Because the Pareto charts encompass the total number of leakers found during the entire 30-year period and are not dependent on the year a leaker was discovered, they are probably reasonable representations of the distribution of total leakers at Anniston. As argued above, it is very likely that leakers that went undetected early in the Army's monitoring activities (primarily in Period I) were eventually detected when detection sensitivity improved and monitoring became comprehensive.[8] Thus, any error introduced on a year-

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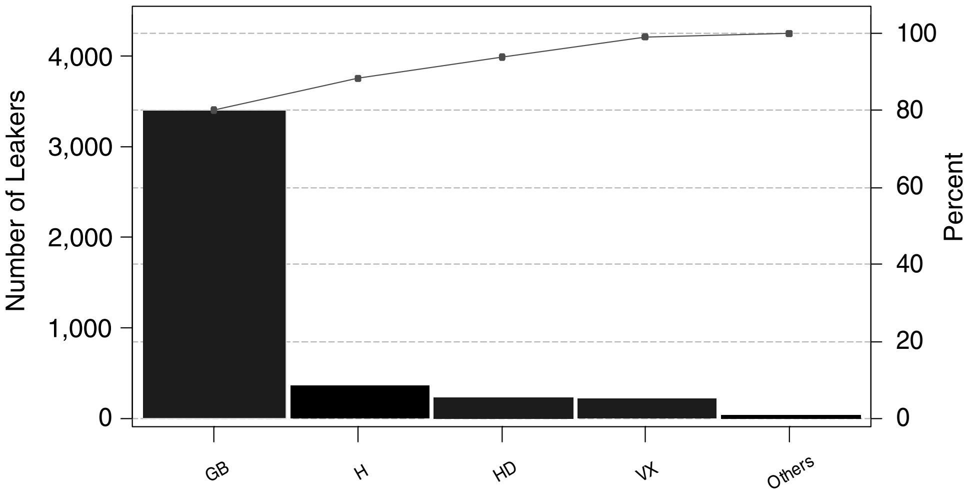
[8] This observation was confirmed by Lis Wachutka, Quality Assurance Specialist, SBCCOM, Aberdeen Proving Ground, Maryland, who noted in a private communication on December 22, 2003, that at least 99 percent of the external leakers over the 30-year period have been detected.



	GB	H	HD	VX	Others
Count	3,395	359	229	220	37
Percent	80.1	8.5	5.4	5.2	0.9
Cumulative (%)	80.1	88.5	93.9	99.1	100.0

FIGURE 3-5 Pareto chart indicating Category 1 leaks by agent (across all sites and including all munition types). Note: The term “other” refers to data for which there is no information as to the particular munition or to data for an agent not listed on the horizontal axis, such as lewisite.

to-year basis by imprecise monitoring procedures is probably not a significant factor over the course of a period.

Similar analyses can be done for other sites, for various combinations of sites, and for any number of subsets of data. One example of another analysis is contained in the PMCD report *Assessment of the Storage Monitoring Inspection Program for M55 GB Rockets*, which found that the limited inspection conducted under the SMI program was sufficient to determine the stability of the GB stockpile as a whole (U.S. Army, 1997). That report further concluded that the Army would be justified in continuing the SMI program, but that a more rigorous and robust protocol could enhance the SMI results (U.S. Army, 1997). Another example is a more focused and detailed assessment of a particular leaker lot of M55 rockets stored at the Anniston site. This is the subject of the report *Statistical Analysis of the Leakage History for Anniston M55 GB Rocket Lot 1033-45-181*, by the Science Applications International Corporation (SAIC, 2002).

Plotting data in Pareto charts (vertical bar graphs with bars in order of size from left to right) enables easy visualization of the data on leakers. Figure 3-5 is a Pareto chart showing the number of Category 1 leaks by agent type across all sites and all munition types for all the years covered by the STS database (Periods I, II, and III). It includes destroyed munitions as well as those still in storage. As indicated, 80.1 percent of the leakers contained GB; 8.5 percent, H; 5.4 percent, HD; and 5.2 percent, VX.

Figure 3-6 shows total Category 1 leaks by Department of Defense Identification Codes (DODICs) for lots and lot clusters of munitions at all storage locations.[9] Six of the first seven DODICs (H520, C766, D543, D483, K725, and D542) identify GB-filled M55 rockets, which account for over 80 percent of the leakers. The information contained in Figures 3-5 and 3-6 again illustrates that by far the largest number of leakers in the stockpile involve GB-filled munitions. These two figures aptly demonstrate the rationale of the Army for its increased inspections in recent years of GB-filled munitions, particularly M55 rockets, relative to other munitions.

Over three-quarters of Category 1 leaks to date have occurred at just two sites: Deseret Chemical Depot and Anniston Chemical Activity, as shown in Figure 3-7. This observation points to the desirability of a site-centric approach for the conduct of statistical analy-

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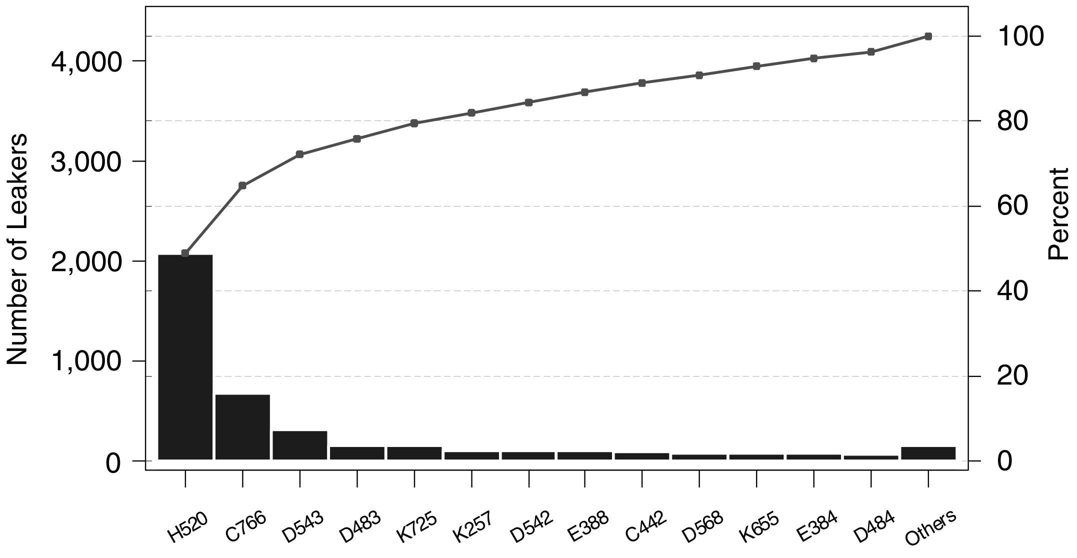
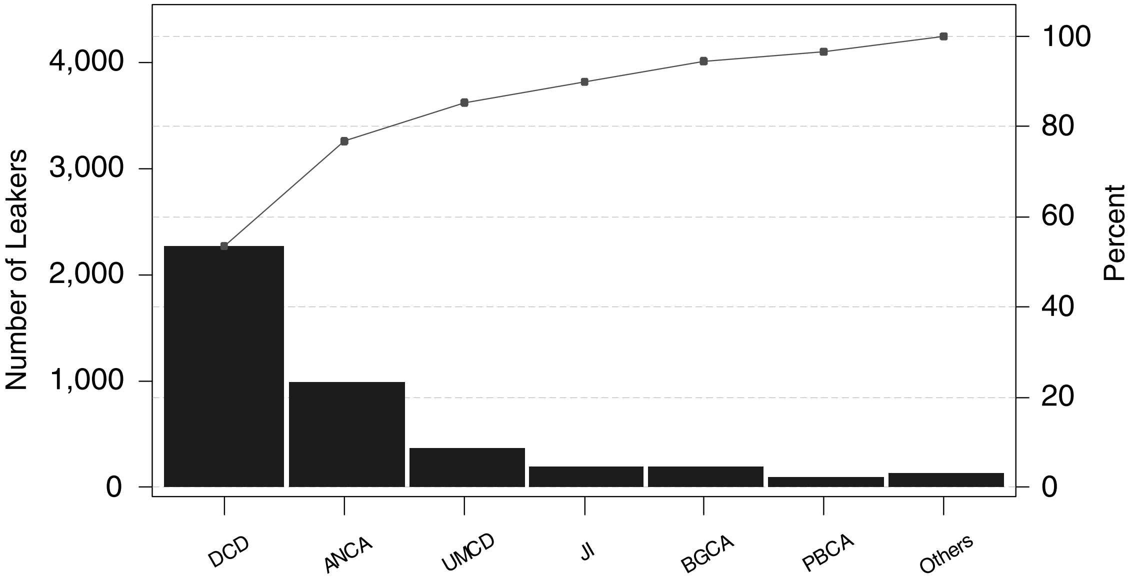
[9] DODICs are definitive identifiers of a type of munition.



	H520	C766	D543	D483	K725	K257	D542	E388	C442	D568	K655	E384	D484	Others
Count	2,076	680	306	157	155	106	102	100	95	83	82	76	69	153
Percent	49	16	7	4	4	3	2	2	2	2	2	2	2	4
Cumulative (%)	49	65	72	76	80	82	84	87	89	91	93	95	96	100

FIGURE 3-6 Pareto chart of Category 1 leaks by DOD Identification Code for all sites.



	DCD	ANCA	UMCD	JI	BGCA	PBCA	Others
Count	2,271	984	364	201	195	89	136
Percent	53.6	23.2	8.6	4.7	4.6	2.1	3.2
Cumulative (%)	53.6	76.8	85.4	90.1	94.7	96.8	100.0

FIGURE 3-7 Pareto chart of Category 1 leaks by site for all sites. See List of Acronyms in front matter for acronyms.

TABLE 3-5 Period III Category 1 Leaks at Each Site by Year

Year	ANCA	BGCA	DCD	JI	PBCA	PCD	UMCD	All
1992	45	24	44	5	2	1	5	126
1993	33	11	72	2	1	0	8	127
1994	50	2	88	0	3	2	0	145
1995	99	5	62	6	0	0	3	175
1996	107	5	46	64	1	12	2	237
1997	40	0	27	0	1	0	2	70
1998	21	2	113	0	2	0	3	141
1999	75	9	161	0	1	0	3	249
2000	52	7	37	2	2	1	2	103
2001	56	2	196	0	3	0	3	260
All	578	67	846	79	16	16	31	1,633

Note: See List of Acronyms in the front matter for site acronyms.

TABLE 3-6 Period III Category 1 Leaks at Each Site by DODIC

DODIC	ANCA	BGCA	DCD	JI	PBCA	PCD	UMCD	All
C441	4	0	2	1	0	0	0	7
C442	3	0	0	1	0	16	0	20
C698	1	0	2	0	0	0	0	3
C703	11	0	0	4	0	0	0	15
C766	0	0	217	0	0	0	0	217
D483	0	0	153	0	0	0	0	153
D484	0	0	5	0	0	0	0	5
D542	0	0	28	0	0	0	2	30
D543	0	46	79	0	0	0	0	125
E382	0	0	7	0	0	0	0	7
E384	0	0	0	69	0	0	0	69
E388	0	0	33	1	0	0	1	35
H520	543	21	248	1	15	0	21	849
K257	12	0	0	2	0	0	0	14
K655	4	0	13	0	0	0	4	21
K665	0	0	0	0	1	0	0	1
K725	0	0	39	0	0	0	3	42
K732	0	0	8	0	0	0	0	8
NA	0	0	12	0	0	0	0	12
All	578	67	846	79	16	16	31	1,633

Note: See List of Acronyms in the front matter for site acronyms.

ses—that is, an approach in which the particular mix of agent and munition types at a site is considered in determining whether apparent leaker rates are indicative of a trend over time.

Tables 3-5 through 3-9 present some examples of how Period III (1992-2001) data can be arrayed to highlight areas and munitions of concern and to help direct monitoring and management of the stockpile and processing sequence. In these cases, the data are from the inspections done according to Army protocols during Period III. Tables 3-5, 3-6, and 3-7 offer site-centric perspectives of leaker occurrences according to year, DODIC, and agent type, respectively. Leaker occurrences could be related to the ages of the leaker muni-

TABLE 3-7 Period III Category 1 Leaks at Each Site by Agent Type

Agent	ANCA	BGCA	DCD	JI	PBCA	PCD	UMCD	All
GB	547	21	739	72	15	0	27	1,421
H	0	46	84	0	0	0	0	130
HD	18	0	13	5	0	16	4	56
HT	1	0	2	0	1	0	0	4
VX	12	0	8	2	0	0	0	22
All	578	67	846	79	16	16	31	1,633

Note: See List of Acronyms in the front matter for site acronyms.

TABLE 3-8 Period III Category 1 Leaks by Agent Type and DODIC

DODIC	GB	H	HD	HT	VX	All
C441	7	0	0	0	0	7
C442	0	0	20	0	0	20
C698	0	0	0	3	0	3
C703	0	0	15	0	0	15
C766	217	0	0	0	0	217
D483	153	0	0	0	0	153
D484	0	5	0	0	0	5
D542	30	0	0	0	0	30
D543	0	125	0	0	0	125
E382	7	0	0	0	0	7
E384	69	0	0	0	0	69
E388	35	0	0	0	0	35
H520	849	0	0	0	0	849
K257	0	0	0	0	14	14
K655	0	0	21	0	0	21
K665	0	0	0	1	0	1
K725	42	0	0	0	0	42
K732	0	0	0	0	8	8
NA	12	0	0	0	0	12
All	1,421	130	56	4	22	1,633

TABLE 3-9 Period III Category 1 Leaks by Agent Type and DODIC for ANCA Site

DODIC	GB	HD	HT	VX	All
C441	4	0	0	0	4
C442	0	3	0	0	3
C698	0	0	1	0	1
C703	0	11	0	0	11
H520	543	0	0	0	543
K257	0	0	0	12	12
K655	0	4	0	0	4
All	547	18	1	12	578

tions for each year through additional analysis. Table 3-8 presents recorded leakers during Period III by agent type across all sites. The contribution from the ANCA stockpile to the population of leaking munitions for Period III is shown in Table 3-9.

The raw data shown in Table 3-5 were analyzed using an appropriate regression analysis and analysis of variance. The data can be analyzed using individual data points or totals by year. The regression analysis of total number of leakers versus year, as seen in Figure 3-8, shows no significant increase in the number of leakers over time. If the data are analyzed differently, however, a trend might appear. For example, data for all sites rather than just ANCA suggest an increase of leakers with time.[10]

Figure 3-9 is a Pareto chart showing the frequency of GB M55 rocket leakers by GB subtype at ANCA. Figure 3-10 is a Pareto chart of the GB M55 rocket population in the ANCA stockpile by GB subtype. These charts were based on Period III data for Category 1 leaks. The percentage of leakers by GB subtype and the percentage of GB rockets by subtype in the total population do not match. Specifically, the proportion of PR-RS rockets that were observed to have leaked in Period III is 3.07 percent (378/12,325), compared with the 1.38 percent (543/39,210) in the total GB M55 rocket inventory at ANCA in the same period. This is a statistically significant difference in the proportion of leaks ($p \leq 0.001$) between PR-RS

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[10] It should be noted, however, that this apparent trend is primarily a result of including DCD weapons, where, of course, all GB munitions have been destroyed.

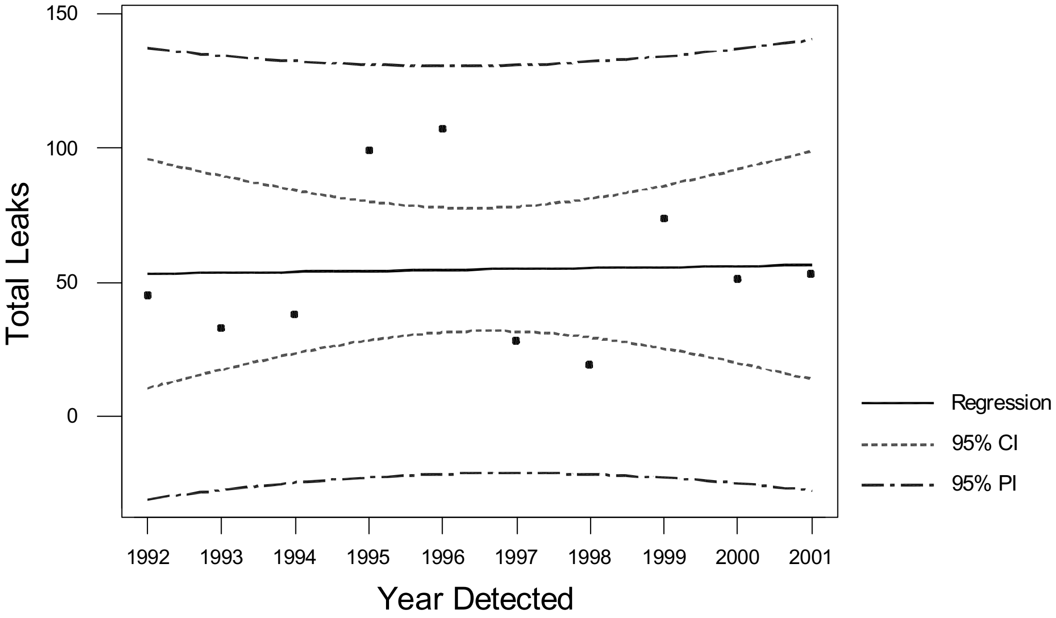
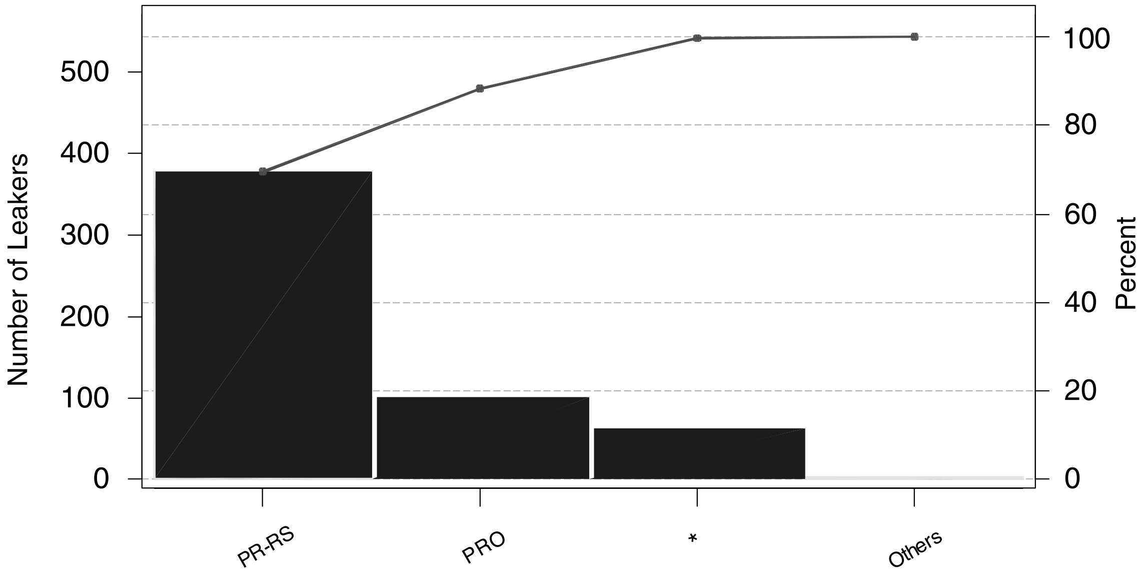
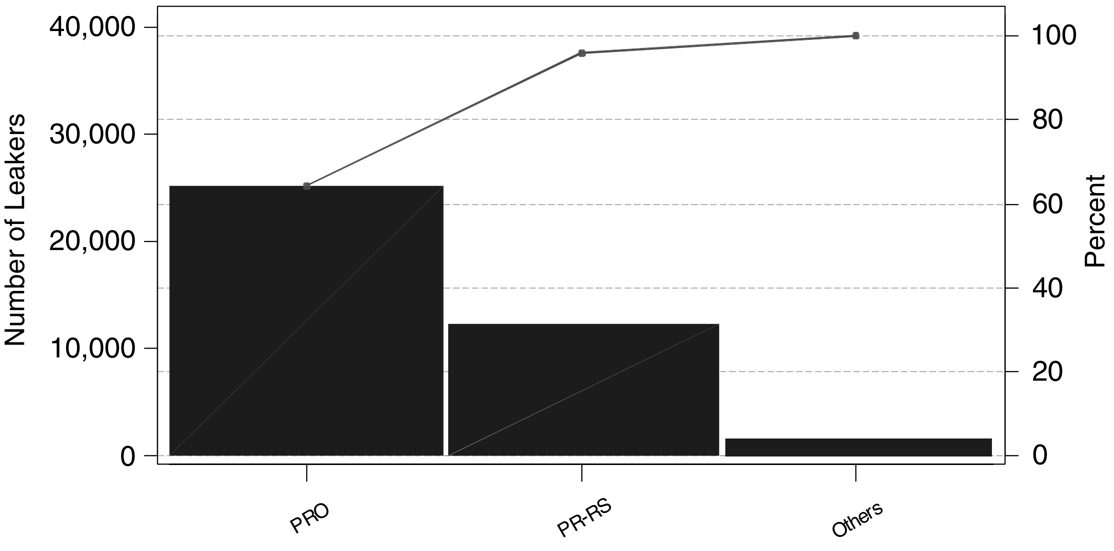


FIGURE 3-8 Regression analysis of aggregated-by-year-of-leak totals at ANCA versus year detected.



	PR-RS	PRO	*	Others
Count	378	101	62	2
Percent	69.6	18.6	11.4	0.4
Cumulative (%)	69.6	88.2	99.6	100.0

FIGURE 3-9 GB rocket leaks by agent subtype at ANCA from 1992 through July 2002. Note: *indicates no information available to specify subtype; “Others” indicates subtypes other than PRO, PR-RS.



	PRO	PR-RS	Others
Count	25,235	12,325	1,650
Percent	64.4	31.4	4.2
Cumulative (%)	64.4	95.8	100.0

FIGURE 3-10 GB rocket population by agent subtype at ANCA prior to start of disposal operations (2003). Note: "Others" indicates subtypes other than RO, PR-RS.

and the total population. Similarly, the 0.40 percent (101/25,235) of leakers for PRO is significantly lower ($p \leq 0.001$) than the 1.38 percent of leakers in the total population. More important, perhaps, is the observation that PR-RS leakers are more than seven times as frequent as PRO leakers. These findings give management further information to pinpoint the munitions that should be of greatest concern.

Since all of the munitions currently in the stockpile are more than 30 years old, any analysis of time of leakage onset for individual munitions based on data from Periods I, II, and III would be of limited use for monitoring the remaining life of the stockpile regardless of the quality of the early data. It is important to note, however, that the time since redistillation or restabilizing of the GB is about 30 or 35 years. Chapter 2 discusses the possibility that autocatalytic reaction(s) might occur. One possible concern is that the rapidly rising portion of the curve for the autocatalytic reaction has not been reached (see Figure 2-3). If, in fact, it is still to be reached, the stability of the stored munitions could be significantly compromised and leakage rates could rise substantially.

Statistical treatment of the information in the STS database by available software tools such as Minitab can be used to examine a very large number of possible interactions and to develop findings that could provide qualitative guidance for monitoring the existing stockpile until its destruction is complete. However, any such findings cannot be used for gelled and/or foaming munitions because they are not represented by leakers. With requisite data, Minitab (or equivalent statistical software programs) could be used to examine whether or not there are correlations between DODICs and the number of gelled rockets.

SUMMARY

Statistical analysis offers a means for gaining understanding of and insights into the condition of stockpiled chemical munitions. It can enable the Army to recognize developing trends in leaker frequencies and other manifestations of anomalies. Such analyses generally involve a three-step process:

- Compiling a good database,
- Comparing graphical depictions of the data, and
- Employing more rigorous statistical analysis techniques to learn whether a conclusion drawn from a graph is valid.

Such a process is not easy to establish at the beginning of a program unless the objectives are clear and a standard and consistent methodology for data recording and monitoring of the population(s) of interest is established. In this case, the objectives of the Army's munition inspection program have changed over time, leading to changes in data requirements and means of collection.

This chapter has discussed the various monitoring and inspection protocols used by the Army over the years to identify leaking munitions in the stockpile. Of these approaches, the SMI procedures (provided in Army Supply Bulletin SB742-1) used over the past 10 years have provided a consistent data set (U.S. Army, 1998a). In addition, SBCCOM and the U.S. Army Technical Center for Explosives Safety of the Defense Ammunition Center have maintained separate databases on the occurrence of leakers in the chemical stockpile. The committee examined both but used the SBCCOM database for this study, adding several new data fields in the process (such as age of munitions and type of agent) to facilitate the analyses. The results of its work are as follows:

- The committee looked at the chemical stockpile as a whole, and the Anniston chemical stockpile in particular, for evidence that the leaker rate is increasing with time. As for the rate of leakers increasing with time, the possibility of the onset of autocatalytic reactions of the stabilizer makes it important to continually monitor the stockpile for possible upturns in the leakage rates.
- A relatively small number of munition types contain the bulk of the leakers. Most of these are GB-filled munitions, the bulk of which are M55 rockets. While H munitions appear to leak at a higher rate than GB munitions, the former constitute a much smaller number of total munitions in the stockpile. Also, VX, HD, and HT munitions leak much less often than either GB or H munitions.
- A significantly higher proportion of M55 rocket subtype PR-RS leaks than of subtype PRO. Further inspections should focus on this disparity and attempt to determine its causes and significance for monitoring and inspecting the stockpile for its remaining life.

4

Operational and Risk Implications of Anomalies

INTRODUCTION

Chapters 1, 2, and 3 present an historical overview of stockpile anomaly occurrences to the extent these could be discerned from Army records. The text and data in the *Stockpile Tracking System Lot Book, Final Revision 2,* dated July 2001 (the STS Lot Book) were especially helpful in the current effort (U.S. Army, 2001a). This publication, from the office of the PMCD, was the single most complete and authoritative source of both qualitative and quantitative material on stockpile composition and condition.

This chapter considers all types of anomalies from the perspective of their effect on disposal operations, including their risk implications. It considers (in addition to leakers) the occurrences of atypical agent and munition handling anomalies during processing and the corrective actions employed to respond to unexpected conditions.

U.S. Army records, primarily as presented in the STS Lot Book and end-of-campaign reports for JACADS and TOCDF, are insufficient to quantify the observations and effects on stockpile disposal operations attributable to the processing of anomalous munitions and containers. While these records provide anecdotal information and discussions of corrective actions taken, they do not quantify the effects on schedule, cost, or worker risk. Some limited quantitative information has been developed, however, and is presented later in the chapter.

This chapter covers the risk implications of the various anomalies, corrective actions that have been taken to facilitate the processing of anomalous items, and—in a qualitative way—the effects of those anomalies on cost and schedule. Effects on worker safety and stakeholder perceptions are also covered but—here, too—only in a qualitative way.

RISK IMPLICATIONS COVERED IN QUANTITATIVE RISK ASSESSMENTS

In accordance with the PMCD *Guide to Risk Management Policy and Activities* (U.S. Army, 1998b), the storage, worker, and general public risks from agent exposure were extensively investigated in developing Phase 1 and Phase 2 quantitative risk assessments (QRAs) for the baseline incineration facilities at the Tooele, Anniston, Umatilla, and Pine Bluff sites.

In the final analysis, the public risks calculated in all of the QRAs performed to date show that the risk associated with continued storage, while quite small, is much larger than the risk associated with disposal operations. Thus, public risk is substantially dependent on the duration of the potential exposures from stored stockpile components. Recognizing this risk, the Army has an extensive program for monitoring and managing stockpile integrity.

Risk assessment can be thought of as the systematic approach to answering three questions: What can go wrong? What is the likelihood of something going wrong? What are the consequences? Each set of answers to these questions defines a scenario. A complete set of scenarios forms the basis for defining risk (Kaplan and Garrick, 1981). This framework is also valuable in considering changes in risk such as may occur through degradation.

Chemical mechanisms related to stockpile degradation are discussed in Chapter 2. Activities that address the risks posed by degraded stockpile items are considered in the Phase 1 and Phase 2 QRAs for the four baseline incineration sites and the Aberdeen and Newport sites. The end result of all these assessments is that degradation-related mechanisms and activities contribute very little to risk across all sites. The degradation anomalies discussed in this report cause processing complications that increase worker risk and delay disposal, prolonging public exposure to storage risk. Because the greatest number of leaking M55 GB rockets is at Anniston, the fraction of the total risk due to degradation across all sites is highest for that site, although the absolute risk of this fraction is small. The assessed degradation-related risk at Anniston is less than 0.1 percent of the total assessed risk from disposal operations at the site and much less than 0.1 percent of the total risk of storage.[1] As represented in the QRAs, this risk from anomalous munitions primarily derives from the longer time munitions remain in storage when disposal campaigns are extended.

Degradation mechanisms for which risk considerations have been investigated or postulated by the Army in the site-specific QRA include these: (1) leaking M55 rockets, (2) increased energetics sensitivity, (3) degraded ton containers, and (4) autoignition of M55 rockets.

Leaking M55 Rockets

Leakage occurs in both storage and processing areas. QRA analysts say there has been no clear evidence for an increase in the rate of leakage. The QRAs therefore assumed that the historical leakage rate over several decades for each munition type would remain constant. The potential for accidents during leaker processing increases as more leakers are encountered. This is expressed in the QRA analysis by extending the duration of the agent campaigns for leaker processing.[2]

Examples of risks associated with leaking M55 rockets that were addressed in the QRAs include those arising from overpacking operations during storage.[3] Also, because overpacked munitions involve more extensive handling during demilitarization, they lengthen the disposal campaigns, thus increasing the time in storage of the remaining munitions.

The risk associated with routine monitoring of igloos is not explicitly considered in the QRA analyses; this risk is considered by the analysts to be "very small" owing to (1) the exterior monitoring that is done before workers enter the igloos and (2) the protective clothing worn by the workers.[4] Nevertheless, an increase in leakage frequency would mean an increased number of entries by workers, which in turn would result in increased risk to workers, however small.

Energetics Sensitivity

The potential effect of agent on the energetic components of M55 rockets was addressed in a 1996 PMCD study (U.S. Army, 1996a). Seven compounds were identified as being potential by-products of reactions in the fuze and warhead section of leaking rockets. Each by-product compound was categorized in terms of its likelihood of formation and the resulting hazard that such formation would present. Three of the compounds formed—cuprous azide, cupric azide, and lead picrate—were identified as the most hazardous because of their great sensitivity and theoretically possible reaction chemistries. However, the study concluded that mechanical barriers within the rocket make it highly unlikely that the required reactants would come together. For that reason, the QRAs ignore the effects of agent on burster sensitivity.[5]

Tests performed on rocket propellant following contamination by GB agent showed that changes in the

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[1] SAIC responses to committee degradation risk questions, August 14, 2002.

[2] SAIC responses to committee degradation risk questions, August 14, 2002.

[3] SAIC responses to committee degradation risk questions, August 14, 2002.

[4] SAIC responses to committee degradation risk questions, August 14, 2002.

[5] SAIC responses to committee degradation risk questions, August 14, 2002.

impact sensitivity were minimal and thus would not be a factor in the risk analysis (U.S. Army, 2000a).

Container Degradation

In 1998, an assessment of degradation of the plugs on ton containers concluded that corrosion of plugs is not expected until after 2005 at the Tooele site and after 2015 at the Anniston, Aberdeen, Pine Bluff, and Umatilla sites (Bizzigotti et al., 1998).[6]

Although there has been some evidence of plug degradation for GB and mustard agent ton containers, no increased incidence of leakage has been observed, i.e., the leakage rate remains very small and apparently stable. In addition, many of the brass plugs used have already been replaced with steel plugs, thus reducing the likelihood of corrosion and leakage in the future.[7]

No degradation of VX-filled ton containers has been documented since storage in this type of container was begun more than 40 years ago. Regular inspections of VX-filled ton containers at Newport and other storage sites have not shown any degradation of the containers.[8] Consequently, degradation mechanisms for these containers have not been identified in over 40 years of observation, and they have not been represented in hazard and operability studies or QRAs conducted in preparation for disposal facility operation.

In mustard agent ton containers, attack on the steel surfaces by hydrogen chloride or by the mustard agent itself is a degradation mechanism. The possibility of corrosion-induced failure is addressed in the hazard and operability studies but was not deemed to specifically warrant consideration in the QRAs. The committee believes that periodic monitoring of the containers will improve the probability of early detection and thus avoid any significant impact from this failure mechanism.[9]

Autoignition of M55 Rockets

As discussed in Chapter 2, the components of the M28 propellant used in M55 rockets degrade slowly under storage conditions, generating heat and nitrogen oxides. This degradation can be accelerated if the propellant is contaminated with GB and/or the rocket is overpacked.

The median frequency of autoignition of M55 rockets has been estimated to be 1.0 to 5.9×10^{-5} per year for overpacked rockets (see Table 4-1) and 1.8×10^{-7} to 1.4×10^{-6} for nonoverpacked (undetected) leakers (see Table 4-2). Table 4-3 compares these estimated frequencies with the total estimated frequencies of other causes of ignition, which are 1.4 to 5.3×10^{-3} per year.[10] In addition, the QRAs indicate that the scenarios associated with storage of M55 rockets represent the largest contribution to the public health risk (U.S. Army, 2002c).

The Army has concluded that existing procedures adequately address the potential degradation of the propellant used in 105-mm cartridges and 4.2-inch mortar rounds. The committee believes that if continued monitoring of the propellant for these munitions indicates degradation, then the propellant and chemical agent can be easily separated using existing maintenance procedures.[11]

Chapter 3 outlines how statistical analysis can be used to characterize GB rockets by agent subtype. A distinguishing feature of these subtypes is the relative frequency with which leakers have occurred. As additional leakers occur, the time required to completely

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[6] The analysis of Bizzigotti et al. (1998) indicates that the first plug failure due to corrosion is not expected at the Tooele site until after 2005. For the 6,398 HD ton containers with a total of 38,388 plugs at Tooele, 66 plug failures from corrosion were predicted from 2006 through 2015. This represents a 0.17 percent failure rate of the plugs, or a 1.0 percent failure rate for the ton containers, which have six plugs each.

[7] SAIC responses to committee degradation risk questions, August 14, 2002.

[8] Newport Chemical Agent Demilitarization Facility answers to committee questions on degradation risk, August 14, 2002.

[9] Aberdeen Chemical Agent Demilitarization Facility responses to committee questions on degradation risk, August 14, 2002.

[10] Median frequencies of 1.0 to 5.9×10^{-5} per year are equivalent to one chance in 100,000 to one chance in 16,950 per year. Median frequencies of 1.0×10^{-7} to 1.4×10^{-6} per year are equivalent to one chance in 5,600,000 to one chance in 710,000. Frequencies of 1.4 to 5.3×10^{-3} per year are equivalent to one chance in 710 to one chance in 190 per year.

[11] Draft of an assessment of the chemical weapons stockpile generated by the Army in 1992, provided to the committee by PMCD on February 27, 2002.

TABLE 4-1 Median Site-Specific Annual Autoignition Probability for Overpacked Rockets

	Probability of Autoignition in Each Year			
Site	2000	2005	2010	2020
Anniston	2.9×10^{-5}	4.2×10^{-5}	5.0×10^{-5}	5.9×10^{-5}
Umatilla	9.8×10^{-6}	1.5×10^{-5}	1.9×10^{-5}	2.3×10^{-5}
Blue Grass	1.0×10^{-5}	1.3×10^{-5}	1.5×10^{-5}	1.7×10^{-5}
Pine Bluff	1.0×10^{-5}	1.3×10^{-5}	1.4×10^{-5}	1.6×10^{-5}

Source: Adapted from U.S. Army (2002c).

TABLE 4-2 Median Site-Specific Annual Autoignition Probability for Nonoverpacked Leaking Rockets

	Probability of Autoignition in Each Year			
Case	2000	2005	2010	2020
Anniston	1.4×10^{-6}	1.3×10^{-6}	1.2×10^{-6}	1.2×10^{-6}
Umatilla	5.6×10^{-7}	6.8×10^{-7}	7.7×10^{-7}	8.9×10^{-7}
Blue Grass	4.9×10^{-7}	5.6×10^{-7}	6.1×10^{-7}	6.8×10^{-7}
Pine Bluff	1.8×10^{-7}	2.4×10^{-7}	2.8×10^{-7}	3.2×10^{-7}

Source: Adapted from U.S. Army (2002c).

TABLE 4-3 Comparison of Site-Specific Autoignition Probabilities with the Probabilities of Other Accidental Ignition Events (probability in 1 year)

Site	Overpacked Rocket Autoignition Probability	Nonoverpacked Rocket Autoignition Probability	Lightning Initiation Probability[a]	Earthquake Initiation Probability[a]
Anniston	3×10^{-5}	1×10^{-6}	2×10^{-3}	1×10^{-4}
Umatilla	1×10^{-5}	6×10^{-7}	6×10^{-4}	8×10^{-4}
Blue Grass	1×10^{-5}	5×10^{-7}	2×10^{-3}	2×10^{-4}
Pine Bluff	1×10^{-5}	2×10^{-7}	5×10^{-3}	3×10^{-4}

[a] Lightning and earthquake initiation probabilities are from the following QRA reports: for Anniston (SAIC, 1997a), for Umatilla (SAIC, 1996), for Blue Grass (SAIC, 1997b), and for Pine Bluff (SAIC, 1997c). These numbers may change as the QRAs for these sites are updated.

Source: Adapted from U.S. Army (2002b).

destroy the M55 inventory, as well as the overall stockpile, probably will be extended. Such delays in destroying the stockpile, especially the M55 rockets, prolong public risk. Prioritizing the destruction of M55 rockets by GB subtype at each site could be an option for reducing the disposal risk to the public if such scheduling does not otherwise adversely affect the overall scheduling for M55 rocket disposal and increase exposure to storage risk.

The above are the only distinct anomalies evaluated in the QRAs. Other anomalies, such as frothing mustard agent munitions, can impact schedule, but they were not evaluated in the QRAs.

SUMMARY OF IMPLICATIONS OF ANOMALIES AND CORRECTIVE ACTIONS

General

Stockpile anomalies can be categorized into two main groups:

- Stable defects are those originating during manufacture or from handling mishaps. They do not cause further degradation once they occur and are often of a mechanical nature.
- Progressive defects are the result of chemical activity subsequent to manufacture. These defects include leakers, gelled agent, corrosion, and the frothing of agent from the agent cavity during either storage or disassembly.

Agent and munitions defects (anomalies) by their very nature can be disruptive and dangerous and can have adverse impacts on processing. Their causes can be complex and are often interactive. They are often associated with specific agent and/or munition lots; this is reflected in the STS Lot Book, which records lot number along with anomaly descriptions. Stable defects may or may not be identifiable in storage. If the defect can be isolated in advance, a timely decision to accept the impact on processing operations or to attempt to mitigate the impact through process and/or equipment modification will lead to minimum schedule disruption. Similarly, if progressive defects are identified during storage by monitoring, sampling, and testing, a timely decision to accept the impact or to implement special handling procedures and/or other process and equipment modifications can be made. Information on anomalous items in the stockpile, when systematically collected and tabulated, can yield the data points needed for statistical analysis and trend detection aimed at mitigating operational disruption. For this purpose, it is desirable that reporting protocols and formats be standardized for consistency in gathering and recording information across all storage sites. Available records, such as end-of-campaign reports, do not allow linking system and equipment downtimes directly to the processing of anomalous stockpile items.

Corrective actions employed to address anomaly conditions of all types include the following:

- Modification of process rate, sequence, schedule, and standard operating procedures, as required, to minimize risk and mechanical disruption;
- Modification of the RCRA permit to enable a facility to handle an anomaly efficiently (by, for example, allowing a different processing sequence);
- Modification and/or replacement of equipment;
- Revisions of operator training and improvement of procedures;
- Notification and education of stakeholders; and
- Rejection, isolation, and eventual special processing of munitions.

Nearly every anomaly encountered during processing will interrupt or slow disposal operations. Moreover, investigations to determine root causes and develop corrective actions and operational changes also contribute to delays in processing. The magnitude of such activities depends on the type of anomaly, its potential effect on worker and public safety, and its impact on operations. The types of anomalies that have been found are discussed briefly below.

Progressive (Chemical-Related) Anomalies

Progressive anomalies include the following:

- agent and propellant stabilizer depletion
- gelling of agent
- crystallization of agent
- sludging of agent
- high-solids-content agent
- frothing and foaming mustard agent
- hydrogen formation
- propellant contamination
- external leakage of agent
- internal leakage of agent

The chemistry that causes some of these anomalies is presented in Chapter 2; only the actions taken during processing will be covered here. The last two leakage anomalies were discussed at length in Chapter 3 and will not be discussed in this chapter except insofar as they cause secondary effects.

Corrective actions that have been taken for progressive anomalies include the following (Thomas, 2002b).

Gelled or Crystallized GB Agent

Gelled or crystallized GB agent requires adjustment of the processing rate and modification of the RCRA permit to allow agent to be destroyed along with the body of the munition in the deactivation furnace system (DFS) or the metal parts furnace (MPF), depending on the munition involved.[12]

High Solids Content HD

Mustard agent that has a high solids content requires adjustment of the processing rate to reflect extended agent drain time, modification of the RCRA permit to allow increased agent loading in the MPF, and destruction of the agent along with the body of the munition in the MPF. Among the problems encountered was damage to the multipurpose demilitarization machine (MDM) equipment when crimped burster tubes could not be reinserted into projectile bodies because of excessive agent heel. Workers in demilitarization protective ensemble (DPE) suits would then have to service the equipment to remedy the breakdown (U.S. Army, 1999b).

Foaming and Frothing HD

To handle projectiles that exhibited foaming and frothing mustard during disassembly, vacuum nozzles were redesigned to envelop the projectile ogive and limit agent spillage (U.S. Army, 1999b). Freezing the munitions and processing them in the MPF with 100 percent heel proved to be feasible (NRC, 2001b). The changed agent loading of the MPF required RCRA permit modification. Processing rates were adjusted as necessary to conform to permit limits (U.S. Army, 1999c).

Hydrogen Formation and Resulting Pressurization

Advance detection of pressurized conditions due to the formation of hydrogen gas is desirable, especially for ton containers. The Army is experimenting with venting to safely relieve pressure. Special safety measures are required to minimize the possibility of explosion when hydrogen pressurization is encountered.

Propellant Contamination

Careful monitoring is necessary to detect physical changes and temperature rise that would indicate propellant contamination by leaking agent. Separation of the propellant from the projectiles is relatively easily and safely accomplished for 105-mm projectiles and 4.2-inch mortar rounds. Internal leakage of M55 rockets is more difficult to respond to because it is difficult to detect.

External Agent Leakage

If a leaker is detected while the munition is in a stockpile igloo, it is overpacked and removed to a separate storage igloo, where it can be monitored more frequently. Overpacked munitions and those developing leaks during transport to the MDB are processed separately by workmen in DPE suits with due concern for the higher risk of operations with leaking munitions. The significant schedule impact to be expected from this type of handling is discussed later in this chapter.

Internal Agent Leakage

Internal leakage is generally undetectable because current monitoring protocols do not call for intrusive monitoring. Consequently, no advance corrective action is possible. If evidence of internal leakage appears during processing, the munition may require handling as a reject item. This involves, first, isolating the munition and, then, special processing by workmen in DPE suits using special tools and techniques.

Stable Anomalies Related to Manufacturing and Handling

Stable anomalies include the following:

- heavy metals in the agent
- improper fabrication of burster tubes

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[12] See *Assessment of Processing Gelled GB M55 Rockets at Anniston* (NRC, 2003).

- welding and brazing defects
- PCBs in M55 rocket shipping and firing tubes
- agent contamination from ton container reuse
- poor sample-plug fit and the use of brass container plugs
- flawed munition casing blanks
- problems with disassembly
- corroded M23 mine adapter plates

Several corrective activities have been taken or are planned to address these stable anomalies.

Heavy Metal in the Agent

The pollution abatement system (PAS)—particularly in third-generation baseline incineration system facilities equipped with the activated carbon PAS filter system (PFS)—may be effective in meeting RCRA permit requirements for heavy metal control.

Improper Fabrication of Burster Tube

Improper burster tube fabrication is an anomaly that shows up in numerous ways—tubes welded into the munitions casing, imperfect agent cavity seal due to burster tube roughness, tubes installed upside down, out-of-specification burster tube fabrication, the use of aluminum tubes instead of specified steel, and overlong tubes. Corrective action involves routine processing where possible but processing as a reject munition when required.

Welding and Brazing Defects

Welding and brazing defects can result in either external or internal agent leakage. Bomb casing seams and the attachment of the lifting lug are typical problem areas. Weld or braze material has been found to be cracked or porous in certain defective lots, permitting agent migration and leakage. If external leakage occurs, the munition must be overpacked and specially processed. Internal leakers are handled in a manner similar to munitions with improper burster tube fabrication anomalies—that is, routinely when possible; as rejects when necessary.

PCBs in M55 Rocket Shipping and Firing Tubes

PCBs are normally destroyed during routine processing with no special provision required for permit compliance.

Agent Contamination from Ton Container Reuse

Cases of contamination with chemicals not coming from the stored agent have been traced to residual material from earlier use of the containers. The permit needed to be modified to allow these unexpected substances to be processed at disposal facilities. Among the substances requiring permit modification is arsenic, which is believed to have come from earlier storage of lewisite.

Poor Sample-Plug Fit and the Use of Brass Container Plugs

To secure an agent-tight seal, ton containers subject to leakage at threaded plug holes have required refitted plugs or retrofit, with steel plugs replacing brass plugs, which are subject to acid attack when agent deteriorates.

Flawed Munition Casing Blanks

In a very small number of cases, flawed steel munition casings developed cracks and subsequently leaked. The affected munitions are overpacked and stored separately.

Disassembly Problems

Manufacturing error, metal corrosion within threaded sections, incompatibility of soft aluminum projectile casings and metal gripper jaws in processing machinery, and careless handling are generating or can generate anomalous conditions that make disassembly of munitions difficult or impossible with the equipment intended for this purpose. One of the more successful corrective actions was the development and employment of the gimbal cam device at JACADS and its subsequent deployment at other facilities. This modification to the projectile/mortar disassembly

(PMD) equipment solved the majority of these problems without interrupting the routine processing cycle (U.S. Army, 2000b). The few munitions that cannot be handled in this way are set aside for special processing at the end of the campaign. For example, nose-cone-removal grippers that become fouled require corrective action by workers wearing appropriate protective clothing.

Corroded M23 Mine Adapter Plates

The corrective action for corroded M23 mine adapter plates processed at JACADS was to slow the DFS rotation rate so the burster would detonate in a thicker-walled section of the kiln. Most remaining M23 mines were fabricated with plastic rather than metal adapter plates. The behavior of these plastic plates during processing is not yet known (U.S. Army, 2001c).

WORKER RISK INCIDENT TO THE STORAGE AND PROCESSING OF ANOMALOUS MUNITIONS

Facility and process design are intended to provide maximum safety for workers, the public, and the environment. Anomalous munitions add to the inherent risk since they may fall outside design parameters and established procedures. Chemical agents, with their extremely high toxicity, will always add to the existing risk of working in a complex chemical processing facility. Thus, assuring worker safety will always be a challenge.

During disposal operations, risks to workers from anomalous stockpile munitions and containers can arise for one or more reasons:

- *Exposure to leaking munitions.* Leaking munitions present a risk of exposure to chemical agent in the form of a liquid, a vapor, or both. Risk to workers is minimized by standard operating procedures that prescribe steps for handling leakers safely. Monitoring to detect the presence of agent before a worker can be exposed is routine. DPE suits used during nonroutine processing of exceptional munitions, such as overpacked leakers, are intended to minimize potential agent exposure. However, additional risk is imposed through the need for protective clothing. Even though complete protection from agent exposure is provided, proper management of DPE operations is necessary to preclude severe worker fatigue and hyperthermia.
- *Operational impact from degraded agent.* An extraordinarily high solids content, or agent gelling, or agent crystallization all delay or even prevent the extraction of agent from munitions, thus extending the processing schedule. At TOCDF, the presence of gelled GB in M55 rockets led to a process change—namely, the destruction of agent in the DFS rather than in the LIC. As a result, state regulatory authorities imposed a conservative limit on the rate of rocket processing that extended the GB campaign schedule significantly.[13] In addition to extending the processing times, which prolongs the potential for operational exposures, risk to workers is also affected when problems with high solids, gelled agent, or crystallized agent must be dealt with by workers in DPE suits.
- *Maintenance and cleanup activities.* Certain anomalies encountered during processing necessitate that workers clean explosives from the explosive containment room (ECR) floor at regular intervals. Agent spills resulting from foaming and frothing mustard and those that occur during the correction of mechanical anomalies must be decontaminated by workers. Debris falling from munitions or ejected by processing machinery must be collected and disposed of safely. PMD jaws require cleaning periodically, especially if they have been used to process aluminum projectile compounds. These activities must all be carried out by workers in DPE suits.
- *Pressurized hydrogen gas.* Hydrogen gas that has formed from mustard agent degradation in munitions and containers to perhaps as high as 200 psig presents a significant risk to workers because of its wide flammability/explosivity limits.
- *Pressure fluctuations in the DFS during mine processing.* The inability to remove the energetic components of the M23 mine can cause small detonations within the DFS and consequent pressure puffs (U.S. Army, 2001c).

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[13] See *Assessment of Processing Gelled GB M55 Rockets at Anniston* (NRC, 2003).

CSDP PROGRAMMATIC IMPACTS

General

Anomalies, by definition, are nonroutine occurrences that involve nonnormal stockpile munitions or containers. In some cases, process planning in the CSDP was broad enough to accommodate the impact of the anomaly. In other cases, anomalies have had a negative effect on program execution. They have caused schedule extensions, cost increases, permit modifications, process modifications, stakeholder confusion and loss of confidence, and greater worker risk.

Schedule and Cost

The committee recognizes that the presence of anomalous items in the stockpile delays normal disposal operations and increases the duration of exposure to stockpile risk. Knowledge about the types and locations of anomalous items helps minimize delays, but there are limited programmatic data available to help anticipate the extent of delays. In some cases, cost data can be used as a surrogate for the extent of delays and the additional operational requirements associated with handling and disposal of anomalous items.

Since each baseline incineration system facility costs approximately $300,000 per day to operate or to maintain in a standby mode, delays in conducting disposal operations due to anomalous stockpile items can have significant cost ramifications. Very little, if any, quantitative data exist on the effects of anomalous stockpile items on the schedule or cost of the stockpile disposal program. There is, however, significant anecdotal information that anomalous munitions and containers extend processing schedules and increase costs. Some cost and schedule information has been developed that gives an idea of the significant impacts of processing anomalous stockpile items on disposal operations.

At TOCDF, the cost of processing a standard M55 rocket was about $2,000 per rocket, and that of processing a leaking or gelled rocket was more than three times as high ($7,200).[14] The impacts on cost were essentially time related. Drainable rockets were processed at a rate of six or more per hour, as most of the agent was drained and processed in the LIC.[15] Gelled rockets could only be processed at the rate of about one per hour, a limitation imposed by RCRA permit requirements.[16] The rate at which leaking rockets could be unpacked by a team in DPE suits was a limiting factor. Consequently, about one leaking rocket or gelled M55 rocket was processed every hour on a sustained basis, with a maximum rate of about two per hour.

The processing of 4.2-inch mortar rounds filled with mustard agent at JACADS encountered a number of anomalies. These included frothing of agent and gelled agent such that the agent could not be drained. These and other issues, such as not being able to reseat the burster casing, increased the time required to complete the demilitarization of the mortar rounds from a scheduled 4 months to 5 months. Such prolongation significantly increases the cost of a program—for example, the approximate cost of operating the JACADS facility for a month was about $10 million.[17]

Anomalies vary with respect to frequency, distribution, and effect. Some have been associated with specific lots, as shown in the STS Lot Book. Some occur so infrequently that there is very little effect on the cost and schedule of disposal operations. To the extent that certain anomalous munitions are believed to have been completely processed and further occurrences are considered unlikely, their effect on future operations is moot. Others have now been reduced to routine handling through the introduction of equipment or processing modifications. However, there is no assurance that old problems thought to have been solved will not recur or that new problems will not be discovered. Should this occur, the effects on stockpile disposal schedules and costs will depend on the number and locations of the munitions involved and the particular consequences that would need to be addressed. Systematic, standardized monitoring can help to identify new anomalies and will allow the program to deal with them efficiently.

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[14] Tim Thomas, Program Manager for Chemical Demilitarization, personal communication to Peter Lederman, July 31, 2003.

[15] Tim Thomas, Program Manager for Chemical Demilitarization, personal communication to Peter Lederman, July 31, 2003.

[16] The RCRA requirement for processing gelled GB M55 rockets at TOCDF limited processing to 1.6 rockets per hour if only rockets were being processed or 1 rocket per hour if the rockets were being coprocessed with other munitions.

[17] Tim Thomas, Program Manager for Chemical Demilitarization, personal communication to Peter Lederman, July 31, 2003.

Stakeholder Perceptions and Reactions

Three anomalies have come to the public's attention through news stories and other sources: the occurrence of leakers, gelled GB M55 rockets, and the potential for autoignition of M55 rockets. Significant public attention has been focused on the overall CSDP, particularly the debate over baseline incineration technology versus neutralization (hydrolysis) processes (the latter will be used at the Aberdeen, Newport, Pueblo, and Blue Grass sites). However, except to the extent they might contribute to heavy metal emissions or occasionally upset conditions in furnace operations, anomalies do not appear to be a major issue with the public. The public continues to be told about leaking munitions in storage igloos by various news media, and although they are a matter of concern, the public seems to believe the Army is managing the problem adequately. The U.S. Congress started the CSDP in the mid-1980s out of concern about the stability of M55 rockets, and the Army has consistently told the public that the continued storage of these munitions poses the greatest risk. However, some individuals and groups believe that incineration (versus hydrolysis with extended storage) poses a more immediate risk.

Nonetheless, there is general agreement in the public sector that early destruction of the stockpile is a proper objective. While the public insists on protection during disposal operations, differences of opinion exist among public stakeholders on the particulars of how prompt, safe destruction can best be achieved—for example, should there be onsite or offsite disposal of secondary wastes from disposal facilities? If the stockpiles were completely dormant, the public would probably consider that time invested in the study of ever safer processes was justified. However, the discovery of leakers and the uncertainty surrounding autoignition of rockets have strengthened some residents' insistence on disposing of the stockpile as rapidly as possible.

In parallel with the planning, construction, and operation of stockpile disposal facilities, the Army has funded the Chemical Stockpile Emergency Preparedness Program (CSEPP). This program to prepare the communities surrounding each site for the agent disposal operations has been a significant component of the cost of the CSDP, which has a current life cycle cost estimate of $24 billion to complete disposal activities at all storage sites. The emergency management plans and infrastructure that guide CSEPP preparations for disposal operations are applicable as well to unintended releases of agent from storage areas as a consequence of accidents (e.g., autoignition) or natural occurrences such as earthquakes or lightning strikes. As noted previously, the significant quantities of chemical munitions and bulk containers in the storage igloos at each site present greater risks to the general public than do the more limited quantities of agent that are being handled in disposal facilities at any given time (NRC, 1994a, 2002).

Regulatory officials have supported the concept of prompt destruction while requiring strict adherence to permit regulations. In most jurisdictions, the regulatory requirements are clear and reasonable given the complexities that arise from legal requirements, public concerns, and political and activist pressures.

SUMMARY

The presence of anomalous items in the aging chemical stockpile is well documented. Anomalies contribute to the risk that the stockpile poses to the general public, the environment, and, especially, to workers. Since the stockpile was originally intended for use in battle, the impact of anomalous munitions on disposal operations was not anticipated, and in some cases the anomalies have necessitated substantial process and permit modification. Moreover, there is no assurance that all anomalies to be encountered before the entire stockpile has been destroyed have already been discovered. Available data do not clearly link stockpile degradation with age; however, autocatalysis could still emerge as an important and dangerous new condition affecting stockpile storage risk. Anomalies, especially leakers and the possibility of rocket autoignition, are of continuing concern to the general public, political leaders, regulatory officials, and several activist organizations. Continuing degradation of the stockpile involving various anomalous manifestations, both known and—possibly—yet to become apparent, will continue over the duration of the disposal program. The extent to which anomalies will be encountered is difficult to predict, although in some cases (e.g., solids content, gelling), estimates have been made. This situation places a premium on the following activities:

- Regular testing, monitoring, and data recording and interpretation in a standardized mode;
- Detailed assessment of operational risks to workers using a HAZOPs analysis or QRA and devel-

opment of procedures and training to safeguard workers associated with identifiable anomalous operations;

- Credible statistical analysis of improved databases to discover possible trends at the earliest possible time;
- Regular intersite communication through direct contact and the program's lessons-learned database to ensure that anomaly detection is made known as soon as possible to all concerned;
- Regular public advisories on demilitarization operations with as much information disclosure as can be permitted consistent with security concerns; and
- Sustained and systematic efforts to destroy the aging stockpile, with emphasis on attending to those munition types and anomalies that pose the greatest actual or potential risks.

5

Findings and Recommendations

Finding 1. To perform the statistical analyses presented in this report, the Stockpile Committee, with assistance from the Army, expanded the parameters measured or inferred from existing databases on the chemical stockpile condition. These additional data fields may be instructive and useful to the Army. The Minitab software that was used is an example of the statistics programs used by industry for analysis. Statistical software of this type can also support an overall program to improve performance, including safety performance.

Recommendation 1. The Army should collect data on degraded agent and other munition anomalies in a manner that provides for maintaining the parameters in the data matrix format developed by the committee or in a similar format. The Army should establish additional data fields, such as documenting inspection activities in which no leaks are found. The Army should also consider the use of a statistical program such as Minitab or an equivalent program to assist in the overall quality of stockpile analyses and safety improvement.

Finding 2. The data on leaking munitions and containers in the chemical agent stockpile from 1992 onward were obtained using a consistent set of protocols. However, the information required for doing certain trend analyses, such as the age of the munition when leaking was detected and agent subtype, is not readily discernible and often not available.

Recommendation 2. The Army should continue using its current monitoring protocols. It should set up a program for acquiring data, maintaining it in a database, and entering it into a statistical software package. Staff will have to be given adequate training in statistical analysis.

Finding 3. The sampling program as currently conducted is biased toward munitions and containers holding GB agent. What data there are indicate that VX leaks are relatively rare. However, one concern is that the stabilizer in VX munitions may be dropping to critical levels.

Recommendation 3. The Army should verify that VX leaks are much less frequent than GB leaks by monitoring VX munitions and containers more closely. The status of stabilizers in VX munitions should be ascertained.

Finding 4. The database on leaking chemical munitions and containers developed by the Army and expanded to include additional fields by the committee is useful for predicting leaker trends, but not for predicting trends for other anomalies such as gels and foaming or frothing rounds. The search for causes and effects of leaks in munitions and for remedial actions to address them could similarly be applied to other stockpile anomalies. End-of-campaign reports are one source of information on anomalies other than leaks.

Recommendation 4. The Army should carefully analyze the data in end-of-campaign reports from chemical stockpile disposal operations and any other available information to determine if a predictive technique can be developed for anomalies other than leaking munitions—for example, gelled agents.

Finding 5. The agent decomposition mechanisms described in Chapter 2 include a number of reactions with positive temperature coefficients ($E_{act} > 0$). Corrosion reaction rates are also expected to increase with temperature, implying that the occurrence of leaks may increase at higher ambient temperatures. The available data did not validate the hypothesis of a temperature dependence.

Recommendation 5. The Army should consider instrumenting some existing storage facilities for the continuous monitoring of temperature, particularly those facilities where materials most susceptible to degradation are stored—namely, munitions with problematic GB subtype lot numbers. The temperature data could then be correlated with leaker rates to identify any temperature dependence. If such a dependence is shown to exist, the Army could consider mitigating measures, including temperature control in the igloos and the reevaluation of processing sequences for the various GB munitions.

Finding 6. Pressurized hydrogen gas has formed from mustard agent degradation in some munitions and containers. This can present a significant risk to workers during disposal operations.

Recommendation 6. Special safety measures are required during disposal of mustard agent munitions and containers to minimize the risk of hydrogen gas exploding.

Finding 7. The degradation mechanisms for GB agent outlined in Chapter 2 imply that degradation can proceed by autocatalysis once inhibitor is exhausted. Autocatalytic reactions are characterized by a slow induction period followed by a rapid rise in reaction rate. While the available data do not support an acceleration in leaker frequency, the current state of reaction within GB rockets could still be on a relatively flat portion of the reaction rate curve, indicating that—most probably—only the usual reactions with stabilizer present are occurring. However, there is a possibility that the rapidly rising portion of the curve that would be characteristic of an autocatalytic reaction is being approached.

Recommendation 7. The Army should maintain an aggressive monitoring and data analysis program, particularly in the case of GB munitions and containers, in order to identify any significant upward trend in the rate of leakers as early as possible. Expeditious disposal of GB munitions can help to avoid an encounter with the rapidly rising portion of the curve that would characterize an autocatalytic reaction resulting from GB degradation.

Finding 8a. Corrosion has been observed on valves and plugs of GB ton containers. This corrosion could cause agent leaks or spills.

Finding 8b. The corrosion that has been observed in burster tubes of 105- and 155-mm projectiles was caused by agent leaking into the burster as a result of incorrectly brazed joints. In such cases, corrosion is the result of a leak, not the source of the leak. In time, this corrosion may result in the release of agent. Munitions in this condition may be in the stockpile.

Recommendation 8. GB munitions and GB in containers should be destroyed as soon as possible.

Finding 9. The frequency of monitoring M55 rockets is based, in part, on observed leakage frequencies. Given that the number of GB M55 rocket leakers is greater than the number of VX M55 rocket leakers, monitoring by the Army focuses on the former.

Recommendation 9. In view of the toxicity of VX, the Army's monitoring protocols should be reviewed to increase confidence that the frequency of leakers and the mechanisms associated with VX degradation are well understood.

Finding 10. Continuing degradation of M55 rocket propellant, even when accelerated by agent contamination, is at present only a minor contributor to storage risk. However, the expeditious destruction of GB M55 rockets is an effective way to reduce risk to the public since accidental ignition due to lightning or earthquakes remains the largest contributor to storage risk. Significant delays in the destruction of GB M55 rockets could necessitate monitoring the condition and stability of the propellant more intensely as agent continues to degrade and perhaps contribute to propellant instability.

Recommendation 10. If destruction of the GB M55 rockets is significantly delayed, the condition and stability of the M28 propellant in these rockets should be closely monitored.

Finding 11. It may be possible to prioritize the destruction of M55 rockets by GB subtype and thereby reduce the likelihood of future leaks.

Recommendation 11. If the committee's analyses of the role of GB subtypes in leaker development can be substantiated by the Army, consideration should be given to prioritizing the order of destruction of M55 GB rockets by GB subtype, as long as this process does not adversely impact the overall M55 GB rocket destruction schedule.

Finding 12. Currently available records, such as end-of-campaign reports, do not allow for directly linking system and equipment downtimes to the processing of anomalous munitions. The early communication of anomaly detection by direct contacts between all sites and by means of the program's lessons-learned database is important for all concerned.

Recommendation 12. The Army should assemble corrective actions from lessons learned to address anomalous conditions of all types, including the modifications of process rates, sequences, schedules, and procedures, and it should ensure the prompt, direct, and adequate distribution of this information to all disposal sites.

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Appendixes

Appendix A

Autoignition and the M55 Rocket

As a consequence of the applicability of the Army's broad experience with energetics in conventional weapons, there is no reason to expect autoignition of either the fuze or burster components of chemical munitions. However, the M55 rocket also contains 19.1 lb of M28 propellant, which is of a double-base composition, containing nitroglycerine (NG), nitrocellulose (NC), and 2-nitrodiphenylamine (NDPA) as a stabilizer. The NG and NC components degrade slowly under storage conditions, generating heat and releasing nitrogen oxides (NO_x). These oxides react with trace moisture to form nitrogen acids, which lead to corrosion problems and heat generation. The NDPA stabilizer reacts with the NO_x to form, successively, three disubstituted and two trisubstituted daughter products, each of which can further react with NO_x, although with lower effectiveness. Each NDPA molecule (including subsequent daughter reactions) can theoretically combine with up to six NO_x molecules. Because NDPA has only a limited capacity for absorbing NO_x, which diminishes for its daughter species, the rate of propellant degradation increases as aging proceeds. This process also generates thermal energy. If the heat generation rate exceeds the rate of heat dissipation through the rocket and its packing, the propellant temperature will increase, thereby increasing degradation rates and, ultimately, the likelihood of autoignition. In addition to the stabilizer depletion that takes place normally in propellant under storage conditions, concerns have also been raised about GB leakage into propellant grains and the impact that such leakage has on propellant stability. Further, when leaking GB M55 rockets are overpacked, the ability to dissipate heat from the rocket to the surroundings is reduced. Overpacking can thus contribute to heating of the propellant and consequently to higher reaction rates, which might increase the possibility of autoignition.

The original stabilizer concentration in the M28 propellant was a nominal 1.8 percent, although, as noted earlier, a small sample of M55 rockets evaluated in 1985 showed propellant NDPA levels ranging from about 1.6 to 2.2 percent (NRC, 1994). MITRE Corporation studies done prior to 1994 suggested that if the rockets were stored at 95°F, the primary NDPA would be depleted to 0.5 percent by 2007 (see, for example, Perry et al., 1993). At the 0.5 percent concentration level, Army guidelines call for increasing surveillance of the munitions, since autoignition has been observed to occur when levels are 0.2 percent or lower. However, this does not consider the additional stabilization capacity provided by the NDPA-daughter species. A subsequent Army study included the effect of stabilization by the daughter species and estimated that there would be a 50 percent likelihood of an autoignition in the M55 rocket stockpile in the time frame from 2041 to 2120 (U.S. Army, 1994).

In September 1996, the Army assembled a panel of outside experts to assess the likelihood of autoignition of M28 propellant in the M55 stockpile. This group,

TABLE A-1 Calculated Best-Estimate Autoignition Probabilities for M55 Rocket Sites

Year	Tooele	Anniston	Umatilla	Pine Bluff	Blue Grass
2010	7.8×10^{-17}	9.0×10^{-16}	1.4×10^{-15}	1.2×10^{-15}	1.7×10^{-15}
2015	5.11×10^{-14}	5.2×10^{-13}	8.3×10^{-13}	6.6×10^{-13}	9.1×10^{-13}
2020	5.2×10^{-12}	5.2×10^{-11}	8.2×10^{-11}	4.9×10^{-11}	8.5×10^{-11}
2025	2.0×10^{-10}	1.7×10^{-9}	2.7×10^{-9}	1.8×10^{-9}	2.7×10^{-9}
2030	3.8×10^{-8}	3.1×10^{-8}	4.8×10^{-8}	3.0×10^{-8}	4.7×10^{-8}

Source: U.S. Army (2002b).

through expert elicitation techniques that considered detailed mechanisms and uncertainties, developed further insights on the effectiveness of NDPA and its daughter products in capturing NO_x generated during M28 propellant degradation, estimated that NDPA levels would have to be less than 0.2 percent to allow autoignition, and suggested that autoignition might not occur immediately after depletion of the stabilizer (U.S. Army, 1997). Using all the information developed, estimates of the likelihood of autoignition were prepared for all sites having M55 rockets (Table A-1).

The study estimated that in 2010, the frequencies of autoignition at the sites were on the order of 10^{-15} per year or less; by 2020, the frequencies had risen to around 10^{-10} per year. Science Applications International Corporation (SAIC) uses a frequency of 10^{-8} per year as the criterion for inclusion of a risk contributor in a quantitative risk analysis (QRA), and autoignition risks would not be above this threshold until 2025. It is common practice in QRAs to establish a quantitative value to screen out scenarios that do not singularly or collectively contribute significantly to the risk metrics of interest. According to the available analyses, autoignition will not significantly contribute to risk for the anticipated operational life of the sites. Further, the contribution of autoignition to overall storage risk is negligible, since the frequencies of ignition by a lightning strike at the sites storing M55 rockets vary from 6×10^{-4} to 5×10^{-3} per year.

The expert group also advised the Army to focus special attention on the effect that leaking GB may have on the stability of M28 propellant. Experience has shown that about 0.5 percent of GB M55 rockets have leaked (in contrast to 0.02 percent of the VX M55 rockets). As leakers are discovered, they are overpacked. When 99 overpacked GB leakers at TOCDF were sampled 11 to 32 years after overpacking, some of the overpacks showed pressure buildup due to continuing NO_x generation. Further, NDPA levels were measured and found to be lower than would be expected in the absence of GB contamination. A second expert elicitation conducted in November 1998 evaluated the effect of agent contamination on the likelihood of autoignition.[1] Since VX rocket leakers are rare, attention was focused on GB rockets. The expert panel concluded that M28 propellant degradation was enhanced by the presence of GB, but that additional work was needed to clarify the characteristics of the interactions.

The Army selected Midwest Research Institute to perform both experimental studies and analysis of leaker sample tests to assess the effects of agent contamination on M28 stability (U.S. Army, 2000, 2002a). Experiments were conducted at elevated temperatures (50°C and 65.5°C) to increase reaction rates. Only modest increases in stabilizer depletion rates occurred with small amounts of GB contamination, and NG and NC also were depleted along with the stabilizer. However, at concentrations above about 6 percent GB in the propellant, the stabilizer depletion rate increased rapidly. A detailed model was developed to predict degradation (in terms of remaining effective stabilizer) and thermal behavior for GB-contaminated propellant grains. A significant feature of this model was that vapor transport was a major pathway by which GB agent could reach the propellant in addition to direct liquid leakage. This pathway became increasingly important at higher temperatures (due to higher vapor pressures) and in sealed containers.

Thermal modeling included detailed heat transfer paths through the rocket and in the two types of overpack systems. Heat generation from internal chemical

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[1] Notes from conference Expert Elicitation on Autoignition of Agent-Contaminated M28 Rocket Propellant, Science Applications International Corporation, November 18-20, 1998.

reactions was also modeled. The possibility of leakage that was not externally detected, i.e., leakers that were not overpacked, was also considered. Where the analysis showed that the peak heat generation rates exceeded the rate of heat transfer out of the system, autoignition was assumed to occur.

The analysis confirmed that the degradation process over time results in increasing NO_x generation, which in turn further increases degradation as the NO_x pressure increases. Overpacking may be accelerating degradation. Controlled venting of overpacks may reduce degradation rates and heat buildup.

A comprehensive Army report in March 2002 concluded that the probability of an autoignition event from propellant stabilizer depletion (including consequent thermal effects) is as follows (U.S. Army, 2002b): for nonoverpacked (undetected) leaking GB M55 rockets, $P_{ai} = 1.8 \times 10^{-7}$ to 1.4×10^{-6} per year, and for overpacked leaking GB M55 rockets, $P_{ai} = 1 \times 10^{-5}$ to 6×10^{-5} per year. Estimates were reported for the years 2000, 2005, 2010, and 2020; the above ranges include the median values to the year 2020 (U.S. Army, 2002b).

The probabilities of propellant ignition by other means range from 6×10^{-4} to 5×10^{-3} per year. By comparison then, the degradation of GB-contaminated propellant leading to autoignition appears to be a fairly small part of the total storage risk. All of these values are subject to uncertainties of about an order of magnitude.

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Appendix B

Leakers by Munition Type

MC-1 GB BOMBS

Metallurgical analysis carried out by the Army Materials and Mechanics Research Center to determine the cause of GB leakage in MC-1 750-lb bombs determined that weld crater cracks, as well as other weld defects such as porosity, cold cracks, and incomplete weld penetration, provided a continuous leak path (U.S. Army, 1986a). An example of one of these defects is shown in Figure B-1.

Additional leakers resulted from a poor fit of threaded alloy steel plugs into the tapped holes that had been drilled to obtain samples for analysis as part of the SUPLECAM program. This problem is limited to those known units from which samples were obtained in this manner.

155-MM GB PROJECTILES

GB 155-mm projectiles were examined with the following results (U.S. Army, 1984a, 1985a):

- In three samples with a two-piece burster, a large amount of porosity was observed at the brazed joint between the burster tube and the sealing plate; this allowed leakage.
- The region of the press fit exceeded the specified surface roughness in a sample of a one-piece burster, which might allow some leakage.
- Cracks were found in the welded joint between the burster tube and shell of one sample, probably allowing leakage.

The evidence strongly suggests that the brazing alloy line defects constitute a major cause of the GB leakage for 155-mm GB projectiles with two-piece burster tubes. As discussed below, similar defects were observed with 105-mm GB projectiles having two-piece burster tubes.

105-MM GB PROJECTILES

Twelve GB 105-mm M360 projectiles were examined in 1981 as part of the Stockpile Reliability Program (U.S. Army, 1983). Six of these projectiles were nonleakers, one had never been filled with chemicals, and five were leakers. Projectiles that had leaked were those with two-piece burster tubes in which an end plug of resulfurized steel was brazed to the main casing section. The agent had leaked through defective (porous/incomplete) brazed joints and reacted with moisture and air, leading to agent hydrolysis. This in turn made the agent corrosive and resulted in attack of the steel at the braze metal and at the sulfide stringers in the end plug. The brazed metal-steel junction may have caused some galvanic attack, which in turn may have increased the damage to the steel at the edge of the brazed joint. In this case, the initial leak of agent was through a de-

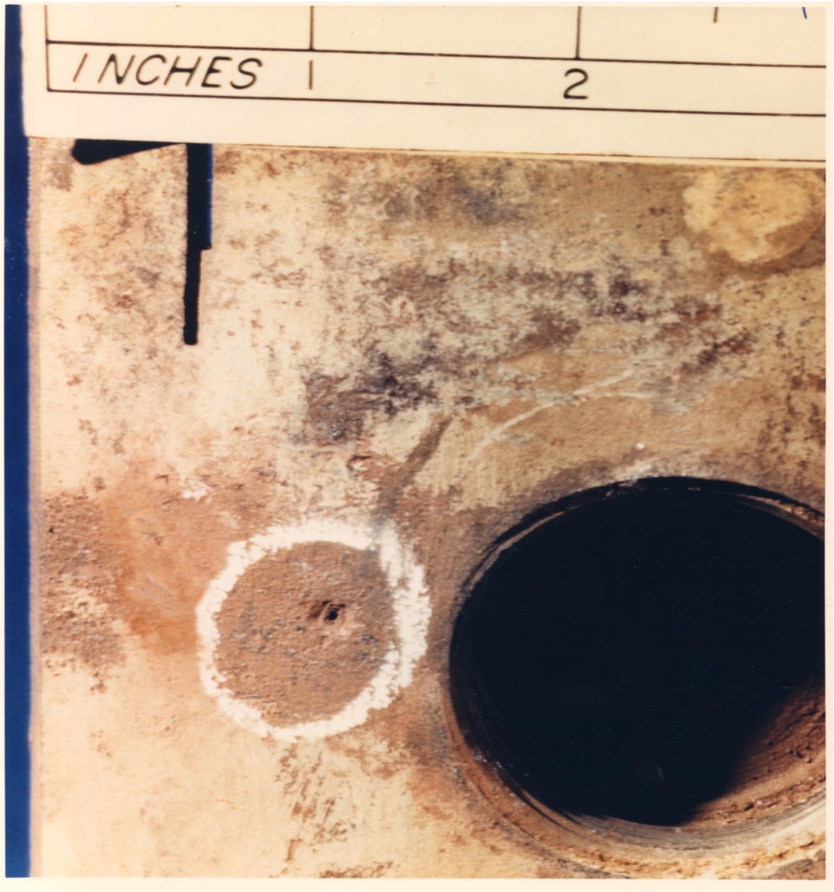

FIGURE B-1 Crater crack in MC-1 750-lb GB bomb. Source: Lis A. Wachutka, Soldier and Biological Chemical Command, Stockpile Management Team, sent by e-mail March 19, 2002.

fective brazed joint to the inside of the burster. In time, this led to corrosion of the end plug and an increased leak path. The units with one-piece burster tubes had neither the brazed joint nor the resulfurized steel end plug and therefore did not have this problem.

8-INCH GB PROJECTILES

A comprehensive metallurgical analysis of three leaking 8-inch M426 GB projectiles was conducted to determine the cause of agent leakage (U.S. Army, 1984b). A through-the-wall crack was observed in the nose end of one of the leaking projectiles. In the other two leaking projectiles, a through-the-wall crack was observed in the burster tubes. These cracks were the cause of agent leakage. In the first case, GB agent leaked from the inside of the shell to the exterior. For burster tube cracks, agent leaked from the exterior to the interior of the tubes. In all cases, manufacturing defects were thought to be responsible for the cracks rather than corrosion. The shell crack most likely formed during the press-fitting of the burster tube into the shell due to the combined effects of preexisting surface flaws and the generation of hoop stresses. The burster tube cracks resulted from improper fabrication procedures.

M55 GB ROCKETS

M55 GB rockets have an aluminum alloy warhead. GB agent reacts with the aluminum, causing general corrosion, pitting, and, eventually, leakers. Leaking rockets were first found in 1966 (U.S. Army, 1966).

As discussed earlier in the chapter, four subtypes of GB were loaded into various lots of M55 GB rockets (U.S. Army, 1985b). In 1985, the Army found a direct correlation between leakers and the subtype of GB agent filled into the rockets, as shown in Table B-1.

TABLE B-1 M55 Rocket Leaker Detection by GB Agent Type

Type of GB Agent	Number of Rocket Lots	Number of Rockets	Number of Leakers Detected	Percent of Stockpile Found to Be Leaking[a]
PRO	294	330,000	203	0.06
PR-RS	5	15,000	96	0.64
RD-RS	10	14,000	77	0.55
RO-RS	9	10,000	476	4.80

[a] These leaks were detected by periodic surveillance and were external to the rocket.
Source: U.S. Army (1985b).

Three GB rockets that had not been leakers previously were found to have external leaks after being transported to the disposal facility. Two rockets were from one PRO subtype lot and one was from an RD-RS lot. The Army estimated with 95 percent confidence that up to 1.8 percent of the rockets could develop leaks as the result of handling and movement and concluded that all rockets had the potential to become leakers while in storage or as a result of movement (U.S. Army, 1985b).

The 1985 investigation found that GB agent purity and its degradation by-products correlate with the historical leaker rate and the degree and severity of corrosion found in metallurgical examinations. The authors observed that there appears to be a correlation between acid content and leakers (U.S. Army, 1985b). However, as shown in Table B-2, acidity levels for the PRO, PR-RS, and RD-RS GB subtypes are similar, but the percent of PRO-filled rockets that leaked is much smaller than that of PR-RS or RD-RS filled rockets. This suggests that some factor other than acidity is affecting corrosion behavior.

Table B-3 identifies the distribution of GB rocket lots by agent type. All the rockets containing the most corrosive subtype of GB agent, RO-RS, have already been destroyed. Extreme pitting depth and corrosion were reported on metal parts from rockets containing all four agent subtypes. Table B-4 reports the condition of the warheads examined in this study. However, since the samples were selected because they appeared to have leaks, they were not representative of the condition of the overall stockpile of rockets when the study was conducted. The Army stated that a better characterization of the condition of the overall stockpile of rockets at that time is given by Table B-5 (U.S. Army, 1985b).

Pitting in the aluminum rocket warheads was reported to be worst at the agent liquid level line. Pitting at this location, which is encountered quite frequently in corrosion events, results from attack at the liquid/vapor interface, which may be due to condensation of moisture at the liquid surface. The extent of attack has been correlated to the acidity of the agent.

Burster casing corrosion (pitting) was less severe than that on the warhead body. This was attributed to the fact that the burster casing is always below the agent liquid level. Of the 43 burster casings examined, 31 had no pits, 9 had a few shallow pits (less than 30 per-

TABLE B-2 Acidity Levels for Various Types of GB-Filled M55 Rockets

Type of GB Agent	Acidity Level ($mg\ H^+/100\ g$)	95 Percent Confidence Interval	Percent of Stockpile Found to Be Leaking
PRO	25.2	21.2 to 29.2	0.06
PR-RS	29.2	15.6 to 42.8	0.64
RD-RS	22.2	9.6 to 34.8	0.55
RO-RS	61.8	43.7 to 79.8	4.80

Source: Adapted from U.S. Army (1985b).

TABLE B-3 Distribution of GB Rocket Lots by Storage Location and GB Agent Type

	Number of Rocket Lots (number sampled)				
Storage Location	PRO	PR-RS	RD-RS	RO-RS	Total
Anniston	22(3)	5 (5)	0	0	27 (8)
Johnston Island[a]	45	0	0	0	45 (0)
Lexington-Blue Grass	34(3)	1 (1)	0	0	35 (4)
Pine Bluff	126	0	0	0	126 (0)
Tooele[a]	74 (6)	0	7 (7)	10 (10)	91 (23)
Umatilla	70 (10)	1 (1)	1 (1)	0	72 (12)
Total	371 (22)	7 (7)	8 (8)	10 (10)	396 (47)

[a] GB munitions at these locations have been destroyed.
Source: U.S. Army (1985b).

cent of the wall), 2 had pits with 30 to 50 percent penetration, and 1 had severe pitting, with five of the pits having greater than 65 percent penetration. The burster with severe pitting was found to be leaking.

There was a puzzling inverse relationship between warhead corrosion and burster casing corrosion. Warheads with severe corrosion had burster casings with no corrosion. The two bursters with medium pit depths (30 to 50 percent) came from warheads with little corrosion. The leaking burster casing came from a warhead that also had little corrosion. The one factor in common was that the agent acidity associated with the three burster casings with medium to severe pitting was low, i.e., an average of 9 mg H^+/100 g.

Gelled agent did not have a consistent effect on warhead corrosion. Two samples had general corrosion with no deep pits. This agent had no acidity. A third warhead had severe pitting, with two pits exhibiting 58 to 71 percent penetration. Agent acidity from this warhead was high, 65.3 mg H^+/100 g.

TABLE B-4 Condition of M55 Rocket Warheads Examined: Average Number of Pits in the Warhead Sample as a Function of Warhead Condition and Pit Depth

			Percent of Wall Penetrated					
Type of GB Agent	Warhead Condition	Sample Size	0-14	15-41	42-57	58-71	72-100	Comment
PRO	Good	11	0	0.1	0	0	0	
	Fair	1	2	4	1	0	1	
	Poor	1	62	56	1	0	1	Leaker
PR-RS	Good	2	1.5	0	0	0	0	
	Fair	5	5	2	0	0	0	Burster tube leak
RD-RS	Good	2	0.5	0	0	0	0	
	Fair	2	0	0	0	0	0	Even corrosion
	Poor	4	28	8	0.5	0	0.25	One leaker
RO-RS	Good	2	1	1	0	0	0	
	Fair	1	0	0	0	0	0	Seal ball pitting
		2	12	0	0	0	0	Gelled agent
		1	6	1	0	0	0	
	Poor	3	50	40	5	1	0	
		1	39	10	3	2	0	Gelled agent
		3	43	25	5	2	3	Known leakers

Source: U.S. Army (1985b).

TABLE B-5 Results of Visual Inspection for Sampled M55 Rocket Warheads

Type of GB Agent	No. of Samples Examined	No. of Pitted Warheads	Percentage of Pitted Warheads	95 Percent Confidence Interval
PRO	44	4	9	3-22
PR-RS	14	4	29	8-58
RD-RS	20	7	35	15-59
RO-RS	16	9	56	30-80
Total	94	24	26	17-35

Source: U.S. Army (1985b).

M2A1 4.2-INCH HD ROUNDS

In 1986, 4.2-inch HD rounds from Pueblo Army Depot were studied (U.S. Army, 1986b). Both were from the same box and had been stored in the vicinity of four other rounds that were confirmed as heavy leakers. One round had only the deterioration associated with storage. The second round had significant deterioration on the forward end (including the fuze, ogive, and body section). Analyses of deposits on this round confirmed the presence of mustard agent. The deterioration of this round was attributed to corrosion from the mustard agent.

TON CONTAINERS

GB

Four brass valves on ton containers of GB were examined in a 1986 report (U.S. Army, 1986c): one that had been at the bottom of a GB ton container, one that had been at the top of a different GB ton container, and two new valves. Three plugs that had been exposed to GB in different ton containers also were examined. The bottom valve had corroded in the threaded section from the inside in a nonuniform fashion. The top valve and plugs showed no visible dimensional change, but the interior surfaces of the plugs were covered with a black deposit. The brass (60 Cu/38 Zn/2 Pb) in both the valves and plugs had undergone intergranular corrosion as well as selective attack of the beta (zinc-rich) phase.[1]

Mustard Agent

Reaction of degraded HD with the iron in the steel container produced hydrogen, which can build up to high pressure in the headspace (U.S. Army, 2001). Pressures of 8 to 136 psig have been found in ton containers and up to 200 psig in projectiles. This hydrogen presents two hazards. First, it could cause degraded plugs to pop out of the container. Second, it could ignite when the container is opened and an ignition source is present. For this reason, workers will need special training for such operations, and areas where such containers are opened will need electrical services and ventilation systems designed for the possible presence of hydrogen.

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[1] The alloy composition has a two-phase structure, alpha and beta, with undissolved lead. The beta phase has a higher zinc content than the alpha phase. Intergranular corrosion occurs at the grain (crystalline phase) boundaries, and the grains of the beta phase appear to have been more rapidly attacked than the grains of the alpha phase (ASM, 1961; see pp. 1013-1038, especially p. 1024).

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Appendix C

Biographical Sketches of Committee Members

Peter B. Lederman, *Chair*, graduated with a Ph.D. in chemical engineering from the University of Michigan. He recently retired as executive director, Hazardous Substance Management Research Center, and executive director, Office of Intellectual Property, New Jersey Institute of Technology. Dr. Lederman has over 50 years of broad experience in all facets of environmental management, control, and policy development; considerable experience in hazardous substance treatment and management; and over 18 years of experience as an educator. He is a registered professional engineer, a diplomate in environmental engineering, and a national associate of the National Academies. Dr. Lederman has also worked at the federal (EPA) and state levels with particular emphasis on environmental policy. His expertise is in chemical engineering, hazardous waste treatment, and educational and corporate leadership.

Charles I. McGinnis, *Vice-Chair*, with an M.Engr. in civil engineering from Texas A&M University, retired from the U.S. Army as a major general and was former director of civil works for the U.S. Army Corps of Engineers and more recently served in senior positions at the Construction Industry Institute in Austin, Texas. He has also served as the director of engineering and construction for the Panama Canal Company and later as vice president of the company and lieutenant governor of the Canal Zone. As director of civil works, he was responsible for a $3 billion per year planning, design, construction, operation, and maintenance program of water-resource-oriented public works on a nationwide basis. He has considerable experience with engineering and construction. He is a registered professional engineer in Texas and Missouri.

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

John J. Costolnick graduated from Northwestern University with an M.S. degree in chemical engineering and is a registered professional engineer. He retired as vice president for engineering of Exxon Chemical Company. He worked for Exxon for more than 35 years, serving in positions of increasing responsibility, from manufacturing manager and plant manager, to vice president for agricultural chemicals and vice president for basic chemical technology. Mr. Costolnick has considerable experience in chemical operations and manufacturing.

Elisabeth M. Drake, a member of the National Academy of Engineering, graduated from Massachusetts Institute of Technology (MIT) with a Ph.D. in chemical engineering. She retired in 2000 as the associate director of the MIT Energy Laboratory. She has had considerable experience in risk management and communication; in technology associated with the transport, processing, storage, and disposal of hazardous materials; and in chemical engineering process design and control systems. Dr. Drake has also served on several National Research Council committees relating to chemical demilitarization. Dr. Drake has a special interest in the interactions between technology and the environment. She belongs to a number of environmental organizations, including the Audubon Society, the Sierra Club, and the National Wildlife Federation.

Deborah L. Grubbe graduated from Purdue University with a B.S. in chemical engineering with highest distinction and received a Winston Churchill Fellowship to attend Cambridge University in England, where she received a certificate of postgraduate study in chemical engineering. She is a registered professional engineer and engineer of record for DuPont. She is currently corporate director for safety and health for DuPont. Previously, she was operations and engineering director for DuPont Nonwovens, accountable for manufacturing, engineering, safety, environmental, and information systems. Ms. Grubbe is a board member of the American Institute of Chemical Engineers Engineering and Construction Contracting Division and has held committee leadership positions with the Construction Industry Institute. She has considerable expertise in safety, chemical manufacturing technology, and project management and execution.

David A. Hoecke graduated from Cooper Union with a B.S.M.E. He is currently president and CEO of Enercon Systems, Inc. His expertise is in the fields of waste combustion, pyrolysis, heat transfer CFD modeling, and gas cleaning. In 1960, he began working for Midland-Ross Corporation as a project engineer, rising to the position of chief engineer for incineration by 1972. In 1974, he founded his own company and has since been responsible for the design and construction of numerous combustion systems, including solid waste incinerators, thermal oxidizers, heat recovery systems, and gas-to-air heat exchangers.

David H. Johnson graduated from the Massachusetts Institute of Technology with a Sc.D. in nuclear engineering. He currently serves as vice president and general manager of ABS Consulting in Irvine, California. He has more than 20 years of experience in risk-based analysis for industry and government applications. He has considerable expertise in and knowledge of all facets of probabilistic risk assessments, including probabilistic modeling and investigation of the impacts of industrial endeavors. His primary expertise is in risk assessment and management.

John L. Margrave, a member of the National Academy of Sciences, graduated from the University of Kansas with a B.S. in engineering physics and a Ph.D. in physical chemistry. Dr. Margrave is currently the chief scientific officer at the Houston Advanced Research Center and the E.D. Butcher Professor of Chemistry at Rice University. His expertise is in high-temperature chemistry, materials science, and environmental chemistry. His research interests include various areas of physical/inorganic chemistry, including matrix-isolation spectroscopy/metal atom chemistry; high-temperature chemistry, including mass spectrometry; high-pressure chemistry; environmental chemistry; and nanoscience/technology. Dr. Margrave previously served on two National Research Council committees in the chemical demilitarization area.

James F. Mathis, a member of the National Academy of Engineering, graduated from the University of Wisconsin with a Ph.D. in chemical engineering. Dr. Mathis was vice president of science and technology for Exxon Corporation, where he was responsible for oversight of $700 million in worldwide research and development programs, and was chair of the New Jersey Commission on Science and Technology until his retirement in 1997.

Frederick G. Pohland, a member of the National Academy of Engineering, graduated from Purdue University with a Ph.D. in environmental engineering. He is currently a professor and the Edward R. Weidlein Chair of Environmental Engineering at the University of Pittsburgh, as well as director of the Engineering Center for Environment and Energy and codirector of the Groundwater Remediation Technologies Analysis Center. He is a registered professional engineer and a diplomate in environmental engineering. He has taught and written extensively in the areas of solid and hazardous waste management, environmental impact assessment, and innovative technologies for waste minimization, treatment, and environmental remediation.

Robert B. Puyear graduated from Purdue University with an M.S. degree in industrial administration and from the Missouri School of Mines and Metallurgy with a B.S. in chemical engineering. Currently he is a consultant specializing in corrosion prevention and control, failure analysis, and materials selection. Previously he worked for Union Carbide for 16 years, developing high-performance materials for chemical and aerospace applications, and for Monsanto for 21 years as a corrosion specialist, including managing its Mechanical and Materials Engineering Section.

Charles F. Reinhardt, who holds an M.D. from Indiana University School of Medicine and an M.Sc. in occupational medicine from Ohio State University School of Medicine, retired after more than 30 years with the DuPont Company. Working at DuPont initially as a plant physician, Dr. Reinhardt joined its Haskell Laboratory in 1966 and served first as a physiologist, rose to chief of the physiology section, and then became a research manager for environmental sciences. In 1971, he became assistant director of the laboratory and in 1976 was named its director, a position he held until his retirement in 1996. An expert in occupational medicine and toxicology, he has served on numerous National Research Council panels and committees, including the Committee on Toxicology.

W. Leigh Short, with a Ph.D. in chemical engineering from the University of Michigan, was a principal and vice president of Woodward-Clyde responsible for the management and business development activities associated with the company's hazardous waste services in Wayne, New Jersey. Dr. Short has expertise in air pollution, chemical process engineering, hazardous waste services, feasibility studies and site remediation, and project management. He has taught courses in control technologies, both to graduate students and as a part of EPA's national training programs. He has served as chairman of the NO_x control technology review panel for the EPA.

Jeffrey I. Steinfeld graduated from Harvard University with a Ph.D. in physical chemistry. He is currently a professor of chemistry at the Massachusetts Institute of Technology. He has taught and written extensively for 37 years at MIT, specializing in high-sensitivity monitoring techniques, pollution prevention, and environmental research and education. His interests include applying scientific knowledge to environmental decision making and ensuring stakeholder involvement in issues that have political, economic, social, scientific, and technical impact.

Rae Zimmerman, with an A.B. in chemistry from the University of California at Berkeley, an M.S. in city planning from the University of Pennsylvania, and a Ph.D. in planning from Columbia University, is currently a professor of planning and public administration and director of the Institute for Civil Infrastructure Systems (ICIS) at the Robert F. Wagner Graduate School of Public Service of New York University. She has directed and/or advised federal, state, and local government agencies on planning and implementation of environmental policies, programs, and plans. Active in the areas of environmental impact assessment; socioeconomic, community, and land use impact evaluations; risk assessment; institutional analysis (legal, financial, and administrative); permitting and regulatory support; and public participation and/or public perception studies, she has been involved in extensive development and implementation of public participation and communication programs for government-sponsored water resources projects and hazardous waste cleanup in connection with environmental permits, plans, and environmental impact statements. She is a fellow of the American Association for the Advancement of Science and a past president of the Society for Risk Analysis.