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WORKING PARTY ON EVALUATION OF CHEMICAL WEAPON DESTRUCTION TECHNOLOGIES**

CRITICAL EVALUATION OF PROVEN CHEMICAL WEAPON DESTRUCTION TECHNOLOGIES

(IUPAC Technical Report)

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Critical evaluation of proven chemical weapon destruction technologies

(IUPAC Technical Report)

Abstract: A critical evaluation is made of the chemical weapon destruction technologies demonstrated for 1 kg or more of agent in order to provide information about the technologies proven to destroy chemical weapons to policy-makers and others concerned with reaching decisions about the destruction of chemical weapons and agents. As all chemical agents are simply highly toxic chemicals, it is logical to consider the destruction of chemical agents as being no different from the consideration of the destruction of other chemicals that can be as highly toxic—their destruction, as that of any chemicals, requires the taking of appropriate precautions to safeguard worker safety, public health, and the environment. The Chemical Weapons Convention that entered into force in 1997 obliges all States Parties to destroy any stockpiles of chemical weapons within 10 years from the entry into force of the Convention—by 2007—with the possibility of an extension for up to 5 years to 2012. There is consequently a tight timeline under the treaty for the destruction of stockpiled chemical weapons and agents—primarily held in Russia and the United States. Abandoned or old chemical weapons—notably in Europe primarily from World War I, in China from World War II as well as in the United States—also have to be destroyed. During the past 40 years, more than 20 000 tonnes of agent have been destroyed in a number of countries and over 80 % of this has been destroyed by incineration. Although incineration is well proven and will be used in the United States to destroy over 80 % of the U.S. stockpile of 25 800 tonnes of agent, considerable attention has been paid particularly in the United States to alternative technologies to incineration because of several constraints that are specific to the United States. Much of the information in this report is based on U.S. experience—as the United States had, along with the Russian Federation, by far the largest stockpiles of chemical weapons and agents anywhere in the world. The United States has made much progress in destroying its stockpile of chemical weapons and agents and has also done more work than any other country to examine alternative technologies for the destruction of chemical weapons and agents. However, the national decisions to be taken by countries faced with the destruction of chemical weapons and agents need to be made in the light of their particular national conditions and standards—and thus may well result in a decision to use different approaches from those adopted by the United States. This report provides information to enable countries to make their own informed and appropriate decisions.

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INTRODUCTION

1. The aim of the IUPAC Working Party on Evaluation of Chemical Weapon Destruction Technologies has been to provide information about the technologies that have been proven to destroy chemical weapons to policy-makers and others concerned with reaching decisions about the destruction of chemical weapons and agents. The Working Party has recognized that each country faced with destruction of chemical weapons will need to take decisions on how to achieve this by considering both the quantity and nature of the chemical weapons in that country, the requirements of the Chemical Weapons Convention, and its own national laws and regulations in deciding where and how to destroy them safely with minimum impact on public health and the environment. Consequently, this report is designed to provide appropriate and relevant information on the proven available destruction technologies in order to help countries arrive at informed national decisions appropriate for that country.

2. The Working Party has examined the technologies for the destruction of chemical weapons that have been demonstrated on 1 kg or more of toxic chemical agent. In carrying out this study, the Working Party has first taken note of the mandate for destruction that stems from the requirements of the Chemical Weapons Convention (CWC) opened for signature in January 1993, entered into force on 29 April 1997 and, in December 2001, has 144 States Parties [1]. The CWC requires that all declared chemical weapons be destroyed within 10 years after the entry into force of the Convention—in other words, by 29 April 2007—with a possible extension, should that be necessary, for up to five years to 29 April 2012. The CWC also sets out requirements for the destruction of old and abandoned chemical weapons [2] that will continue to be found for decades in countries where chemical weapons have been produced, tested, stored, and used. There are thus two principal categories of chemical weapons:

   a. Stockpiled chemical weapons, which have to be destroyed by 29 April 2007 with a possible extension to 29 April 2012; and

   b. Old and abandoned chemical weapons, in unknown types and quantities, which will be found from time to time and will need to be destroyed also by 29 April 2007 unless the Executive Council decides to modify the provisions on the time limit.

3. A historical perspective is then provided giving an indication of the nature of the chemicals that have been used as chemical weapons during the past century and then addresses the nature of the problem. Many chemical weapons have been destroyed or disposed of by methods that are no longer accepted—and indeed, the CWC specifically prohibits **dumping in any body of water, land burial, and open pit burning.** During the past 40 years, over 20 000 agent-tonnes of chemical weapons have been destroyed; more than 80 % by incineration and the remainder by neutralization. It should be noted that the unit used in this report for the quantities of chemical weapons destroyed is agent-tonnes and **not** the weight of munitions. Following the entry into force of the CWC, a total figure has been published by the Organization for the Prohibition of Chemical Weapons (OPCW) for the chemical agents declared and destroyed. The figure as of 30 June 2001 for the total declared is 69 862 agent-tonnes, and the total destroyed is 5 734 agent-

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1. Available at http://www.opcw.org
2. The definitions of these terms in the Chemical Weapons Convention are provided in Chapter I of this report.

tonnes. The principal contributors to the global stockpile are the United States and the Russian Federation; the United States has declared its stockpile as comprising some 31 495 agent-tons (short tons) [3] which corresponds to 28 570 agent-tonnes whereas the Russian Federation has declared [4] a stockpile of about 40 000 agent-tonnes. As India and one other country (known from non-OPCW information to be South Korea) have also declared chemical weapons, the combined stockpiles for these two countries can be deduced as being about 1 500 agent-tonnes. As of October 2001, the United States had destroyed using incineration over 20 % [5] of its stockpiled chemical weapons—or some 6 700 agent-tonnes. In addition to stockpiled chemical weapons, there are also quantities of old and abandoned chemical weapons in several countries around the world—notably in Europe primarily from World War I, in China from World War II as well as in the United States—which also need to be destroyed.

4. In considering the technologies for the destruction of chemical weapons, it is important to recognize that the destruction technology is only one part of the overall process of safely disposing of these unwanted materials. The technology destroys the agents and decontaminates their containers while creating residual process streams (or effluent streams) whether gas, liquid, or solid. The treatment of these effluent streams to permit discharge to the environment with minimum impact on public health and the environment is as important as the destruction technology itself. Because chemical agents were produced to cause harm, there was never any necessity to ensure that the agents produced were particularly pure, as the original considerations were simply that the agent should be effective and should have sufficient stability to be stored for a number of years prior to use. The destruction and disposal is consequently made more complex because the agent is likely to contain impurities and materials, such as solvents, which were present when it was originally produced, as well as degradation products generated during storage. Many stockpiled chemical weapons are over 40 years old, and consequently the nature of their contents is variable and uncertain. This variation in the material to be destroyed means that the requirement is to identify technologies and effluent treatments that are robust in that they are capable of dealing with the impurities and the variations in agent composition.

5. This report first addresses transportation of chemical weapons and bulk agent from storage depots or other locations where chemical weapons have been found to sites at which they are destroyed. The various options for the removal of the agents from weapons are then considered. The next two chapters examine the high-temperature and low-temperature destruction technologies, respectively, which have been used—or are being considered for use—with chemical agents. The options for gas, liquid, and solid effluent treatment are then addressed. A subsequent chapter considers how to deal with abandoned chemical weapons that will be found intermittently in unknown types and quantities in many countries for decades to come. References are provided to assist those seeking additional detail.

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[3] U.S. Department of Defense News Release, *U.S. Chemical Weapons Stockpile Information Declassified,* Reference Number No. 024-96, 22 January 1996. Available at http://www.defenselink.mil/news/ Jan1996/b12496_bt024-96.htm

[4] Government of the Russian Federation, Resolution No. 510 of 5 July 2001, *On Making Amendments and Additions to the Resolution by the Government of the Russian Federation of March 21, 1996 (No. 305) on Approving the Federal Special Program "Chemical Weapons Stockpiles Destruction in the Russian Federation"*. Available at http:www.armscontrol.org

[5] A. Johnson-Winegar. *The U.S. Chemical Demilitarization Program,* Statement before the Senate Armed Services Committee, Sub-Committee on Emerging Threats and Capabilities, U.S. Senate, 12 July 2001.

6. A final chapter considers the technologies and constraints that have to be considered by a country faced with making informed decisions about destruction of chemical weapons. The Working Party is acutely aware that much of the information presented in this report is based on U.S. experience [6], and one of us (Richard S. Magee) had been Chairman of the U.S. National Research Council 1996 Panel on "Review and Evaluation of Alternative Chemical Disposal Technologies". However, this is hardly surprising as the United States had, along with the Russian Federation, by far the largest stockpiles of chemical weapons and agents anywhere in the world. The United States has made much progress in destroying its stockpile of chemical weapons and agents and has also done more work than any other country to examine alternative technologies for the destruction of chemical weapons and agents. This report therefore draws heavily on the U.S. experience. **However, the national decisions to be taken by countries faced with the destruction of chemical weapons and agents need to be made in the light of their particular national conditions and standards—and thus may well result in a decision to use different approaches from those adopted by the United States.** National decisions in other countries will need to consider the stockpile size and the nature of the chemical weapons in those countries in deciding both where and how to destroy them in accordance with the requirements of the Chemical Weapons Convention and to do this safely with minimum impact on public health and the environment. The aim of this report is to provide information on the available destruction technologies in order to help countries arrive at informed national decisions appropriate for that country.
7. In order to maximize the benefits of the report in helping countries arrive at informed national decisions appropriate for that country in respect of chemical weapons destruction technology, this report uses the commonly used terminology for chemical warfare (CW) agents and provides a tabulation here to relate these common terms for CW agents to their IUPAC chemical names.

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[6] Indeed, it should be noted that because one of us (Richard S. Magee) had been Chairman of the U.S. National Research Council 1996 Panel on "Review and Evaluation of Alternative Chemical Disposal Technologies", language used in that NRC Report has been reviewed, updated, and modified where appropriate—or left unchanged where appropriate.

CW agent	IUPAC name	Alternative names
AC	hydrogen cyanide	
Adamsite	10-chloro-5,10-dihydrophenarsazine	DM
BBC	2-bromo-2-phenylacetonitrile	CA; α-bromobenzylcyanide; 1-bromo-1-tolunitrile
BZ	3-quinuclidinyl benzilate	3-quinuclidinyl benzilate
CA	2-bromo-2-phenylacetonitrile	BBC; α-bromobenzylcyanide; 1-bromo-1-tolunitrile
CS	(2-chlorobenzylidene)malonodinitrile	
CG	phosgene	carbonyl dichloride
CK	cyanogen chloride	
Clark I	chlorodiphenylarsine	DA; diphenylchloroarsine;
Clark II	cyanodiphenylarsine	DC; diphenylcyanoarsine; diphenylarsinous cyanide
CN	α-chloroacetophenone	1-chloroacetophenone; 2-chloro-1-phenylethan-1-one
DA	diphenyarsinous chloride	Clark I; diphenylchloroarsine
DC	cyanodiphenylarsine	Clark II; diphenylcyanoarsine
DM	10-chloro-5,10-dihydrophenarsazine	Adamsite
GA	*O*-ethyl *N,N*-dimethyl phosphoroamidocyanidate	tabun
GB	*O*-isopropyl methylphosphonofluoridate	sarin
GD	*O*-pinacolyl methylphosphonofluoridate	soman; 3,3-dimethylbutan-2-yl methylphosphonofluoridate; *O*-(1,2,2-trimethylpropyl)-methylphosphonofluoridate
H	bis(2-chloroethyl) sulfide	mustard; sulfur mustard; bis(2-chloroethyl) sulfane
HN-3	tris(2-chloroethyl) amine	nitrogen mustard
Lewisite	2-chlorovinyldichlorarsine	L; 2-chloroethenylarsonous dichloride; 2-chlorovinylarsinous dichloride
Nitrogen mustard	substituted (2-chloroethyl) amines	HN-1, HN-2, HN-3
Sarin	*O*-isopropyl methylphosphonofluoridate	GB
Soman	*O*-pinacolyl methylphosphonofluoridate	GD; 3,3-dimethylbutan-2-yl methylphosphonofluoridate; *O*-(1,2,2-trimethylpropyl)-methylphosphonofluoridate
Tabun	*O*-ethyl *N,N*-dimethyl	GA; phosphoroamidocyanidate
VX	*O*-ethyl *S*-2-diisopropylaminoethyl methyl phosphonothiolate	*O*-ethyl *S*-2-diisopropylaminoethyl methyl phosphonothioate
VR	*O*-isobutyl *S*-[2-diethylamino ethyl] methyl thiophosphonate	Russian VX; *O*-isobutyl *S*-[2-diethylamino ethyl] methyl phosphothioate

I. MANDATE FOR DESTRUCTION

1. The principal developments regarding chemical weapons occurred in World War I when they were first used in April 1915, leading to the development of retaliatory capabilities and the extensive use of chemical weapons during the later years of that war. The first chemical warfare agents were readily available industrial and other civil-use chemicals such as ethyl bromoacetate, chlorine, hydrogen cyanide, and phosgene. World War I saw the use of a large variety of toxic chemicals (see Table 1) including mustard gas [7], which became the agent of choice by the end of that war except where nonpersistent agents were needed.

Table 1 CW agents extensively used in World War I[a].

Agent	First used	Code/symbol
Tear gases and other irritants		
Xylyl bromide	1915	
Benzyl bromide	1915	
Bromoacetone	1915	
Ethyl iodoacetate	1915	
Diphenylchloroarsine (Clark I)	1917	DA
Diphenylcyanoarsine (Clark II)	1918	DC
α-Bromobenzylcyanide	1918	BBC or CA
Choking gases		
Chlorine	1915	
Phosgene	1915	CG
Diphosgene	1916	
Chloropicrin	1916	PS
Blood gases		
Hydrogen cyanide	1916	AC
Cyanogen chloride	1916	CK
Blister agents		
Mustard	1917	H
Phenyldichloroarsine	1917	PD
Ethyldichoroarsine	1918	DICK

[a] Table developed from Table 3.1 in T. Stock and K. Lohs, "Old chemical munitions and warfare agents: Detoxification and degradation", in *The Challenge of Old Chemical Munitions and Toxic Armament Wastes, SIPRI Chemical and Biological Warfare Studies*, T. Stock and K. Lohs (Eds.), No. 16, Oxford University Press (1997).

2. At the end of World War I, stockpiles of chemical weapons and of agents were destroyed by available expeditious means, such as dumping, burying, open-pit burning, or release into the atmosphere. The period between the end of World War I and the start of World War II saw relatively little development of new chemical warfare agents as many countries hoped that chemical weapons would never again be used in war. Many nations signed and ratified the Geneva Protocol [8] of 1925, which prohibited the use in war of asphyxiating, poisonous or other gases, and of all anal-

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7. It should be noted that many chemical warfare agents described as "gases" are actually liquids; for example, mustard gas and several tear gases.
8. League of Nations. *Protocol for the Prohibition of the Use in War of Asphyxiating, Poisonous or Other Gases, and of Bacteriological Methods of Warfare, Signed at Geneva, 17 June 1925,* Treaty Series, Vol. XCIV, 1929, Nos. 1, 2, 3 and 4, No. 2138, p. 65.

ogous liquids materials or devices. Some States, however, signed with reservations that would allow States to retaliate in kind with chemical (or biological) weapons should these be used against the State.

3. World War II saw a major concern that chemical weapons might be used, and both sides acquired stocks of chemical weapons. In addition, Germany developed a new class of chemical agent based on toxic organophosphorus compounds known as the G nerve agents. Although both sides had large stocks of weapons and agents (see Table 2), chemical weapons were not used in World War II apart from by Japan, and the end of the war saw the discovery by the Allied Forces of the German nerve agents, which were then studied extensively in the post-war years, resulting in the identification of a further class of even more toxic agents—the V nerve agents. It should, however, be noted that these nerve agents were not found by scientists in military laboratories seeking more effective chemical warfare agents, but were discovered by scientists engaged in industrial chemistry.

Table 2 CW agents stockpiled in World War II [8].

Agent	Code/symbol
Tear gases and other irritants	
Ethyl iodoacetate	
Diphenylchloroarsine (Clark I)	DA
Diphenylcyanoarsine (Clark II)	DC
α-Bromobenzylcyanide	CA
Adamsite	DM
1-Chloroacetophenone	CN
Choking gases	
Phosgene	CG
Diphosgene	
Chloropicrin	PS
Blood gases	
Hydrogen cyanide	AC
Cyanogen chloride	CK
Blister agents	
Mustard	H
Phenyldichloroarsine	
Lewisite	L
Bis(2-chloroethylthioethyl)ether	
Tris(2-chloroethyl)amine	HN-3
Nerve agents	
Tabun	GA

Most of the national stockpiles of weapons and agents were abandoned or destroyed at the end of World War II. Such abandoned chemical weapons are discovered from time to time in a number of countries and need to be destroyed safely.

4. Following World War II and the recognition of the potential role for nuclear weapons, a number of countries in the 1950s and the 1960s decided to abandon their offensive chemical warfare programs. Consequently, by the latter years of the 1960s, proposals were being made in Geneva for an international treaty that would prohibit the development, production, acquisition, and storage of chemical weapons. It was to take some 20 years for these negotiations to be brought to a successful conclusion with the opening for signature on 13–15 January 1993 of the Chemical Weapons Convention, which entered into force on 29 April 1997.

5. The Chemical Weapons Convention totally prohibits the development, production, transfer, acquisition, stockpiling, and retention of chemical weapons and their use and requires all States Parties to undertake "*to destroy chemical weapons it owns or possesses, or that are located in any place under its jurisdiction or control, in accordance with the provisions of this Convention*" [9]. The scope of the Convention is broad in that chemical weapons are defined as being:

   > *Toxic chemicals and their precursors, except where intended for purposes not prohibited under the Convention, as long as the types and quantities are consistent with such purposes* [10]

   and toxic chemicals are defined as

   > *Any chemical which through its chemical action on life processes can cause death, temporary incapacitation or permanent harm to humans or animals. This includes all such chemicals, regardless of their origin or of their method of production, and regardless of whether they are produced in facilities, in munitions or elsewhere.* [11]

   It is thus evident that **all** chemicals are covered by the prohibition of the Convention unless they are intended for purposes not prohibited under the Convention and are in types and quantities that are consistent with such purposes.

6. The requirement for the destruction of chemical weapons is detailed in Article IV of the Convention, which requires that:

   > *Each State Party shall destroy all chemical weapons.... Such destruction shall begin not later than two years after this Convention enters into force for it and shall finish not later than 10 years after entry into force of this Convention.* [12]

   The destruction requirements are further elaborated in Part IV(A) of the Verification Annex, which *inter alia* require that the "*chemicals are converted in an essentially irreversible way to a form unsuitable for production of chemical weapons, and which in an irreversible manner renders munitions and other devices unusable as such*." [13]

7. In addition, Part IV(A) sets out provisions for the order of destruction of chemical weapons, which is based on the obligations specified in Article I and the other Articles of the Convention. Paragraph 16 of Part IV (A) states that:

   > *16. For the purpose of destruction, chemical weapons declared by each State Party shall be divided into three categories:*

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9. Organization for the Prohibition of Chemical Weapons. *Convention on the Prohibition of the Development, Production, Stockpiling and Use of Chemical Weapons and on their Destruction,* Article I, para. 2. Available at http://www.opcw.org
10. CWC, Article II, para. 1.
11. CWC, Article II, para. 2.
12. CWC, Article IV, para. 6.
13. CWC, Verification Annex, Part IV (A), para. 12.

Category 1:	*Chemical weapons on the basis of Schedule 1 chemicals and their parts and components;*
Category 2:	*Chemical weapons on the basis of all other chemicals and their parts and components;*
Category 3:	*Unfilled munitions and devices, and equipment specifically designed for use directly in connection with the employment of chemical weapons.*

8. Paragraph 17 of Part IV (A) sets out the requirements placed on the State Party for the destruction of chemical weapons in the three categories:

Category	Start of destruction	Completion of destruction
1	Not later than 2 years after EIF for the State Party	Not later than 10 years after EIF of the Convention
2	Not later than 1 year after EIF for the State Party	Not later than 5 years after EIF of the Convention
3	Not later than 1 year after EIF for the State Party	Not later than 5 years after EIF of the Convention

EIF = entry into force

It will be noted that the requirement is the more demanding the later that the Convention enters into force for a particular State Party as the completion deadlines are after the **entry into force of the Convention** (i.e., 29 April 1997).

9. Specific requirements are also specified for the amounts of Category 1 chemical weapons to be destroyed again as a function of time after the **entry into force of the Convention:**

Phase	Amount to be destroyed	Time by which to be destroyed
1	Not less than 1 %	Not later than 3 years after EIF of the Convention
2	Not less than 20 %	Not later than 5 years after EIF of the Convention
3	Not less than 45 %	Not later than 7 years after EIF of the Convention
4	All Category 1 chemical weapons	Not later than 10 years after EIF of the Convention

10. The Verification Annex also includes a provision allowing a State Party, if it believes that it will be unable to ensure destruction of all chemical weapons within the 10-year time frame, to apply to the Executive Council for an extension of the deadline for the completing the destruction of its chemical weapons [14]. The Convention, however, states that "*any extension shall be the minimum necessary but in no case shall the deadline for a State Party to complete its destruction of all chemical weapons be extended beyond 15 years after entry into force of this Convention.*" [15]

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14. CWC, Verification Annex, Part IV (A), para. 24.
15. CWC, Verification Annex, Part IV (A), para. 26.

11. An exception is made in respect of "old chemical weapons and abandoned chemical weapons", which are defined in the Convention as:

> *"Old Chemical Weapons" means:*
>
> *(a) Chemical weapons which were produced before 1925; or*
>
> *(b) Chemical weapons produced in the period between 1925 and 1946 that have deteriorated to such an extent that they can no longer be used as chemical weapons.*
>
> *"Abandoned Chemical Weapons" means:*
>
> *Chemical weapons, including old chemical weapons, abandoned by a State after 1 January 1925 on the territory of another State without the consent of the latter.* [16]

12. Part IV (B) of the Verification Annex sets out the requirements for the destruction of both old and abandoned chemical weapons. In respect of old chemical weapons produced before 1925 the significant requirement is that

> *6. A State Party shall treat old chemical weapons that have been confirmed by the Technical Secretariat as meeting the definition in Article II, paragraph 5 (a), as toxic waste. It shall inform the Technical Secretariat of the steps being taken to destroy or otherwise dispose of such old chemical weapons as toxic waste in accordance with its national legislation.* [17]

The logic in regarding these particular old chemical weapons as toxic waste will be apparent when it is recalled that the wide range of toxic chemicals used in World War I (see Table 1) were generally available toxic chemicals or industrial chemicals, that could be readily chlorinated, which were used as chemical weapons and were not made expressly for this purpose.

13. In regard to old chemical weapons produced between 1925 and 1946, the principal consideration is whether or not they can still be used as chemical weapons. If the Technical Secretariat confirms that they meet the definition in Article II, paragraph 5(b)—namely that they **have deteriorated to such an extent that they can no longer be used as chemical weapons**—then the requirement in the CWC is that

> *7. ...a State Party shall destroy old chemical weapons that have been confirmed by the Technical Secretariat as meeting the definition in Article II, paragraph 5 (b), in accordance with Article IV and Part IV (A) of this Annex. Upon the request of the State Party, the Executive Council may, however, modify the provisions on time-limit and order of destruction of these old chemical weapons, if it determines that doing so would not pose a risk to the object and purpose of this Convention. The request shall contain specific proposals for modification of the provisions and a detailed explanation of the reasons for the proposed modifications.*

Other chemical weapons produced between 1925 and 1946 that do not meet the definition in Article II, paragraph 5(b) shall be destroyed in the same way as chemical weapons produced from 1 January 1946 onwards—in accordance with Article IV and Annex IV (A) of the Verification Annex.

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16. CWC, Article II, paras. 5 and 6.
17. CWC, Verification Annex, Part IV (B), para. 6.

14. For abandoned chemical weapons, the requirement is that these be destroyed. These will be treated in the same way as declared chemical weapons—in accordance with Article IV and Annex IV (A) of the Verification Annex—unless the abandoned chemical weapons also meet the definition of old chemical weapons in Article II 5(b) when the Executive Council of the CWC may agree to modify or in exceptional cases suspend the provisions for destruction so long as doing so "*would not pose a risk to the object and purpose of this Convention*" [18]. Should the abandoned chemical weapons not meet the definition of old chemical weapons in Article II 5(b) then the Executive Council may, on the request of the State Party on whose territory these weapons have been abandoned, in exceptional circumstances modify the provisions on the time limit and the order of destruction, if the Executive Council determines that doing so would not pose a risk to the object and purpose of the Convention.

15. Consequently, under the CWC there are essentially two principal categories of chemical weapons:

    a. Those declared by States Parties that are essentially chemical weapons or chemical warfare agents in the stockpile of that State, and that have to be destroyed during the period commencing two years after entry into force of the CWC for that State and being completed not later than 10 years after entry into force of the CWC (i.e., by 29 April 2007).

    b. Old chemical weapons that have been produced before 1925, which shall be destroyed as toxic waste.

16. Abandoned chemical weapons form an intermediate group, which may be destroyed in the same way as stockpiled chemical weapons or possibly, with the agreement of the Executive Council, destroyed in the same way as old chemical weapons, as toxic waste. In effect, chemical weapons are either **stockpile** munitions or agents that are still in storage or **non-stockpile** munitions or agent that have been buried often on battlefields, on present and past military bases, along transportation routes or dumped at sea. Such non-stockpile munitions or agents may also fall into the categories of old chemical weapons or abandoned chemical weapons. Insofar as **non-stockpile** munitions or agent are concerned, Article IV of the CWC also states that:

    > *17. The provisions of this Article and the relevant provisions of Part IV of the Verification Annex shall not, at the discretion of a State Party, apply to chemical weapons buried on its territory, before 1 January 1977 and which remain buried, or which had been dumped at sea before 1 January 1985.*

    Consequently, there is no requirement for States Parties to recover such buried or dumped chemical weapons, but should a State party decide to recover them, then they have to be destroyed in accordance with the requirements specified in the CWC.

17. There is, therefore, a clear incentive for States to destroy their stockpiled chemical weapons in a timely way in order to meet the CWC requirements as well as to remove the hazard associated with stockpiled chemical weapons and chemical warfare agents that are gradually aging. The overall hazard associated with stockpiled chemical weapons and agents is greater than that associated with destruction of these weapons and agents. Consequently, taking no action is **not** a responsible option. There are no benefits from delaying action to destroy chemical weapons and chemical warfare agents.

18. The time constraints imposed by the CWC—namely, the need to start destroying stockpiled chemical weapons within two years after entry into force of the CWC for that State and com-

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[18] CWC, Verification Annex, Part IV (B), para. 17.

pleting the destruction no later than 29 April 2007—means that it is only practicable to consider destruction technologies that are mature and have already been proven to be effective in destroying chemical agents. Although there is the possibility that the Executive Council may accept a request to modify the provisions on the time limit, the basic requirement in the Convention is that such old or abandoned chemical weapons shall be destroyed before 29 April 2007. It is, however, equally true that old or abandoned chemical weapons may well continue to be found for many years in States in which chemical weapons have been used or stockpiled, the acceptability of mature destruction technologies—and hence the possible need for new technologies for destroying these old and abandoned chemical weapons—will depend on what the environmental requirements for that State are in regard to gas, liquid, or solid materials released from the waste disposal process. Such environmental standards are likely to be increasingly more stringent regardless of what is being destroyed.

19. States Parties that have declared chemical weapons under the CWC are also required to meet additional requirements. Once a State Party has declared its chemical weapons it **shall not remove any of these chemical weapons except to a chemical weapons destruction facility** [19]. It is also required to submit a general plan for the destruction of chemical weapons providing an overview of the entire national chemical weapon destruction program of the State Party. The Verification Annex specifies [20] that:

> *Each State Party shall ensure that its chemical weapons destruction facilities are constructed and operated in a manner to ensure the destruction of the chemical weapons; and* ***that the destruction process can be verified under the provisions of this Convention.*** [Emphasis added]

20. The State Party is required to provide detailed information for each destruction facility including [21]:

> *(d) Detailed technical descriptions, including design drawings and instrument specifications, for the equipment required for: removing the chemical fill from the munitions, devices, and containers; temporarily storing the drained chemical fill; destroying the chemical agent; and destroying the munitions, devices, and containers;*
>
> *(e) Detailed technical descriptions of the destruction process, including material flow rates, temperatures and pressures, and designed destruction efficiency;*
>
> *(h)* ***A detailed technical description of measures to facilitate inspections in accordance with this Convention;***
>
> *(l)* ***Suggested measures for international verification***. [Emphasis added]

21. This detailed information is then reviewed by the Technical Secretariat so that [22]:

> *35. After a review of the detailed facility information for each destruction facility, the Technical Secretariat, if the need arises, shall enter into consultation with the State Party*

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19. CWC, Article IV, para. 4.
20. CWC, Verification Annex, Part IV (A), para. 14.
21. CWC, Verification Annex, Part IV (A), para. 31.
22. CWC, Verification Annex, Part IV (A), para. 35.

> *concerned in order to ensure that its chemical weapons destruction facilities are designed to assure the destruction of chemical weapons****, to allow advanced planning on how verification measures may be applied and to ensure that the application of verification measures is consistent with proper facility operation, and that the facility operation allows appropriate verification*** [Emphasis added].

22. A State Party is therefore required to consult the OPCW about the proposed chemical weapons destruction facility so as to ensure that (1) the destruction technology meets the requirement [23] of the CWC that the chemical agents are **converted in an essentially irreversible way to a form unsuitable for the production of chemical weapons, and which in an irreversible manner renders munitions and other devices unusable as such** and (2) the operation of the destruction facility complies with the CWC requirements for verification of the destruction of chemical weapons.

23. The IUPAC Working Party on Chemical Weapon Destruction Technologies has consequently limited its consideration in this report to those technologies that are **known** to have been used **to destroy 1 kg or more of an actual chemical agent** and appear to have the potential to be used to destroy ton quantities in the time scales required by the Convention.

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[23] CWC, Verification Annex, Part IV (A), para. 12.

II. OVERALL PERSPECTIVE

1. It is important to set the problem of the destruction of chemical weapons into an overall perspective, which considers both what can be learned from the recent historical record about the destruction of chemical weapons as well as what quantity of chemical weapons remain to be destroyed.

A. Experience in the destruction of chemical weapons

2. The 20th century has seen the use and destruction of vast amounts of chemical weapons. It is clear that following World War I and again following World War II large numbers of stockpiled weapons and significant quantities of bulk agent were disposed of or destroyed by methods that were acceptable at that time but are no longer acceptable today. For example, volatile or gaseous chemicals such as phosgene would be released into the atmosphere, and large quantities of chemical agents were disposed of by open-pit burning. Other methods included the dumping of chemical weapons into the sea, frequently by loading ships with unwanted weapons and then scuttling the ships at sea. In 1972, the Oslo Convention for the Prevention of Marine Pollution by Dumping of Wastes and Other Matter, dated 29 December 1972 and amended on 12 October 1978 and 1 December 1980, prohibited sea dumping [24]. Another common method of disposal was to dispose of unwanted chemical weapons by digging trenches and burying the munitions; such land-buried munitions are increasingly being unexpectedly found during building works and excavations, particularly in States in which chemical weapons were used or stockpiled. The CWC makes it clear that its provisions in Part IV of the Verification Annex, relating to the destruction of chemical weapons, "*shall not, at the discretion of a State Party, apply to chemical weapons buried on its territory before 1 January 1977 and which remain buried, or which have been dumped at sea before 1 January 1985*." [25] The CWC states that it is up to each State Party to "*determine how it shall destroy chemical weapons,* ***except that the following processes may not be used: dumping in any body of water, land burial or open pit burning****…*" [Emphasis added] [26]

3. In contrast to the previously favored methods of burial or ocean dumping which had been used to dispose of large quantities of chemical weapons, the past three or four decades have seen the destruction of significant quantities of chemical weapons using more environmentally conscious

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24. Oslo Convention for the Prevention of Marine Pollution by Dumping of Wastes and Other Matter, dated 29 December 1972 and amended on 12 October 1978 and 1 December 1980. Available at http://sedac.ciesin.org/entri/texts/marine.pollution.dumping.of.wastes.1972.html
25. CWC, Article III, para. 2.
26. CWC Verification Annex, Part IV (A), para. 13.

destruction methods. Table 3 is based on a summary [27,28] published in 1997 of experience during the 35 years from 1958 to 1993, which shows that some 14 500 tonnes of mustard and nerve agents have been destroyed either by incineration (I), neutralization (N), or a combination of these two techniques (N/I).

Table 3 Destruction of chemical warfare agents, 1958–1993.

Site	Agent	Amount[a]	Method	Date
Rocky Mountain Arsenal, USA	H	2786 tonnes	I	1969–74
Rocky Mountain Arsenal, USA	GB	3799 tonnes	N	1973–76
Tooele (CAMDS)[b], USA	GB	34.5 tonnes	I	1981–86
JACADS[c] Johnston Atoll, USA—OVT (operational verification test) data	GB	36 tonnes	I	1991
Tooele (CAMDS), USA	VX	7 tonnes	I	1984
JACADS Johnston Atoll, USA—OVT data	VX	49 tonnes	I	1992
JACADS Johnston Atoll, USA—OVT data	HD	51 tonnes	I	1992
DRES Canada	H	700 tonnes	N/I	1974–76
DRES Canada	H	12 tonnes	I	1990–91
DRES Canada	VX, GA, GB	0.3 tonnes	N/I	1990–91
DRES Canada	L	1.5 tonne	N	
Munster, Germany	H, etc.	70 tonnes/yr	I	1980–
Shikhany, Russia	GB, GD, H	300 tonnes	N/I	1980–90
Shikhany, Russia	VR (Russian VX)	30 tonnes	N/I	1980–90
Porton Down, UK	H	20 tonnes	I	1970
Nancekuke, UK	GB	20 tonnes	N	1967–68
Runcorn, UK	H	6000 tonnes	I	1958–60
Iraq (UNSCOM supervised)	H	500 tonnes	I	1992–93
Iraq (UNSCOM supervised)	GA	30 tonnes	N	1992–93
Iraq (UNSCOM supervised)	GB, GB/GF	70 tonnes	N	1992–93

[a] U.S. figures in short tons (2000 lb) converted to tonnes (1000 kg).

[b] CAMDS was a Chemical Agent Munitions Disposal System experimental facility at the Tooele Army Depot, Utah.

[c] This JACADS data is OVT (Operation Verification Test) data obtained prior to the full-scale operation of the Johnston Atoll Chemical Agent Disposal System.

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27. R. G. Sutherland. "The destruction of old and obsolete chemical weapons: Past experience", in *The Challenge of Old Chemical Munitions and Toxic Armament Wastes*, T. Stock and K. Lohs (Eds.), SIPRI Chemical and Biological Warfare Studies, No. 16, p. 141, Oxford University Press (1997); National Research Council, Committee on Alternative Chemical Demilitarization Technologies. *Alternative Technologies for the Destruction of Chemical Agents and Munitions,* Chap. 3, pp. 54–74, National Academy Press, Washington, DC (1993).
28. This summary does not include any information on destruction of chemical weapons by France. It is, however, evident that France has been considering techniques for the destruction of chemical weapons from Frederic Guir, "The technical challenge of dismantling and destroying old and abandoned chemical weapons", in *The Challenge of Old Chemical Munitions and Toxic Armament Wastes*, T. Stock and K. Lohs (Eds.), SIPRI Chemical and Biological Warfare Studies, No. 16, p. 156, Oxford University Press (1997) and from a study of a firing pool technique for the destruction of chemical weapons available as M. Herve Bizeau, "Preliminary technical study for a destruction process", in Defence Research Establishment Suffield, *Reports Presented to the Specialists Meeting on Chemical Weapons Destruction, Geneva, Switzerland, 7–11 October 1991,* Suffield Special Publication No. 152, December 1991.

Analysis of this data shows that some 66 % (9600 tonnes) of the 14 500 tonnes was destroyed by incineration, 27 % (3900 tonnes) by neutralization, and 7 % (1000 tonnes) by neutralization/incineration.

4. Incineration is an inherently attractive approach for destruction of organic compounds as the carbon and hydrogen in the organic compound in the presence of oxygen produce carbon dioxide and water; in addition, the other elements in chemical warfare agents will produce products such as hydrogen chloride (mustard), sulfur dioxide (mustard), phosphorus pentoxide (nerve agents such as GA, GB, VR and VX), hydrogen fluoride (nerve agent GB) and nitrogen dioxide (nerve agents GA, VR and VX). Indeed, chemical warfare agents are combustible and therefore lend themselves to destruction by incineration. The incineration products are far less toxic than the original chemical warfare agents. Further, the exhaust gases are typically scrubbed by passing them through countercurrent liquid absorption beds to reduce the level of pollution in the gases released to the atmosphere to an acceptable level that protects public health and the environment. However, organic compounds containing arsenic present additional problems, as many inorganic arsenicals are confirmed carcinogens.

5. Neutralization involves the reaction of the agent, such as the nerve agent GB, with sodium hydroxide causing the nerve agent GB to hydrolyze, producing as initial products, hydrogen fluoride and iso-propylmethyl-phosphonic acid (2-propyl methyl phosphonic acid); these both react with additional sodium hydroxide to produce the salts, sodium fluoride, and sodium methylphosphonate. The principal disadvantage of the alkaline hydrolysis of nerve agents is the large volume of hydrolysate produced, which can typically result in a five-fold increase in the overall volume. Table 4 provides a summary of information on destruction of chemical agents by neutralization during the period 1953 to 1993.

Table 4 Destruction of chemical warfare agents by neutralization, 1958–1993.

Country	Agent	Quantity (tonnes)	Reactant	Temperature	Disposal
United States	GB	3799	Aq NaOH	Ambient	Hazardous landfill
Canada	H	700	Calcium hydroxide (lime)	95	Incineration
Russia	GA, GB, H	300	Monoethanolamine	100	Incineration
Russia	VR (Russian VX)	30	Phosphoric acid and ethylene glycol	140	Incineration
United Kingdom	GB	20	20 % NaOH	Ambient	Discharge to sea
Iraq	GA	30	Aq NaOH	Ambient	Discharge to limed pit
Iraq	GB, GF	70	Aq NaOH	Ambient	Discharge to limed pit

The hydrolysate requires further treatment such as biodegradation, supercritical water oxidation, or incineration prior to release to the environment. Other chemical warfare agents, such as mustard H, can be neutralized by different processes such as reaction with hot water. However, without exception, the resulting hydrolysate requires further treatment to meet current acceptable environmental release standards.

6. Further insight into the use of incineration and neutralization to destroy chemical weapons can be gained from the ongoing U.S. program to destroy the U.S. chemical weapon and agent stockpile summarized in Table 5.

Table 5 Schedule for and current status of destruction of U.S. stockpiled chemical munitions (as of October 2001)[a].

Site	Agent (short tons)	% U.S. stockpile	Stockpile nature	Technology destruction	Full-scale
Aberdeen	1625 tons	5.2 %	HD containers	Neutralization	2005–2006
Anniston	2254 tons	7.2 %	HD, HT, GB, VX munitions HD containers	Incineration	2002–
Blue Grass	523 tons	1.7 %	H, GB, VX munitions	On hold	
Johnston Atoll	2030 tons	6.4 %	HD, GB, VX munitions & containers	Incineration	1989–2000 Completed
Newport	1269 tons	4.0 %	VX containers	Neutralization	2004
Pine Bluff	3850 tons	12.2 %	HD, HT containers GB, VX munitions	Incineration	2003–
Pueblo	2611 tons	8.3 %	HD, HT munitions	On hold[b]	
Tooele	13 616 tons	43.2 %	HD, L, GA, GB, VX containers H, HD, HT, GB, VX munitions	Incineration	1996– 39.4 % destroyed
Umatilla	3717 tons	11.8 %	HD containers GB, VX munitions	Incineration	2002
Total, agent-tons	31 495	100 %			23.5 % destroyed
Total, agent-tonnes	28 572				

[a] This is based on stockpile information available at http://www.defenselink.mil/news/Jan1996/ b012496_bt024-96.html and information on destruction schedules at individual storage sites available at http://www-pmcd.apgea.army.mil/

[b] Technology decision expected late 2001.

It is thus evident that over 23.5 % of the U.S. stockpile has already been destroyed. Overall, **80.8 % is to be destroyed by incineration, 9.2 % planned to be destroyed by neutralization and 10 % is currently on hold.**

7. On 29 November 2000, the Johnston Atoll Chemical Agent Disposal System (JACADS) had completed destruction of its stockpile of 2031 agent-tons (1843 agent-tonnes) of chemical munitions involving the destruction of more than 400 000 rockets, projectiles, mortars, ton containers of agent, and land mines containing mustard and nerve agent (GB and VX) [29]. As of 3 October 2001, the Tooele Chemical Agent Disposal Facility (TOCDF) had completed destruction of 5365 agent-tons (4867 agent-tonnes) of agent involving the destruction of more than 600 000 rockets,

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29. Office of the Secretary of Defense (Public Affairs). *Chemical Weapons Destruction Complete on Johnston Atoll,* News Release, 30 November 2000. Available at http://www.defenselink.mil/news/Nov2000/ b11302000_bt715-00.html

projectiles, bombs, and ton containers [30]. At both facilities, the agents were destroyed by incineration. Taken together, the agent destroyed at these two facilities represents a total of some 7396 agent-tons (6710 agent-tonnes) and about 23.5 % of the U.S. stockpile of over 31 000 agent-tons (28 000 agent-tonnes). In addition, Table 5 shows that over 80 % of the U.S. stockpile of chemical weapons and agents are to be destroyed by incineration.

8. Much attention has also been paid in the United States to alternative technologies. The initial U.S. approach was to destroy the stockpile by incineration with facilities initially being constructed at Johnston Island in the Pacific Ocean and then at Tooele, Utah. In the early 1990s, there was increased public concern in the United States about the possible dangers from emissions from commercial waste incineration facilities as well as from military incinerators. This led to an examination in 1995 and 1996 of alternative technologies to incineration for the destruction of the bulk chemical agent at Aberdeen, Maryland and Newport, Indiana, which had no filled munitions for destruction. Subsequently, decisions have been taken to destroy the bulk agent at these two sites by neutralization. Continued public pressure for alternative technologies to incineration to destroy assembled chemical munitions has led to the U.S. Congress stopping work on the baseline incineration facilities which were planned for the storage sites at Pueblo, Colorado and Lexington, Kentucky until not less than two alternative technologies have been demonstrated. A decision had been expected in September 2001 on which technology to use at Pueblo, Colorado; there are four options: incineration—known in the United States as "baseline technology"; enhanced baseline technology; and two alternatives—water hydrolysis followed by biotreatment or water hydrolysis followed by supercritical water oxidation. The other element of the U.S. chemical weapon destruction program relates to non-stockpile material, which includes chemical agent identification sets and old chemical weapons that have been buried. Various technologies are being examined for the treatment of the reaction products resulting from neutralization of the agent in non-stockpile material.

9. A more detailed analysis of the U.S. stockpile information enables the individual quantities of the various chemical agents to be calculated.

Table 6 Types and quantities of chemical agents in the U.S. stockpile[a].

Storage depot	GB	GA	VX	Mustard	HT	Lewisite	Total
Aberdeen	–	–	–	1623.8	–	–	1623.8
Anniston	436.5	–	828.7	456.1	532.3	–	2253.6
Blue Grass	305.6	–	127.2	90.6	–	–	523.4
Johnston Atoll	1320.4	–	422.7	289.4	–	–	2032.5
Newport	–	–	1269.3	–	–	–	1269.3
Pine Bluff	483.7	–	147.3	94.2	3124.5	–	3849.7
Pueblo	–	–	–	2551.9	59.1	–	2611.0
Tooele	6048.7	2.1	1356.3	6014.4	181.5	13.0	13 616.0
Umatilla	1014.0	–	363.9	2339.5	–	–	3717.4
Total in agent-tons	9608.9	2.1	4515.4	13 459.9	3897.4	13.0	31 496.7
Total in agent-tonnes	8717.2	1.9	4096.4	12 210.8	3535.7	11.8	28 573.8

[a] This is based on stockpile information for the individual storage sites as shown in January 2001 at http://www-pmcd.apgea.army.mil/

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30. Project Manager Chemical Demilitarization. *Processing Status as of 5 November 2000 for the Tooele Chemical Agent Disposal Facility (TOCDF).* Available at http://www-pmcd.apgea.army.mil/aag_tocdf.asp

B. Chemical weapons awaiting destruction

10. The OPCW in its Annual Report for 2000 has provided a useful tabulation setting out the quantities of chemical weapons declared by States Parties together with the quantities of such agents so far destroyed. Only four of the 134 States Parties have declared chemical weapons under Article IV of the Convention: these are the United States, the Russian Federation, India, and one other State Party. Although the latter State Party is not identified, at its request, by the OPCW, it is generally known from publicly available information that it is South Korea. Information about the U.S. stockpile and its composition is available as is some information about the Russian Federation stockpile.

11. Information on the Russian Federation program to destroy its stockpile of chemical weapons is available from a Russian Federation paper [31] in 1996 to the Preparatory Commission for the OPCW and, more recently, in Resolution No. 510 of 5 July 2001 of the Government of the Russian Federation [32]. This includes a tabulation showing what chemical weapons are stored at which storage facility. This table is reproduced in Table 7 to which have been added information on the quantities of the agents taken from a paper [33] presented by senior members of the Russian Ministry of Defense in March 1996 to a NATO Advanced Research Workshop.

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31. Russian Federation. *Special Federal Programme Destruction of Chemical Weapon Stockpiles in the Russian Federation,* PC-XIV/B/WP.7* dated 25 June 1996.
32. Russian Federation. Government Resolution No. 510 of 5 July 2001, *On Making Amendments and Additions to the Resolution by the Government of the Russian Federation of March 21, 1996 (No. 305) On Approving the Federal Special Programm "Chemical Weapons Stockpiles Destruction in the Russian Federation",* Moscow. Available at http://www.armscontrol.org/pdf/russchemdemil.pdf
33. V. Petrov, V. I. Kholstov, V. P. Zoubrilin, N. V. Zavialova. "Practical actions of Russia on preparations for destruction of stockpiled Lewisite and 'mustard'", in *Arsenic and Old Mustard: Chemical Problems in the Destruction of Old Arsenical and 'Mustard' Munitions,* J. F. Bunnett and M. Mikolajczyk (Eds.), NATO ASI Series, 1. Disarmament Technologies, Vol. 19, p. 79, Kluwer, Dordrecht (1998).

Table 7 Types and quantities of chemical agents in the Russian stockpile.

Location	% stockpile	VR	GB	GD	H	L	H/L	CG
Kambarka (Udmurt Republic)	15.9	–	–	–	–	√ 6349	–	–
Gorny (Saratov Region)	2.9	–	–	–	√ 807	√ 293	√ 157/71[a]	–
Kizner (Udmurt Republic)	14.2	√	√	√	–	√ 129	–	–
Maradykovsky (Kirov Region)	17.4	√	√	√	–	–	√ 149	–
Pochep (Bryansk Region)	18.8	√	√	√	–	–	–	–
Leonidovka (Penza Region)	17.2	√	√	√	–	–	–	–
Shchuch'ye (Kurgan Region)	13.6	√	√	√	–	–	–	√
Total in agent-tonnes	40 000	15 200	11 700	4800	807	6771	306/71[a]	345[b]

√ indicates that a particular agent is present at the particular site location.

[a] The second figure is for a mixture of mustard and lewisite in 1,2-dichloroethane.

[b] Figure for phosgene calculated from the balance remaining from 40 000 agent-tonnes.

The figures shown in Table 7 for the quantities of the different agents are broadly similar to those less officially reported [34] in 1993 of VR 15 200 tonnes, GB 11 720 tonnes, GD 4750 tonnes, H 690 tonnes, H/L 1010 tonnes, Adamsite 3200 tonnes, and CG 5 tonnes, which corresponds to a total stockpile of 36 575 tonnes. Whilst the figures for all three nerve agents are similar, the figures for the other agents show discrepancies when compared to the later information; notably, no Adamsite has been declared to or by the OPCW.

12. Resolution No. 510 provides for the construction of two full-scale chemical weapons destruction complexes outside the town of Shchuch'ye (Kurgan Region) and Kambarka (Udmurt Republic) instead of the seven previously planned and the completion of the destruction of the chemical weapons stored at these facilities by 2011; the completion of construction of the chemical weapons destruction facility outside the village of Gorny (Saratov Region); and the setting up of small-scale facilities for the detoxification of chemical weapons stored at the depots in the village of Maradykovsky (Kirov region), in the town of Pochep (Bryansk Region) and in the village of Leonidovka (Penza Region), for destruction or disposal of detoxification products at chemical industry facilities before the year 2012; and destruction of chemical weapons stored in the town of Kizner (Udmurt Republic) at the chemical weapons destruction complex in the town of Shchuch'ye before the year 2012. The Russian Federation has chosen to use a two-stage neutralization-based process to destroy the chemical agent; these are discussed later in this report but, as an example, sarin, soman, and mustard are neutralized with monoethanolamine and then the reaction products are bitumenized to produce a waste suitable for storage in landfills.
13. The information from the United States and the Russian stockpiles in Tables 6 and 7 are provided together with that available from the OPCW Annual Report of 2000 updated to 30 June 2001 in

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34. Lev Federov. *Rossiya (Moscow)*, No. 50, p. 8, 8–14 December 1993, as reported in News Chronology, Item 931208, *The Chemical Weapons Convention Bulletin*, Issue No. 23, p. 16, March 1994.

(*continues on next page*)

Table 8. In considering the figures in Table 8, it needs to be recognized that the quantity declared to the OPCW is the quantity declared by a State **when** the CWC entered into force for that State and the totals can therefore be different from totals declared by a State in earlier publications as any agent destroyed prior to entry into force of the CWC will not have been declared to the OPCW. Although some of the figures in Table 8 show reasonable correspondence between the total declared to the OPCW and the information on the quantities in the U.S. and Russian stockpiles, there is a significant discrepancy of about 4000 agent-tonnes in respect of the figures for GB and for GD which suggests that the Russian stockpile information may have reported some 4000 tonnes of GD as GB. There is no public information about the nature and amount of the Indian and South Korean stockpiles, although it can be deduced from Table 8 that their combined total is about 1500 agent-tonnes.

Table 8 Types and quantities of chemical weapons declared and destroyed (as of 30 June 2001)[a]. All quantities in agent-tonnes.

Agent	Amount declared to OPCW	Amount destroyed in OPCW Report	U.S. stockpile	Russian stockpile
GB	15 048	4486	8717	11 700
GD	9174	–	–	4800
GA	2	–	2	–
VX	4032	324	4096	–
VR (Russian VX)	15 557	–	–	15 200
Sulfur mustard	13 838	338	12 211	807
Mustard/lewisite	273	–	–	306
Mustard/lewisite in dichloroethane	71	–	–	71
Lewisite	6744	–	12	6771
HT	3535	–	3536	–
Phosgene	5	–	–	345
Precursors (DF, QL) and other chemicals	1614	586		
Total	69 863	5734	28 574	40 000

[a] This is based on information available in Annex 4 in the OPCW Annual Report 2000 updated to 30 June 2001 together with U.S. stockpile information available at http://www.defenselink.mil/news/Jan1996/b012496_bt024-96.html and information on destruction schedules at individual storage sites available at http://www-pmcd.apgea.army.mil/

It is thus apparent that the **amount awaiting destruction, worldwide, as of 30 June 2001, is 64 129 agent-tonnes.**

14. In addition to declarations under Article IV of the Convention, States Parties have also made declarations of old and abandoned chemical weapons under Part IV (B) of the Verification Annex. Information provided in Annex 5 of the OPCW Annual Report for 2000 shows that such declarations have been made by:

Belgium
Canada
China
France
Germany
Italy
Japan
Panama
Slovenia
United Kingdom
United States

Although there have been publications dealing with recovered old chemical weapons in Poland [35] and Austria [36], these countries are not shown in Annex 5 of the OPCW Report for 2000 as having made declarations under Part IV (B) of the Verification Annex of the Chemical Weapons Convention.

12. The total figures for chemical weapons summarized in Table 6 exclude the quantities declared under Part IV (B) of the Verification Annex. Nevertheless, some indications of the numbers of old and abandoned chemical weapons can be gleaned from statements made by the States Parties concerned:

    - The United States in respect of its non-stockpile chemical materiel program reported initially in 1993 that such material was located at some 224 sites at 96 locations in 38 States in the United States and in U.S. territories. In January 2001, the U.S. Army Web site [37] stated that "*There are 99 known or suspected non-stockpile burial locations in 38 States and territories. Some locations have multiple non-stockpile burial sites. Approximately 227 known or suspected non-stockpile sites have been identified.*" It should, however, be noted that the United States includes five categories in its non-stockpile chemical materiel:
        - Binary chemical warfare material
        - Former chemical weapon production facilities
        - Miscellaneous chemical warfare material—unfilled muntions and devices; samples; research, development, testing and evaluation materials; and equipment designed for use directly in connection with chemical weapons
        - Buried chemical warfare materiel—chemical material buried from World War I through the late 1950s, as well as dud munitions from range firing operations
        - Recovered chemical warfare materiel—items recovered during range clearance operations, from burial sites and from research testing ranges

    An NRC report [38] refers to approximately 10 000 Chemical Agent Identification Sets (CAIS) items and 1400 non-stockpile munitions as being currently in storage awaiting destruction. Elsewhere, the NRC report mentions the presence of some bulk containers (55 gallon and "ton" containers) in burial sites.

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35. Z. Wertejuk, M. Koch, W. Marciniak. "Recovered old arsenical and 'mustard' munitions in Poland", in *Arsenic and Old Mustard: Chemical Problems in the Destruction of Old Arsenical and 'Mustard' Munitions,* J. F. Bunnett and M. Mikolajczyk (Eds.), NATO ASI Series, 1. Disarmament Technologies, Vol. 19, p. 91, Kluwer, Dordrecht (1998).
36. J. Stolz. "The storage of old and abandoned chemical weapons in Austria", in *The Challenge of Old Chemical Munitions and Toxic Armament Wastes*, T. Stock and K. Lohs (Eds.), SIPRI Chemical and Biological Warfare Studies, No. 16, p. 187, Oxford University Press (1997).
37. Information at http://www-pmcd.apgea.army.mil/nscmp/IP/FS/definitions/index.asp
38. National Research Council, Committee on Review and Evaluation of the Army Non-Stockpile Chemical Materiel Disposal Program. *Disposal of Chemical Agent Identification Sets,* p. 22, National Academy Press, Washington, DC (1999).

- Japan has said that it is estimated that some 700 000 chemical munitions have been abandoned in China. The agents in the weapons left in China are: mustard, mustard-lewisite, diphenyl cyanoarsine (Clark II), hydrogen cyanide, phosgene, and chloroacetophenone. China has suggested that the number of abandoned munitions might be as high as 2 million (further information on these Japanese chemical weapons abandoned in China is provided in Chapter IX).
- There is less information about the European declarations under Part IV (B) although the UK National Authority in its recent Annual Reports has provided figures for the numbers of actual or suspected old chemical weapons found annually as well as for the numbers of old chemical weapons destroyed annually:

Year	Number of actual or suspected old chemical weapons found	Number of items[a] of old chemical weapons destroyed
1998	234	357
1999	1156	730
2000	532	712

[a]These figures include non-munition chemical weapon related items and items that in the event proved not to be chemical weapon related.

- Information regarding old chemical weapons in Belgium indicates that explosive ordnance units still collect about 3000–3500 munitions a year from the Flanders region with about 10 % (or some 300 to 350) being confirmed as chemical munitions [39]. More recent information [40] is that in 2000, some 24 000 munitions were recovered of which some 867 were confirmed as old chemical weapons.

  It is, thus, clear that in Belgium and the United Kingdom there are several hundreds of old chemical weapons found each year corresponding to an average figure of around 500 to 700.
- Information regarding old chemical weapons in France indicates that in 1998 there were about 146 agent-tonnes (about 148 000 munitions) in storage and that each year a further 30 to 50 tonnes are found [41]. The agents are primarily phosgene, diphosgene, mustard, chloropicrin, and hydrogen. A facility capable of destroying about 100 agent-tonnes a year is being built to destroy these old chemical weapons.
- Information [42] is available that in Italy old chemical weapons and material from the clean-up of the sites where chemical weapons were originally made or stored has been

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39. R. G. Manley. "The problem of old chemical weapons which contain "mustard gas" or organoarsenic compounds: An overview", in *Arsenic and Old Mustard: Chemical Problems in the Destruction of Old Arsenical and 'Mustard' Munitions,* J. F. Bunnett and M. Mikolajczyk (Eds.), NATO ASI Series, 1. Disarmament Technologies, Vol. 19, p. 12, Kluwer, Dordrecht (1998).
40. H. de Bisschop. Private communication, 16 October 2001.
41. B. d'Espagne. *Status and Treatment of Old Chemical Weapons in France*, CWD98: The International CW Demil Conference, CD-ROM format, pp. 108–32 (1998).
42. Italian Chamber of Deputies, Allegato B, Seduta No. 814, 27 November 2000, p. 34740 as reported in News Chronology, Item 001127, *The CBW Conventions Bulletin*, Issue No. 51, p. 31, March 2001.

transferred to the NBC defense establishment at Civitavecchia where large quantities of agents—mustard, phenyldichloroarsine, lewisite, diphenylchloroarsine, Adamsite, and phosgene—and some 40 000 filled chemical weapon projectiles have been accumulated to await destruction. 130 tonnes of mustard were destroyed prior to the entry into force of the CWC, and work is currently under way on the destruction of the Adamsite, phosgene, and chemical-filled munitions.

13. It is not easy to estimate the agent quantities in these old and abandoned chemical weapons. Indeed, some old chemical weapons are found to be empty. The Chemical Agent Identification Sets in the U.S. non-stockpile chemical materiel program typically contain a few hundred grams of agents: the agents include mustard, lewisite, Adamsite, and phosgene. The OPCW information on chemical weapons destruction shows that about 1.7 million munitions/containers corresponding to about 5700 agent-tonnes have been destroyed thus far. Consequently, if an estimated figure of 700 000 is taken for the abandoned chemical weapons in China, then from the other information above, a broad estimate can be made of about 1 million old chemical weapons which, if all were filled with agent, might correspond to over 3000 agent-tonnes.

C. SUMMARY

14. Analysis of the available data on chemical weapon destruction during the period from 1958 to 1993 shows that some 66 % (9600 tonnes) of the 14 500 tonnes was destroyed by incineration, 27 % (3900 tonnes) by neutralization, and 7 % (1000 tonnes) by neutralization/incineration. Since then, the United States has destroyed a further 6700 agent-tonnes by incineration, bringing the total destroyed by incineration to over 16 000 agent-tonnes. As for the chemical weapons awaiting destruction, this is around 64 000 agent-tonnes in stockpiles primarily in the United States and Russia and about 3000 agent-tonnes of old chemical weapons. In percentage terms, over 90 % of the chemical weapons awaiting destruction are in declared stockpiles of munitions and agent and over 5 % in abandoned or old chemical weapons.

15. This Working Party, in its focusing on the experience gained and the technologies available over the past decade, is conscious that much of the information presented in this report is based on U.S. experience as the United States had, along with the Russian Federation, by far the largest stockpiles of chemical weapons and agents anywhere in the world. The United States has made much progress in destroying its stockpile of chemical weapons and agents and has also done more work than any other country to examine alternative technologies for the destruction of chemical weapons and agents. This report consequently draws heavily on the U.S. experience. Insofar as old and abandoned chemical weapons are concerned, the European countries have been dealing with this problem ever since World War I and thus have gained considerable expertise and information on how to deal with such weapons. This information may well be of value in dealing with the abandoned chemical weapons in China and with the U.S. non-stockpile chemical materiel program, which includes recovered old munitions. However, it needs to be stressed that the national decisions to be taken by countries faced with the destruction of chemical weapons and agents need to be made in the light of the particular national conditions and standards and thus may well result in a decision to use different approaches from those adopted by the United States. The aim of this report is to provide information to enable countries to make informed decisions that are appropriate for that country.

III. THE NATURE OF THE PROBLEM

1. What then is the problem that has to be solved in the destruction of chemical weapons and chemical warfare agents? What different categories of munitions, agents, and agent containers have to be addressed, and what actually needs to be destroyed? The requirements of the CWC and the need to destroy weapons and agents safely and to protect the environment are the principal drivers that determine which processes can be used for the destruction of chemical weapons and agents.

2. There are three broad categories of chemical weapons (CW) and chemical warfare agents (CWA) that need to be addressed:

   a. **Assembled chemical weapons stockpile.** These are chemical weapons that are in storage that is controlled and which comprise weapons that are militarily usable. Such weapons will generally be in good condition; however, some may have begun to corrode and leak. The nature of the munition and its agent fill will usually be known.

   b. **Bulk storage agent**. This is agent in bulk storage containers. Depending on storage and maintenance care and activities, the containers are likely to be in good condition. The nature of the agent will usually be known.

   c. **Recovered old munitions and agent containers**. These will frequently have been uncovered unexpectedly by excavations, and the condition and nature of the munition and its agent fill will often be unknown; The destruction of such munitions and decontamination of the containers will frequently require additional steps such as identification of whether the munition has a chemical agent fill, whether it is explosively configured, the nature of the agent fill, and whether this has degraded. Chapter IX of this report addresses the particular problems associated with recovered munitions and agent containers.

3. The principal CWC requirement is for the chemicals to be "*converted in an essentially irreversible way to a form unsuitable for production of chemical weapons, and which in an irreversible manner renders munitions and other devices unusable as such*." [43] The CWC moreover states that it is up to each State Party to "*determine how it shall destroy chemical weapons, except that the following processes may not be used: dumping in any body of water, land burial or open pit burning*." [44] Furthermore, each State Party "*shall ensure that its chemical weapons destruction facilities are constructed and operated in a manner to ensure the destruction of the chemical weapons; and that the destruction process can be verified under the provisions of this Convention*." [45]

4. The criteria as to what is an environmentally acceptable process vary from country to country, as well as with time, as more demanding standards are set for what is permissible to be released into the environment. Whatever destruction method is used for CW and CW agents, the aim needs to be to achieve an appropriately high standard of safety and of environmental responsibility and acceptability. There is a tradeoff to be achieved between these. Environmental emission standards for process residuals need to be set at realistic and scientifically justifiable levels so that the destruction can be carried out safely with minimum health risk both in the short and the long term to those carrying out the destruction and to those living in the vicinity of the destruction facility

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[43] CWC Verification Annex, Part IV (A), para. 12.
[44] CWC Verification Annex, Part IV (A), para. 13.
[45] CWC Verification Annex, Part IV (A), para. 14.

and with the minimal impact on the environment. Unrealistic emission standards can needlessly complicate the destruction process and degrade safety.

5. The risk factors relating to safety can be divided into two broad categories: first, those factors related to handling chemical weapons and chemical agent prior to their introduction into the specific destruction technology and, second, those factors related to the agent-destruction technology and associated system elements. The risk factors related to the handling of weapons and agent, prior to entry into a destruction technology, are common to all the agent-destruction technologies, and include risks during storage, risks during transportation whether within a storage site or to a destruction site, and the risk from the operation used to gain access to the chemical agent. These factors can be exacerbated or ameliorated by unique aspects of a destruction technology. Safety factors are addressed for transportation, for removal of chemical agents from weapons, and within the specific destruction technologies.

6. It also needs to be recognized that there are several components that have to be destroyed or decontaminated. First, there is the CW agent itself, second is the munition/container in which it had been stored, third are the energetic components of the munition (fuzes, primers, explosives, and propellants), and fourth are the packaging materials such as the pallets on which the munitions were stored. Energetics and dunnage need destruction as they are frequently contaminated by agent. Each of these may require a different technique for its destruction or decontamination recognizing that the levels of agent contamination can be very different.

7. There are three principal categories of chemical warfare agent in the stockpiled munitions and bulk agent storage: mustard; lewisite; and the nerve agents (GA, GB, GD, VR and VX). Although incineration can be used for all three types, the incineration of lewisite, which contains arsenic, requires that the arsenic products be collected and not released to the environment. There is a wide range of potential alternative technologies to incineration for the destruction of chemical warfare agents; however, specific technologies have to be matched to the particular agent to be destroyed and the technologies are relatively immature. Not every agent can be readily destroyed by every technology. A further factor relates to the quantity of agent to be destroyed and the process to be used. For large quantities of agent, there are advantages in using a destruction process that can be run continuously, whereas for small quantities of agent, a batch process will suffice and often be more convenient as it lends itself to being used on a batch run basis. Further, agent-contaminated munitions or containers, energetics, and/or packaging materials may require a different technological solution than the neat agent alone.

8. Destruction technologies are conveniently divided into high- and low-temperature processes, together with effluent treatment. In this report, the following processes are regarded as having been sufficiently demonstrated with actual chemical warfare agent and to be considered as candidates for chemical agent destruction within the time frame of the CWC requirement.

High-Temperature Destruction of Chemical Agent

Incineration
Plasma pyrolysis
Molten metal technology
Hydrogenolysis
Destruction of arsenical agents

Low-Temperature Destruction of Chemical Agent

Hydrolysis of mustard Agent HD
Hydrolysis of mustard and nerve agents using aqueous sodium hydroxide
Reaction of mustard and nerve agents using amines and other reagents
Electrochemical oxidation
Solvated electron technology

Effluent treatment is addressed according to its nature under the three headings: gas, liquid, and solid.

9. However, it must be noted that there is a wide variation in the technical maturity of these technologies. The additional development required for some of these technologies makes it highly problematic that they can be sufficiently advanced to be a major contribution within the CWC treaty time lines, which require destruction of all stockpile chemical weapons by 2007. They may, however, have application for the destruction of old and abandoned chemical weapons for which the CWC treaty time line may, should the State party concerned make such a request, be modified by the Executive Council.

IV. TRANSPORT OF CHEMICAL WEAPONS AND BULK AGENT

A. Introduction

1. In considering the transportation of chemical weapons for demilitarization, two fundamental facts need to be recalled. First, chemical weapons are but a few of the immense range of known toxic chemicals, many of which have applications for industrial and commercial peaceful purposes and which are transported routinely in quantity from facility to facility within countries and between countries. Second, chemical agents were designed to be produced at a production facility and then filled into weapons, either at the same production facility, or after transportation in containers to a filling factory. The filled chemical weapons were designed to be shipped from the filling facility to storage depots, then to forward depots and ultimately to the aircraft, artillery, or other delivery vehicle that was intended to deliver the chemical warhead to the military target. In general, but not necessarily always, the chemical weapon is not fitted with a fuse until immediately prior to use. A burster charge is also frequently fitted at the production facility. Consequently, chemical **munitions are designed for transportation without presenting an undue hazard** to either military personnel or to the public. The same was true of bulk storage containers designed to be filled at the production facility and then transported to a storage site and, eventually, to a filling facility.

2. Consequently, in considering transportation of chemical munitions (assumed to be unfuzed) or storage containers to destruction facilities, the basic munition or container is inherently a safe item about which the key question is **whether**, because of the time that has elapsed and of the conditions under which it has been stored between filling of the munition or container up to the time at which its transfer is being considered to a destruction facility, the item is still safe to transfer or whether it requires to be specially packed to minimize any potential risk.

B. Experience

3. During the past few years, experience about transportation of chemical munitions to a destruction facility has been gained in a number of countries. In Europe, chemical weapons and chemical agents were abandoned by military forces in a number of countries. These abandoned chemical weapons and agents were frequently left in ditches or other holes and covered over with soil. Subsequently, many years later, often when the area is being commercially developed or being used agriculturally, old munitions are uncovered whose nature (chemical, explosive, or other) and condition is frequently unknown. The same situation frequently applies to munitions found many years later on old firing ranges where the munition may simply have failed to function when originally fired.

4. A different situation applied to the stockpile munitions, such as those that had been deployed from the United States to Germany, which were then brought back to Johnston Island for destruction. The condition of this stockpile was excellent, and its nature well known. In the United States, a study [46] was carried out in 1984 by the National Research Council to recommend the most effective, economical, and safest means of disposing of the U.S. Army's aging and obsolete stockpile of chemical agents and munitions. The stockpile in 1984 was all at least 16 years old and some of it 40 years or more old. This study included transportation safety considerations, as the committee had intended to make a definitive statement about the relative risks and costs of (1) continuing to store and ultimately to destroy chemical agents and munitions at their current stor-

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46. National Research Council, Committee on Demilitarizing Chemical Munitions and Agents. *Disposal of Chemical Munitions and Agents,* National Academy Press, Washington, DC (1984).

age depots, or (2) transporting some of them to carefully chosen consolidation sites which could then reduce the number of disposal facilities to be constructed. It was recognized that such shipments might be justified if the net risks involved in shipment, storage, and destruction at a few depots was clearly lower than those of storage and destruction at each of the current depots. However, the data for such comparative safety–hazards–risk assessments were not available; the NRC committee noted that the two principal transportation studies that had been carried out in the United States were contradictory. It also observed that any such comparative analysis should recognize that "*the socio-legal-political constraints on transportation are emotional, interdependent and substantial*" and that "*the conclusions from such a transportation safety analysis would no doubt be controversial and inconclusive, and the decision whether to transport or not would almost certainly be made on grounds other than hard evidence.*" Although the committee recommended that the Army should carry out such an assessment, it also said that it believed that disposal at on-site facilities would cost less than transportation to and disposal at large central facilities. In the event, the U.S. Congress decided to prohibit the further study of transport of chemical agent and munitions reflecting public opposition within the United States to such transport. The U.S. experience is thus one in which transportation of chemical munitions was successfully accomplished from Germany to Johnston Atoll, yet for socio-legal-political reasons such transportation was ruled out within the United States. It will be a matter for any State contemplating the destruction of chemical weapons to decide whether to transport them to a central facility for destruction; much will depend on the size and dispersion of the chemical weapon stockpile within that State as well as the state of the stockpile chemical weapons.

5. Yet another situation applied in Iraq following the Gulf War of 1990/1991 when as part of the United Nations Security Council cease-fire resolution [UNSCR 687 (1991)], Iraq was required to surrender all its chemical weapons for destruction under the supervision of UNSCOM. The weapons were at scattered sites, and some had been partially destroyed by bombing; assessments had to made as to what was the safest means of safely disposing of such weapons and whether to transport them to a central site for destruction or for destruction *in situ*.

6. Each of these three transportation situations is considered below:

Buried non-stockpile munitions/old chemical weapons

Removal and transport of old chemical weapons

7. Since old chemical weapons (OCW) are often found scattered over a large area, they have to be collected and transported to an intermediate storage site. As there is uncertainty about the safety of these newly discovered OCW, it is prudent to use sturdy containers to transport them, and these containers need to be gas-tight under pressure and coated so that they are able to withstand the use of aggressive decontaminants. In addition, transportation coordination and planning are essential. For example, in Germany these containers need to be approved by the federal authority that regulates the transport of dangerous goods and explosives. When old chemical weapons are moved, detailed arrangements need to be made with the federal state police and environmental agencies about the route to be taken. If significant quantities of OCW are to be transported, the police restrict access to the roads on which they will be moved, and personnel trained in detection, decontamination, and medical support accompany the transport. Other European countries adopt similar precautions. This is addressed in greater detail later in Chapter IX.

Stockpile munitions

Transportation of chemical weapons to Johnston Island

8. An example of how stockpile munitions can be transported is provided by the U.S. transportation of chemical weapons from Germany to the destruction facility at Johnston Island in the Pacific.

Johnston Island (JI) is located nearly 800 miles southwest of Hawaii and is the site of the chemical stocks that were originally stored in Okinawa and Germany (6.6 % of U.S. total). The Johnston Atoll Chemical Agent Disposal System (JACADS) is the world's first fully integrated chemical munitions destruction facility. Construction of the facility started in late 1985, equipment was installed in 1987, and systemization was initiated in 1988. After extensive training of operators, testing of equipment, operations with training and simulant-filled munitions, and comprehensive pre-operations checks, the facility destroyed its first GB-filled, M55 rockets on 30 June 1990.

9. In March 1989, President Bush requested the Department of Defense to investigate accelerating the project for removing the U.S. chemical munitions that were stored in Europe. The Department of the Army was given the lead and formed a Task Force to coordinate the operations. Plans were initiated, and bilateral meetings were held with the Federal Republic of Germany. Contracts were awarded to procure containers, agent monitors, modular shelters, and mobile laboratories. These contracts were necessary to support any retrograde schedule selected.

10. Transport to Johnston Island of approximately 100 000 nerve agent-filled artillery projectiles stored in the Federal Republic of Germany was initiated in 1990. These munitions had thick steel walls, relatively insensitive explosives, and no fuzes. In addition, they had been maintained in excellent condition. Together, these characteristics resulted in a determination that they are among the safest chemical munitions to transport.

11. Prior to the initiation of the movement, several important actions were completed. The first concerned environmental assessment documents relating to the movement of the munitions. An environmental assessment was prepared to address the sea movement of the chemical munitions to Johnston Island—the preferred destination. Also required was preparation of a second JACADS supplemental environmental impact statement to address storage at Johnston Island and ultimate disposal there of the European stocks. Next, certifications had to be provided to Congress that adequate storage space was available on Johnston Island for these munitions and that the JACADS plant could meet required destruction rates for destroying chemical agent munitions. Both certifications were provided to Congress in July 1990. Lastly, all safety and operational requirements had to be completed. Some of these requirements were fabrication of 6000 secondary steel containers, procurement of air monitoring equipment, procurement of mobile laboratories and shelters, vessel refurbishment, and crew training.

12. The out-load of the chemical munitions started on 26 June 1990, with the removal of the munitions from their storage bunkers and placement into secondary steel containers. These steel containers were then packed into standard transportation vans called MILVANs for ease of handling and transport. Over 5500 MILVANs were used to transport the stockpile. The road convoy movement to Miesau Army Depot started on 26 July 1990. A total of 28 convoys, each escorted by security, decontamination, and firefighting vehicles, were needed to move all the MILVANs to Miesau. Rail convoys then began on 12 September 1990, when two mission trains and an escort train left Miesau Army Depot for the German port of Nordenham. Each mission train carried security and emergency response equipment and personnel. A total of 14 mission trains were used to move the stockpile.

13. At the port, the MILVANs were loaded on board two modified Ready Reserve Fleet vessels, the SS Flickertail State and SS Gopher State. MIDGARD, the civilian port operator, conducted the loading operations under contract to the United States. The U.S./German team that planned and conducted the movement within Germany worked very well together and resulted in executing the movement with no incidents or accidents.

14. The two ships departed Nordenham, Germany on 22 September 1990, escorted by U.S. Navy guided-missile cruisers. The ocean phase of the movement was uneventful, including the three at-sea refueling operations. The route took the ships north of the United Kingdom and Ireland, south around Cape Horn on the southern tip of South America, and then north and west to Johnston Island. The Gopher State docked at Johnston Island on 6 November 1990. The Flickertail State docked on 11 November 1990. Off-load operations were completed on 18 November.

15. The MILVANs were then taken to the "Red Hat" chemical exclusion area where they were downloaded and the munitions placed into storage bunkers like those in Germany. The last munition was placed in a storage bunker in February 1991.

16. Section 364 of fiscal year 1991 Defense Authorization Act (Public Law 101-510) required the Secretary of the Army to prepare a report on the safety aspects of the chemical retrograde movement. The safety report, titled "Safety Aspects of the Retrograde of Unitary Chemical Munitions from the Federal Republic of Germany", was completed and sent to Congress in March 1992. The chemical retrograde movement was an unqualified success because of meticulous planning, training, cooperation of Germany, and dedicated men and women who executed the project.

17. As press attention to the planned European chemical retrograde movement increased, a flurry of inquiries and protests from the South Pacific Forum nations was experienced. To enhance communications with the public on the chemical retrograde project and the chemical destruction process, two information teams were dispatched to the region to brief officials of the South Pacific Forum nations, including Australia and New Zealand. Team members answered many questions, clarified some misperceptions, but were not able to dispel all concerns regarding the chemical retrograde project.

Transportation from Solomon Islands to Johnston Island

18. In 1991, World War II mustard-filled artillery projectiles were found in a remote area of Mbanika Island in the Solomon Islands. Mbanika Island had been a forward support base during the war and was used as a large ammunition storage area for the United States. The government of the Solomon Islands requested their removal. In response, U.S. survey teams were sent to gather information concerning the terrain surrounding the site. The first of these teams arrived in December 1989 and ascertained that the munitions were stable and did not constitute an emergency. Subsequent teams continued surveys and assessments, and in 1990, the then Secretary of Defense assured the South Pacific Forum that the United States would safely dispose of all of the munitions found. The U.S. Pacific Command (PACOM) was designated as Executive Agent for the removal of the weapons. A plan was developed, and the U.S. Army Pacific (USARPAC), with assistance from the Technical Escort Unit, executed the mission.

19. In May 1991, under the watchful eye of the representatives of the Solomon Island government and Australia, a total of 109 mustard-filled projectiles were overpacked into steel cylinders by U.S. personnel. This operation was carried out without incident, although several personnel experienced heat exhaustion. The area was later surveyed and tested for contamination and found to be clean. The overpacked munitions were placed in an Army ocean-going barge and transported to Johnston Island where they were unloaded and placed into storage bunkers. These items were destroyed by JACADS during its disposal campaign.

20. In response to concerns expressed by the South Pacific Forum in August 1991, the Defense Department affirmed that in the future the only chemical weapons that would be transported to Johnston Island for destruction would be those that are clearly U.S. in origin and found in the Pacific region.

Chemical munitions in Iraq

21. Iraq's chemical munitions were dispersed at airbases and storage depots throughout Iraq. The United Nations Special Commission (UNSCOM) established a Chemical Weapons Destruction Advisory Panel (DAP) to assess how best to destroy Iraq's chemical weapons safely and effectively [47]. The question of whether the destruction operation should be carried out at a single location or at each of the chemical munition storage sites was discussed at length. The former option required the movement of chemical munitions, many of which were in poor condition from widely dispersed sites across Iraq to a central location, whereas the latter option required the use of mobile destruction equipment, which could be moved from site to site. Although considered to be technically feasible, the use of mobile equipment was recognized as resulting in additional technical, safety, and environmental problems because of the need to operate at several different sites. After considering all aspects of the problem, the DAP decided to centralize the destruction operations at a single site and to transport all munitions deemed to be safe to this location. As the bulk stocks of chemical agent and most of the precursor chemicals were already at the Al Muthanna CW production site, and much of the infrastructure for the destruction operation, although severely damaged, was at Al Muthanna, it was decided to carry out the destruction operation at Al Muthanna.

22. Before being transported to Al Muthanna, each munition was checked to ensure that it was not fuzed. Leaking munitions were sealed using a variety of techniques, and then checked to confirm that they were no longer leaking. The munitions were then placed in specially designed racks and packed into International Standards Organization (ISO) transport containers, which had been modified to ensure that they were both liquid- and vapor-tight. A deep layer of absorbent material was placed on the floor of each container. As an additional precaution, refrigerated containers were used for the munitions containing mustard agent. This ensured that the mustard agent, which solidifies in its pure form at 14 °C, was maintained in a solid form during its transportation to Al Muthanna. A small number of munitions, judged to be in too poor condition to be moved, were set aside for on-site disposal at a later date.

23. These ISO containers were transported by Iraq under the direction of UNSCOM. Each shipment was accompanied by the necessary security, monitoring, decontamination, and medical personnel and equipment to deal with all foreseeable incidents. Shipments were carefully monitored during the transfer process to ensure that any leaks would be promptly detected and appropriate action taken. Routes for the shipments were planned, as far as possible, to avoid populated areas. On arrival at Al Muthanna, the munitions were placed in storage in a remote area of the site. Using these procedures, all the munitions that could be moved were safely transported to Al Muthanna without incident.

C. Risk perspectives

24. There are two principal munition categories: (1) stockpile munitions or containers that should generally be in good condition despite having been stored for many years, and (2) non-stockpile munitions or containers, which have been (a) buried, (b) otherwise dumped or (c) unexploded ordnance, and whose condition on retrieval is uncertain. In the case of both stockpile and non-stock-

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[47] R. G. Manley. "UNSCOM's experience with chemical warfare agents and munitions in Iraq", in *The Challenge of Old Chemical Weapons and Toxic Armament Wastes,* T. Stock and K. Lohs (Eds.), pp. 241–252, Stockholm International Peace Research Institute, Oxford University Press (1997).

pile munitions or containers, part of the standard procedures that need to be followed in approaching the munitions or containers will be to check that there are no leaking munitions or containers. The second procedure, having established that there are no leaking munitions or containers, is to determine whether or not the munition has a burster charge and if it has been fuzed. Stockpile munitions will generally have a burster charge fitted and may either be fuzed in storage or, more often, fitted with a fuze immediately prior to use. In the case of non-stockpile munitions, much depends on how the munition became non-stockpile and whether the munition had been discarded before or after being fuzed. However, generally, non-stockpile munitions will not be fuzed, although if they are unexploded ordnance they will have been fuzed and the fuse may no longer be safe to handle.

25. Should the munition be found to be leaking, it will then need to be handled by personnel wearing full protective equipment, and the munition will need to be transported in a sealed container which will also probably contain absorbent to ensure that there is no release into the atmosphere of chemical agent. If the munition is found to be fitted with a burster charge or to be fuzed, then explosive ordnance disposal personnel may need to be called to make the munition safe to move and transport. If the state of the munition is uncertain, then it may be necessary to use techniques such as X-ray to determine whether or not the munition has a burster charge or is fuzed. If there is doubt about the status of the munition, or if the fuse cannot be safely removed, then the options of destruction at the particular location or of transportation in a container designed to contain the weapon should it function will need to be considered.

Transportation to storage and destruction sites

26. The decision whether to transport stockpile chemical munitions to a storage-and-destruction site or whether to consider destruction at the location where the stockpile munitions have been discovered will depend on a number of factors, which include the size of the stockpile at the location, the state of the munitions, and in particular whether they have been stored fuzed or not, and the hazards involved in transportation to a storage-and-destruction site. Much will also depend on the national socio-legal-political attitudes to the transportation and destruction of chemical weapons. The decision will depend on the particular circumstances relating to the stockpile chemical weapons.

On-site agent transport risks

27. At a chemical agent and munitions storage-and-destruction site, there are two primary sources of risk: (1) the risk associated with the stockpile itself (stockpile risk) and (2) the risk associated with the destruction of the stockpile (operational risk). The actual risk from either or both of these depends on whether risk-initiating events occur. Such events can be either internal or external in nature: Internal events are events associated with the storage and routine maintenance of the stockpile and with the operation of the destruction facility. External events are events not associated with site operations, such as earthquakes, floods, lightning strikes, and airplane crashes.

28. Agent destruction imposes risks above and beyond the inherent risks associated with the existence and maintenance of the chemical agent and munitions stockpile; however, whereas the short-term risks of destruction of CW agents exceed the short-term risks of storage, the integrated long-term risks of storage are greater. The transportation of agents from storage to the destruction facility, the unpacking and disassembly of munitions and containment systems, and the actual agent destruction processes provide additional opportunities for agent releases caused by internal or external events.

30. Chemical weapons and agents need to be transported from on-site storage facilities (e.g., igloos, warehouses, or open areas) to the disposal facility. The loading, transportation, and unloading of

munitions and agent containers poses a risk to the workers and to the public. Consequently, care needs to be taken in these activities to ensure that risks from agent exposure are minimized.

31. Prior to transport of munitions and containers, the area needs to be checked for any sign of leakage. If agent contamination is found, special procedures should be followed to contain leaking munitions and to decontaminate the area. The munitions or agent containers can then be loaded into a robust, vapor-tight, transport container that is designed to withstand impacts and fire exposure. Alternatively, munitions and containers can be transported without secondary containment. However, this may increase the risk depending on the agent and the chemical weapon configuration. The transport container or munitions/agent container is then moved from the agent storage area to the unpacking area within the disposal building where munitions and agent containers are generally unpacked manually.

V. REMOVAL OF CHEMICAL AGENTS FROM CHEMICAL WEAPONS

1. Chemical weapons consist of a diverse range of chemical agents and associated munitions, which together represent a complex disposal task, regardless of the technology used. Chemical agents can be found in containers (such as various bombs stored without explosives, aerial spray tanks, and ton storage containers) and munitions (such as land mines, missile warheads, bombs, rockets, artillery projectiles, and mortar projectiles). Some munitions may have no explosives or propellant, whereas others contain some combination of fuze, booster, burster, and propellant [48]. Generally, these components are referred to collectively as energetics. They incorporate a variety of chemical compounds that need to be disposed of as part of a chemical weapons disposal operation.

2. Munitions are often stored in configurations suitable for transportation during wartime, such as in boxes or protective tubes. Such packing and handling materials are referred to as dunnage. These materials also need to be disposed of in any program for chemical weapons destruction. However, dunnage may be disposed of at a hazardous waste site, if shown to be agent-free.

A. Disassembly and draining

3. One approach to demilitarization processing is to separate the components of munitions such as the agent, energetics, contaminated metal, and dunnage into separate streams that can be handled safely in downstream processing systems (e.g., hydrolysis, incineration). Since each munition is unique, each needs to be processed separately.

4. Munitions that are explosively configured and/or contain propellant pose a challenge owing to the potential for an explosion during processing. In the U.S. chemical demilitarization operations, such munitions are moved into an explosive containment room that is maintained below atmospheric pressure to prevent leakage of agent outside the enclosure and is designed to withstand overpressures and contain any fragmentation that might result from explosion of munitions during processing. Ventilation from this room is passed sequentially through six charcoal filter beds, with agent monitors after the first, second, and fourth beds.

5. Agent is removed from munitions by means of automated machinery using one of two processes. Agent storage compartment walls in missile warheads, rockets, and mines can be simply punched and drained of agent. Heavy-walled steel artillery projectiles need to be disassembled. Disassembly begins with the removal of explosive elements in the case of armed projectiles. Where possible, mechanical extraction of a burster well gains access to the agent. Agent drainage (and subsequent destruction) can be complicated because of gelling or solidification of the material, which then does not drain from the munition. Gelling occurs mostly in aged mustard. The U.S. experience at JACADS indicated that on average only 60 % of the mustard could be drained from approximately 50 000 projectiles. Consequently, treatment of the metal body parts also involved destruction of significant amounts of gelled agent. This experience led the United States to reconsider the value of draining; 45 000 mortar rounds containing mustard were processed undrained at JACADS. An additional problem experienced with mustard-filled munitions at

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[48] The fuze, a highly sensitive explosive element, initiates an explosive chain by detonating a booster. The booster is an intermediate charge, sensitive enough to be detonated by the fuze and energetic enough to detonate the much larger burster. The burster, the end of the explosive chain, bursts the munition with sufficient energy to disperse the agent held in the munition. Propellants are the energetic materials necessary for the propulsion of the rockets and the artillery projectiles.

JACADS was the foaming/frothing of the agent when the burster well was removed. This resulted in considerable agent spillage and heavy contamination of the disassembly machinery. A concept is now being developed in the United States in which the mustard is frozen in the munition before venting the agent cavity (e.g., by drilling) and processing the frozen agent-filled munitions in a metal parts furnace. This concept is one of four technology approaches being considered for destruction of the chemical stockpile munitions at Pueblo, Colorado. A final technology decision is anticipated by late 2001.

6. Bulk munitions contain agent but no energetics. Such munitions and bulk agent containers bypass the explosion-containment room and are conveyed to a bulk drain station where containers are mechanically punched and munitions are reverse-assembled and then drained within an enclosure; the air of the enclosure also passes through the charcoal filter beds.

7. These operations result in three separate streams of material that are fed to specially designed destruction systems: an agent stream that is stored in a feed tank prior to injection into a liquid incinerator; a mixed stream of energetics, small metal parts, and residual agent that is fed to the rotary kiln deactivation furnace system; and the large metal parts (e.g., ton containers, spray tanks, artillery projectiles) with residual agent but no energetics, that are fed to the metal parts furnace. The separation of these three streams is considered an important safety feature of the U.S. baseline system, enabling the design of the individual disposal system for a specific material stream to be tailored to ensure safe, controllable operations. As a result, most agent is treated in liquid form; energetics and metal parts where only residual agent is present are treated separately. As already mentioned, in the case of mustard-filled munitions, significant quantities of mustard agent may adhere to the metal parts and therefore need to be treated along with the metal parts.

B. Explosive charges for accessing chemical weapons

8. It is not always possible to access the chemical agent by disassembly such as removal of the filling plug or by punch/drill and drain. Extremely thick-walled artillery casings are an example where these techniques are unsuitable. This is particularly true when performing field operations where adequate equipment is not readily available. Such a situation faced UNSCOM's Chemical Weapons Destruction Advisory Panel (DAP) when confronted with the draining operations for some of Iraq's chemical weapons. For example, it was not possible to remove the filler plugs of the Al Hussein missile warheads. Various techniques were investigated for opening these warheads, and the technique finally used was to blow a small hole in the nose of each warhead using a "shaped" charge. The contents were then removed using the vacuum transfer system developed for the aerial bombs. Any residual agent was neutralized by filling the warhead with alcoholic caustic soda and, after soaking for a time, burnt out. Once certified free from contamination, the warheads were destroyed by mechanical means.

9. The Iraqi mustard-filled 155-mm artillery rounds posed a particularly difficult problem as they had no filler plugs and the thick-walled cases were not easy to drill. Owing to the presence of hydrogen gas and other gaseous degradation products in many of the rounds, there was not only considerable internal pressure but also a high risk of ignition during the drilling of the case. After a number of trials, a successful technique was developed for opening these rounds. It involved standing the rounds on their "boat-tails" in specially designed racks on large concrete pads and placing a small, specially designed, explosive charge inside the burster tube of each round. The positioning of the charge was such that when it was fired the explosive force cut the burster tube just below the point where it joined the neck of the shell. The rounds were wired up and opened in batches of 200. Once opened, the outside of the round was first decontaminated and then the

mustard removed by suction in the manner developed for the aerial bombs. When the mustard had been removed, the empty shell cases were filled with alcoholic caustic soda and burnt out.

10. The French have proposed a universal solution for the destruction of old or abandoned chemical weapons: the firing pool. The firing pool technique utilizes the fact that a munition contains an explosive (which is intended to disperse the chemical agent on the battlefield) inside a burster tube. A firing pool is a large pool capable of withstanding repeated explosions. It is filled with an aqueous decontamination solution, and the chemical weapon to be destroyed is placed in the center of the pool and submerged. One chemical weapon is planned to be exploded every 15 min.

11. In the firing pool, the body of the munition is destroyed by the use of controlled explosive charges while the explosion delivers the chemical agent into a decontamination solution. The advantage of this process is its ability to accommodate both the explosive and the chemical components of CW munitions. The firing pool technique was designed initially for explosive experiments with conventional weapons and meets the requirements for the safe handling of explosives. In order to ensure the detonation of the inner burster charge, two additional explosive charges are fitted on opposite sides of the munition. This means that the pool needs to be sufficiently large so that it can contain the blast from the inner burster and the two additional charges.

12. The firing pool approach has its limitations. Old and abandoned chemical weapons were designed with an explosive charge that was just sufficient to make the shell burst, resulting in large pieces of irregularly shaped scrap. If dispersion were as designed, then dispersion of chemical warfare agents in a decontamination solution would be a satisfactory means of destruction. However, it is very difficult to assess the viscosity of some agents after 70 years in a shell. Mustard, for example, is liable to polymerize, and this polymer sticks to even a fragmented shell. As noted, the fragments will be large and few in number. When the scrap is removed from the pool, some of the toxic compound sticks to the metallic parts, resulting in a hazard to both workers and the environment.

13. It is important to recognize that the use of explosive charges to access chemical agent will be **limited** to a few unique situations where other approaches are not feasible or readily available.

C. Water-jet technology for munitions cleaning and cutting

14. In Germany, old chemical weapons (OCW) are stored and categorized by type, to the extent possible so as to facilitate their handling and ultimate destruction, to avoid confusion and to ensure safety. The OCW, which have been removed from various areas, are placed in facilities that provide safe intermediate storage. The munitions that are excavated are generally coated with dirt and have a rough surface because of corrosion. For this reason, prior to further treatment they are cleaned using high-pressure water.

15. When these old chemical weapons are dismantled they are disassembled, the fuzes and explosive charges (bursters) are removed and the chemical fills are drained. In most cases remote-controlled special dismantling equipment—such as defusing tools, machines for drilling, milling and sawing, and chopping benches—needs to be used for these critical and hazardous procedures.

16. This equipment is operated from a dismantling control bunker. In the event of an explosion or the release of toxic chemicals, the personnel are protected from fragments, vapors, and aerosols by thick concrete walls and a highly efficient air filtration system. The dismantling process is constantly monitored and videotaped to provide thorough documentation for later evaluation of the operation.

17. The French search for a munition-opening device that will function in corrosive liquids, like detoxifying solutions, led to consideration of water-jet cutting technology instead of the use of a standard saw. A water jet can easily process several sizes of munitions. It can be used, first, to cut munitions into workable pieces and, then, to clean them at a lower jet pressure in order to ensure complete decontamination of the scrap generated by the process. This solves the problems raised by polymerized derivatives of mustard, which do not flow out of a munition that is pierced by the use of the conventional drilling technique. A fully automated water-jet cutting device that is fitted in a small decontamination pool has been tested at the Centre d'Etudes du Bouchet, the French research center for nuclear, biological, and chemical defense, to evaluate its efficiency.

D. Cryofracture

18. After testing a variety of disposal technologies, in 1983 the U.S. Army selected component disassembly followed by incineration of separated waste streams of agent; energetics; and metal parts followed by processing of off-gases through a pollution abatement system (PAS) as the disposal method of choice. While development was proceeding of this baseline incineration system, the U.S. Army studied alternate technologies to identify methods that might improve operational safety and reduce disposal time and costs. From a comprehensive evaluation of alternatives considered in 1983, which considered a number of disassembly options, cryofracture technology emerged as the most promising backup to simplify the mechanical disassembly of munitions [49].

19. Cryofracture uses liquid nitrogen to cool munitions casings to the point where they become brittle and are easily fractured with either a drop hammer or press. Cryofracture was considered promising at that time, as it removed human handlers from the unpacking end of the demilitarization process, and it offered a simple single process for accessing agent and explosives in a variety of munitions. Cryofracture uses robots to unpack munitions and immerse them in a cryogenic bath of liquid nitrogen, which embrittles steel, rendering it easier to fracture. The weapon or container is then fractured by a hydraulic press, and the metal fragments, explosives, and agent are incinerated simultaneously in a single rotary kiln followed by a pollution abatement system to treat the gaseous effluent.

20. In 1985, the U.S. Congress instructed the U.S. Army to build a prototype cryofracture chemical weapons disposal plant at the Tooele Army Depot, Utah. A cryofracture followed by incineration test using simulated GB munitions was conducted at Tooele in 1986, and development continued in 1987 and 1988, at which time the U.S. Department of Defense ended the development project because it was considered unlikely that the program's timing would permit cryofracture to be integrated into the baseline technology and provide either a cost or time advantage. A report by the National Research Council's Committee on Review and Evaluation of the Army's Chemical Stockpile Disposal Program in 1989 expressed reservations [50] about cryofracture noting that:

> *[Cryofracture] is not especially useful in the disposal of bulk agent or in the disposal of munitions such as rockets, whose aluminium shells rather than growing brittle at lower temperatures, actually become tougher.*

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49. National Research Council, Committee on Demilitarizing Chemical Munitions and Agents. *Disposal of Chemical Munitions and Agents,* National Academy Press, Washington, DC (1984).
50. As reported in National Research Council, Panel on the Current Status of the Cryofracture Process, *Demilitarization of Chemical Weapons by Cryofracture: A Technical Assessment,* pp. 3–4, National Academy Press, Washington, DC (1991).

> *There is no means to control the size of explosive fragments, to separate such elements, or to even assure that burster fragments do not remain assembled to fuzes. Thus, fuzes—which will detonate in a furnace—could well lead to detonation of nearby burster elements. Unsteady very rapid burning of explosive and propellant elements would lead to variable residence times for agents in downstream components, thus making complete combustion difficult to achieve. The combustion of so many different types of components simultaneously, with the potential for generating undesirable complex gases or solids in the process, plus the strong corrosive nature of the chemical agents makes the use of a common kiln a most questionable procedure from the standpoint of both efficiency and safety.*
>
> *Uncertainties in the cryofracture process and still-to-be-proven aspects of its procedures imply, at the very least, that a large effort over a long period of time to develop the system and then prove its safety would be required before demilitarization operations using cryofracture technology could be started.*

21. Despite these objections, the cryofracture research and development program was reactivated in 1989 at the direction of the U.S. Congress with instructions to build a full-scale facility, rather than a prototype, for cryofracture. In 1991, the U.S. National Research Council was asked to reexamine the technical status of the cryofracture process and specifically to:

> *evaluate the technical merits of the cryofracture process on the basis of any new data that may have been acquired and advances in understanding that may have been achieved in the last several years. The Panel will also determine whether the concerns raised in the previous National Research Council report on cryofracture are being addressed in the Army's current research and development program.*

22. The panel did not undertake a comprehensive review of the overall chemical demilitarization program, but rather focused on the cryofracture program. They concluded [51] in their 1991 report that:

> *the initial cryofracture facility under design for installation at Tooele Army Depot in Utah would almost certainly undergo an extended (several-year) start-up. This would mean that the timing for the cryofracture program could not be expected to be shorter than the presently projected timing for the current process, nor would the new technology offer any real possibility of meeting the 2002 deadline for completion of the program, which is expected to be established in a U.S.-Soviet treaty. With almost all the funds for the current process expected to be spent or committed before the initial cryofracture facility is operational, no cost savings in the program from the use of cryofracture appears possible.*

The panel's report also noted that the cryofracture program was not designed to address the NRC concerns about incinerator operation and stated that "*the uncertainty caused by the lack of a protype for the incineration process and the downstream systems make it doubtful that the pollution abatement system (PAS) equipment downstream of incineration can be judged to have a proven design or to have been tested thoroughly*." The report essentially halted all U.S. government support for further development of the cryofracture process.

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[51] National Research Council, Panel on the Current Status of the Cryofracture Process. *Demilitarization of Chemical Weapons by Cryofracture: A Technical Assessment,* Executive Summary, p. iii, National Academy Press, Washington, DC (1991).

23. In 1996, persuaded by public opposition to incineration in Richmond, Kentucky and Pueblo, Colorado, the U.S. Congress enacted Public Law 104-201, which instructed the U.S. Department of Defense (DOD) to "*conduct an assessment of the chemical demilitarization program for destruction of assembled chemical munitions and of alternative demilitarization techniques and processes (other than incineration) that could be used for the destruction of the lethal chemical agents that are associated with these munitions.*" The DOD established a program manager for Assembled Chemical Weapons Assessment (ACWA), who is required under the Public Law to "*identify and demonstrate not less than two alternatives to the baseline incineration process for the demilitarization of assembled chemical munitions.*"

24. General Atomics has proposed a two-step alternative to incineration of chemical agents and munitions at the Pueblo Chemical Agent Disposal Facility [52]. This General Atomics total solution is based on a modified baseline incineration plant design in which the incinerators and their accompanying pollution abatement system are replaced by neutralization and supercritical water oxidation (SCWO) systems. The system design is specific to dealing with an inventory of chemical munitions similar to that at Pueblo, that is, one consisting of projectiles having steel bodies and containing mustard.

25. Projectiles are first unpacked and propellant charges and aluminium tailpieces removed and the energetics (fuzes and bursters) removed inside an explosion containment room. The downloaded projectiles, free of energetics, but still filled with agent, then enter a projectile agent removal system (PAR). The PAR consists of a cryobath loading robot, cryobath, cryobath unloading robot, cryopress, projectile rotary hydrolyzer, and heated discharge conveyer. Projectiles are transferred to the cryobath loading station by conveyor. The loading robot lifts the munition and places it in a cradle on the cryobath conveyor, which then passes through a liquid nitrogen bath in about 40 min, cooling to –200 °C, and becoming completely brittle in the process. At the end of the cryobath, the unloading robot lifts the munition and places it on tooling within the cryopress. A cover closes around the tooling, and the hydraulic press fractures the munition. The cryopress tooling is tilted up, and the projectile fragments and agent are transferred by gravity into the projectile rotary hydrolyzer. Hot water is used to flush any residual frozen agent off the tooling. The projectile rotary hydrolyzer is a 6-foot rotating drum, 40 feet long, with an internal spiral flight integrally welded to the inside of the drum. The agent is warmed and dissolved by a countercurrent flow of hot water inside the hydrolyzer, and is then transferred as a liquid to the agent hydrolysis system where hydrolysis is completed using supercritical water oxidation (SCWO). Metal fragments from fractured projectiles are moved by the action of the hydrolyzer drum rotation and after one hour are discharged into a heated discharge conveyor. This is similar to the baseline incineration equipment with additional heating capacity. Metallic residues are heated to 540 °C and held at that temperature for 15 min, thus achieving a 5X decontamination level [53]. The heated discharge conveyor is nitrogen purged.

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[52] National Research Council, Committee on Review and Evaluation of Alternative Technologies for Demilitarization of Assembled Chemical Weapons. *Review and Evaluation of Alternative Technologies for Demilitarization of Assembled Chemical Weapons,* p. 88, National Academy Press, Washington, DC (1999).

[53] 5X is the U.S. Army's classification for material that is completely decontaminated, is free of agent, and may be released for general use or to the public. For more information on the U.S. Army 5X decontamination, see Appendix H *Excerpt from the U.S. Army's 5X Decontamination Review* in National Research Council, Committee on Alternative Chemical Demilitarization Technologies, *Alternative Technologies for the Destruction of Chemical Agents and Munitions,* National Academy Press, Washington, DC (1993).

26. The National Research Council evaluation [54] in 1999 of alternative technologies proposed for assembled chemical weapons noted that they found no data to indicate that cryofracture would provide better access to liquid agent than more conventional approaches, such as shearing. They made the following finding in respect of cryofracture:

    > *Cryofracture appears to be an effective method for accessing the agent in projectiles and mortars and might provide an improvement over baseline disassembly in accessing gelled or crystallized agent. This remains to be demonstrated.*

    It is also evident that cryofracture, as with any technology for removal of agents from munitions, has to be integrated into a comprehensive demilitarization process.

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[54] National Research Council, Committee on Review and Evaluation of Alternative Technologies for Demilitarization of Assembled Chemical Weapons. *Review and Evaluation of Alternative Technologies for Demilitarization of Assembled Chemical Weapons,* p. 101, National Academy Press, Washington, DC (1999).

VI. HIGH-TEMPERATURE DESTRUCTION OF CHEMICAL WARFARE AGENTS

A. Incineration

Process description

1. Incineration of organic chemicals containing carbon, hydrogen, and oxygen leads to the formation of carbon dioxide and water. As chemical warfare agents also can contain fluorine, chlorine, nitrogen, phosphorus, and sulfur, incineration will produce hydrogen fluoride (GB), hydrogen chloride (H, HD, HT), nitrogen dioxide (GA, VR and VX), phosphorus pentoxide (GA, GB, VR and VX), and sulfur dioxide (H, HD, HT). All of these can be removed by scrubbing. In principle, incineration is an environmentally safe method of toxic waste disposal provided that the temperature used is sufficient to decompose the organic chemical to simple inorganic chemicals.

2. More chemical agent has been destroyed by incineration than by any other technology. The United States commissioned studies of different disposal technologies and tested several in the 1970s, including incineration and chemical neutralization [55]. In 1982, the U.S. Army selected component disassembly and incineration along with associated pollution abatement systems, now known as the baseline system, as the preferred disposal system. A year later, the National Research Council of the U.S. National Academy of Sciences formed a Committee on Demilitarizing Chemical Munitions and Agents to review the status of the stockpile and the technologies for destruction. That committee reviewed the range of technologies, which it identified in its report [56] as being:

   a. chemical processes, such as hydrolysis, caustic neutralization, anhydrous chlorinolysis, and aqueous chlorinolysis;

   b. placement of chemical agent and munitions in underground cavities and destroying them in a nuclear explosion;

   c. conventional thermal processes such as incineration and pyrolysis; and

   d. “novel technologies”, only one of which—called “in-shell combustion”—was advanced enough in 1984 to be seen as potentially useful.

   In its report in 1984, the Committee concluded:

   > *Considering the above advantages and disadvantages of each disposal method, thermal destruction is the preferred means for disposing of the current stockpile of chemical agents and munitions. The Army has already selected thermal destruction as the most appropriate method. The committee supports this decision.*

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55. As reported in National Research Council, Committee on Review and Evaluation of the Army Chemical Stockpile Disposal Program, *Review of Systematization of the Tooele Chemical Agent Disposal Facility,* National Academy Press, Washington, DC (1996), Appendix B, p. 84, reference to Moynihan *et al.*, 1983.
56. National Research Council, Committee on Demilitarizing Chemical Munitions and Agents. *Disposal of Chemical Munitions and Agents,* pp. 5–6, National Academy Press, Washington, DC (1984).

3. Three years later, the NRC established the Review and Evaluation of the Army Chemical Stockpile Disposal Program Committee [57] (known as the Stockpile Committee) to provide the U.S. Army with technical advice on specific aspects of the disposal program. As of January 2001, the U.S. Army had requested and received 23 reports from the Stockpile Committee. These reports have consistently endorsed the U.S. Army's selection of incineration as a safe and adequate technology for the destruction of agent and energetic components and for the reliable decontamination of metal parts to a level suitable for release to commercial industry.

4. Incineration is the technology used by many countries to destroy chemical warfare agents; it is the baseline process used by the United States at the Rocky Mountain Arsenal from 1969 to 1976 when over 3000 tons (2720 agent-tonnes) of mustard agent were incinerated [58], in the Chemical Agent Munitions Disposal System at the Tooele Army Ammunition Plant, Utah, which was not designed for large-scale destruction activities but nevertheless destroyed [59] more than 19 000 projectiles and 14 000 rockets containing nerve agent, GB, and more recently in the Johnston Atoll Chemical Agent Disposal System (JACADS) at Johnston Atoll in the Pacific approximately 750 miles southwest of Hawaii. The JACADS facility had a two-fold mission:

   - to destroy the chemical agents and munitions stored there, and
   - to serve as a demonstration facility for the baseline incineration system.

   JACADS completed its demilitarization operations on 29 November 2000 [60] and has now initiated the process leading to its closure.

5. Construction of the first disposal facility in the continental United States was begun in Utah in 1989. This facility, the Tooele Chemical Agent Disposal facility (TOCDF) is a "second-generation" baseline system that has incorporated into its design and operating procedures many improvements and technological advances based on JACADS operating experience.

6. The "second-generation" baseline process is made up of three stages:

   a. **Stage I.** The separation of chemical agents, energetics, and related materials in preparation for incineration.

   b. **Stage II.** The incineration of agents, energetics (explosives and propellants), and dunnage (packing and shipping materials) and the thermal decontamination of metal parts from munitions and storage containers.

   c. **Stage III.** The treatment and monitoring of gaseous effluents and analysis and disposal of remaining solid and liquid wastes.

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[57] The Review and Evaluation of the Army Chemical Stockpile Disposal Program Committee was established in 1987 at the request of the then Undersecretary of the Army. It was set up under the aegis of the National Research Council Board on Army Science and Technology.

[58] National Research Council, Committee on Demilitarizing Chemical Munitions and Agents. *Disposal of Chemical Munitions and Agents,* p. 21, National Academy Press, Washington, DC (1984).

[59] National Research Council. *Disposal of Chemical Munitions and Agents,* p. 21, National Academy Press, Washington, DC (1984).

[60] Department of Defense, Office of the Assistant Secretary of Defense (Public Affairs). *Chemical Weapons Destruction Complete on Johnston Atoll,* News Release, 30 November 2000. Available at http://www. edefenselink.mil/news/Nov2000/b11302000_bt715-00.html

7. This chapter of the report is only concerned with the incineration in Stage II. The outcome of Stage I are four material feed streams for incineration: agent, energetics (explosives and propellants), metal parts, and dunnage (packing materials and other miscellaneous waste). All of these streams may be contaminated by chemical agent. This division provides an important perspective on destruction complexities. The four types of materials in these streams have widely differing physical properties that influence handling: the extremely toxic liquids may be pumped and stored with relative ease; energetic solids encased in thin metal containers burn vigorously if sufficiently exposed, and require careful treatment to avoid detonation; inert, heavy-walled metal vessels contain residual agent; and miscellaneous dunnage materials have various physical characteristics and chemical makeup. Separation of these materials into controlled processing streams allows optimal design of separate disposal processes for each, while simplifying the control and thereby maximizing the safety of operations. The benefits of separation apply equally to all disposal technologies, and no individual disposal technology is particularly well suited to processing mixed streams. The four main material feed streams may be composed of the following materials:

   Agent: There are three different agent types in the U.S. stockpile—GB, VX, and mustard—in varying degrees of purity and quantity, depending upon site inventory. Liquid agent is drained from bulk containers and munitions.

   Energetics (explosives and propellants): Rockets, land mines, and some artillery projectiles may contain energetic materials, including fuzes, boosters, bursters, and solid rocket propellants. These energetics and associated small metal parts are often contaminated with agent.

   Metal parts: Large metal parts include drained containers without energetic materials (ton containers, bombs, spray tanks, and artillery projectile bodies). All of these materials will be contaminated with agent. Some may contain significant amounts of gelled agent that does not drain readily (particularly mustard).

   Dunnage: Miscellaneous wastes, which can be contaminated, including storage and handling pallets and packing materials, rags, protective clothing, and activated carbon from the ventilation air cleanup system.

8. Two auxiliary processing streams also result from all destruction technologies:

   Decontamination fluids: Fluid materials, such as sodium hydroxide in water, are used throughout the facility, for example, to enable safe access to areas and equipment for maintenance. These fluids may contain minor residual agent contamination and dust or other particulate materials.

   Ventilation air: Air from the process buildings and laboratories contains agent vapors.

9. The U.S. baseline incineration system is shown in Fig. 1. The four material streams are fed to three furnaces—the liquid incinerator (LIC), the deactivation furnace (DFS) for energetics, and the metal parts furnace (MPF) to decontaminate the metal. Although a fourth incinerator, the dunnage incinerator (DUN), was intended, this has not been put into operation. Instead, uncontaminated packing materials are being disposed off-site and testing is underway at JACADS to demonstrate the suitability of the existing incinerators to treat miscellaneous contaminated waste streams.

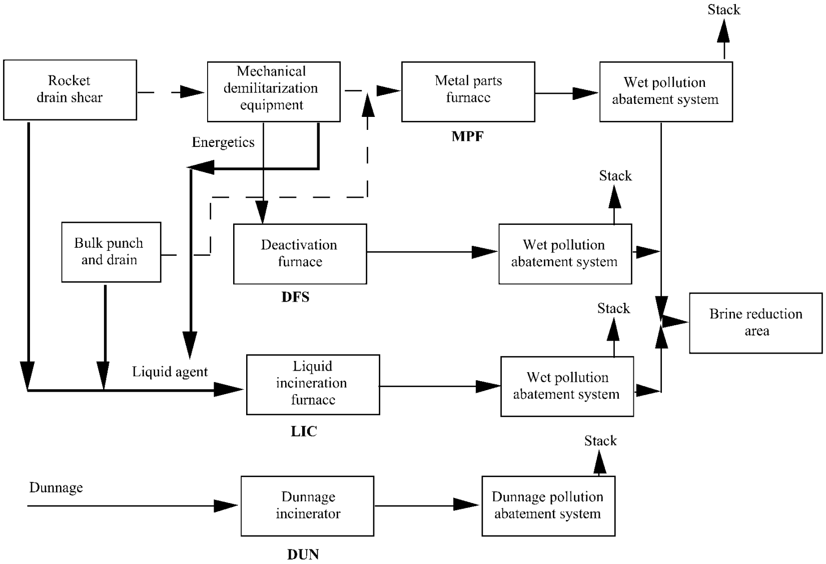

Fig. 1 U.S. baseline incineration system[a].

[a]Based on National Research Council, Committee on Review and Evaluation of the Army Chemical Stockpile Disposal Program, Review of Systematization of the Tooele Chemical Agent Disposal Facility, Appendix B, p. 92, National Academy Press, Washington, DC (1996).

10. *Agent destruction.* Liquid chemical agent drained from the munitions and storage containers is collected in a storage tank from which it is fed into a high-temperature LIC where it is burned at a temperature of 1480 °C. The LIC is a two-stage refractory-lined incinerator designed to destroy the nerve agents GA, GB, and VX, and mustard (H, HD, and HT). The drained agent is atomized by a nozzle and mixed with combustion air. Auxiliary fuel is used to maintain combustion at or above 1400 °C with the flue gases being passed to an afterburner maintained at a minimum temperature of 1090 °C before ducting to the pollution abatement system. The liquid incinerator at JACADS had to be shut down periodically for manual removal of glass-like solidified salts from both agent and decontamination fluid disposal. A slag removal system has been developed to discharge molten salts during operations at the TOCDF; the system has, however, not totally eliminated the slag problem.

11. The afterburner is a critical part of the incineration system as it uses an auxiliary fuel, such as natural gas, propane, or fuel oil, to ensure that temperatures in excess of 1090 °C are achieved to ensure that any residual agent or partial combustion products are destroyed. Spent decontamination fluid is also injected into the afterburner to ensure destruction of any residual agent in such fluid as well as the evaporation and discharge of the water vapor. This fluid also contains salts, which are deposited in the bottom of the afterburner.

12. *Destruction of energetics.* Energetics (fuzes, boosters, bursters, and solid rocket propellant) are burnt in a counterflow rotary kiln (deactivation furnace system) (DFS). Energetics are all contained in thin-walled metallic housings that need to be punched or cut into pieces prior to burning; confined energetics would detonate in the kiln rather than burn. Rockets, after being drained of agent, are sliced into eight pieces to expose energetic material surface area so the material will burn without detonating. Draining and slicing are both done while the rocket is in its fiberglass

launch tube. Bursters from artillery projectiles are also sliced, but after removal from the projectile. Explosive elements from land mines are punched in place to expose the explosive and are not removed from the munition. The pieces, most of which are wetted with agent, are fed carefully into the downstream end of the kiln (downstream in the sense of gas flow) to avoid explosive concentrations within the kiln. Solid pieces move upstream (against the gas flow) as the energetics are burned and then move onto an electrically heated discharge conveyor, where the temperature is maintained at 540 °C for 15 min. This results in a "5X" decontaminated material, which is the U.S. Army's classification for material that is completely decontaminated, is free of agent, and may be released for general use or to the public [61].

13. The resultant mixture of light steel components, melted aluminium, and fiberglass is of no commercial value. Gases discharged from the rotary kiln pass through an afterburner where they are subjected to a temperature of 1090 °C for 2 s.

14. *Metal parts decontamination.* Metal parts that have been drained of agent (such as one-ton agent containers, bombs, spray tanks, artillery projectiles, and burster wells, which were pulled to access the agent) are heated to 540 °C and maintained at that temperature for 15 min in a fuel-fired metal parts furnace (MPF) to produce metal suitable for release as scrap (defined by the U.S. Army as 5X) after deformation to comply with CWC requirements. Residual or undrained (including gelled) agent remaining in the metal parts is vaporized and burned within the furnace; the residence time in the furnace is of the order of 2 h. During this period, the residual agent is vaporized (≈40 min), the metal parts are heated to 540 °C and maintained at that temperature for at least 15 min (heated and maintained ≈40 min), and then the metal parts are allowed to cool in a cool-down zone (≈30 min) to minimize any fugitive emissions, should there be any residue remaining in the metal parts prior to the metal exiting the metal parts furnace. This process takes additional time and can limit the system's throughput. Gases discharged from the metal parts furnace are passed through an afterburner, maintained at 1090 °C, before being treated in the pollution abatement system. The decontaminated metal parts are discharged and shipped to an approved disposal site or sold for scrap.

15. *Pollution abatement system.* The liquid incinerator, the energetics deactivation furnace, and the metal parts furnace all have identical, separate, dedicated pollution abatement systems. Gases leaving the secondary chamber of the liquid incinerator or the metal parts furnace flow to these pollution abatement systems for removal of gaseous pollutants and particles to meet emission standards. Hot gases leaving the energetics deactivation furnace system kiln flow to a refractory-lined cyclone separator, where large particles such as glass fibers from rocket launch tubes are removed. The gases then enter the afterburner and subsequently flow into a similar pollution abatement system.

16. The exhaust gas stream enters the quench tower near the bottom, where it is cooled by contact with a countercurrent spray of brine (actually a solution of sodium hydroxide in water which reacts with acidic gases to form sodium chloride and other salt solutions) pumped from the packed-bed scrubber sump. Acidic or acid-forming gases [e.g., hydrogen chloride, hydrogen fluoride, nitrogen oxides (NO_X), and sulfur dioxide, depending on the chemical agent incinerated]

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[61] For more information on the U.S. Army 5X decontamination, see Appendix H *Excerpt from the U.S. Army's 5X Decontamination Review* in National Research Council, Committee on Alternative Chemical Demilitarization Technologies, *Alternative Technologies for the Destruction of Chemical Agents and Munitions,* National Academy Press, Washington, DC (1993).

in the exhaust gas react with the caustic brine to form salts, which remain in solution in the brine. The cooled gas stream exits from the top of the quench tower and enters a variable throat venturi where it is scrubbed to remove particulates. The venturi has a variable throat to maintain a constant pressure drop independent of the flow of exhaust gases. The brine streams from the quench and venturi scrubber are then returned to the scrubber tower sump. Process water is added to the packed-bed scrubber sump to make up for water evaporated in the quench tower. An 18 % caustic (sodium hydroxide) solution is added, as necessary, to the sump to maintain the brine pH above 8 or 9.

17. The exhaust gas stream from the venturi scrubber enters the scrubber tower below the clear liquor reservoir tray, moves upward through the packed-bed section, and exits at the top of the tower, after passing through a mist-eliminator pad. In the packed-bed section, the gas stream comes in contact with a brine solution flowing countercurrently through the bed. Acidic gases in the exhaust gas stream are further scrubbed with caustic brine. The brine solution from the packed bed falls back to the reservoir tray, and it's recycled back to the top of the packed-bed section. Excess brine overflows into the tower sump. Brine density is controlled by pumping a brine stream into the brine reduction area storage tanks and replacing it with processing water.

18. The scrubbed gases enter a candle mist-eliminator vessel. Mist-eliminator candles (i.e., candle-shaped fabric filters) remove very fine mist and submicron particulate matter that were not removed in the venturi scrubber. The cooled and cleaned exhaust gases are pulled through an induced draft blower located upstream of the stack shared by the three pollution abatement systems.

19. Emissions testing at JACADS and TOCDF has demonstrated the ability of these incineration systems to consistently meet all emissions[a] standards for particulates, organic compound destruction, and emissions of oligochlorodibenzodioxins/oligodichlorobenzofurans. Examples of recorded data [62] were as follows: particulate emissions were on average 14.7 gr/dsm^3 (103 runs), agent destruction was complete (40 runs), i.e., no agent measured in the stack gases, and dioxins and furans (36 runs) were near detectable levels-ITEQ (average) of 0.037 ng/dsm^3. Finally, PCB destruction in the DFS exceeded the 99.9999 % regulatory requirement.

Scientific principles

20. Incineration is the thermal decomposition and subsequent oxidation at high temperatures of the organic chemicals that are the chemical warfare agents. For mustard gas, the incineration process can be shown as being the following:

$$2(ClCH_2CH_2)_2S + 13.5O_2 = 8CO_2 + 6H_2O + 4HCl + 2SO_2$$

For GB, the incineration process can be shown as

$$2(CH_3)_2CHO(CH_3)POF + 13O_2 = P_2O_5 + 8CO_2 + 9H_2O + 2HF$$

and for VX as

$$2C_{11}H_{26}NO_2PS + 38.5O_2 = 22CO_2 + 26H_2O + P_2O_5 + 2SO_2 + 2NO$$

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[a] Particulate emissions in the United States are frequently expressed as grains per dry standard (20 °C, 1 atm) cubic meter shown as gr/dsm^3 (15.4 grains are equivalent to 1 gram).

62. National Research Council. *Carbon Filtration for Reducing Emissions from Chemical Agent Incineration*, p. 58, National Academy Press, Washington, DC (1999).

or as

$$2C_{11}H_{26}NO_2PS + 39.5O_2 = 22CO_2 + 26\ H_2O + P_2O_5 + 2SO_2 + 2NO_2$$

21. In the baseline system, liquid chemical agent drained from the munitions and storage containers is collected in a storage tank from which it is fed into a high-temperature liquid incinerator (LIC) where it is burned at a temperature of 1480 °C. The LIC is a two-stage refractory-lined incinerator designed to destroy the nerve agents GA, GB, and VX, and mustard gas (H, HD, HT). The drained agent is atomized by a nozzle and mixed with combustion air. Auxiliary fuel is used to maintain combustion at or above 1400 °C with the flue gases being passed to an afterburner maintained at a minimum temperature of 1090 °C for 2 s before ducting to the pollution abatement system.

22. In the pollution abatement or scrubbing system the various acidic or acid-forming products from the incineration are reacted with sodium hydroxide in the caustic brine solution involving reactions such as the following:

    Reaction with HCl:

    $$NaOH + HCl = NaCl + H_2O$$

    Reaction with HF:

    $$NaOH + HF = NaF + H_2O$$

    Reaction with SO_2:

    $$NaOH + SO_2 = NaHSO_3$$

    $$NaHSO_3 + NaOH = Na_2SO_3 + H_2O$$

    $$O_2 + 2Na_2SO_3 = 2Na_2SO_4$$

    Reaction with SO_3 (if formed rather than SO_2):

    $$NaOH + SO_3 = NaHSO_3$$

    $$NaHSO_3 + NaOH = Na_2SO_4 + H_2O$$

23. Agent-drained munitions and bulk items are fed by conveyor into the MPF which maintains all metal parts at a temperature of 540 °C for at least 15 min. Metal parts for projectiles and bulk items have a residence time of approximately 2 h. Exhaust gases pass to an afterburner maintained at 1090 °C and are then ducted to the pollution abatement system. The decontaminated metal parts are discharged and after deformation shipped to an approved disposal site or sold for scrap. Under these conditions, the incinerators emit no detectable agent in the stack gases.

Technology status

24. By 1988, incineration had been used to destroy 2800 agent-tonnes of CW (or 60 000 munitions) at Rocky Mountain Arsenal and at the Chemical Agent Munitions Disposal System (CAMDS) at the Tooele Army Ammunition Plant, Utah. It has also been used in other countries such as Canada, Germany, Iraq, and the United Kingdom to destroy over 9500 agent-tonnes of chemical agent. By January 2001, the total amount of chemical agent disposed of by incineration has exceeded 15 000 agent-tonnes.

25. The baseline incineration system was developed largely at the CAMDS experimental facility at Tooele Army Depot, Utah. The first full-scale operational plant, the Johnston Atoll Chemical Agent Disposal System (JACADS) in the Pacific, began chemical weapon destruction in June 1990 and completed this 10 years later in November 2000, and the Tooele Chemical Agent

Disposal Facility (TOCDF), in Utah, the first full-scale chemical agent disposal facility in the continental United States began operations in August 1996. Together, these two sites contain 49.6 % of the total U.S. stockpile of chemical agent of 31 495 agent-tons (28 572 agent-tonnes). As of the beginning of January 2001, JACADS had destroyed all its chemical weapons (1843 agent-tonnes), while TOCDF had destroyed over 4360 agent-tonnes, some 35 % of its stockpile. In total, over 20 % of the U.S. chemical agent stockpile had been destroyed safely and without any known health or environmental impact. Three other sites—Umatilla, Oregon; Anniston, Alabama; and Pine Bluff, Arkansas—have baseline incineration systems under construction. When completed, over 80 % of the U.S. stockpile will be destroyed at baseline incineration system sites.

Stability, reliability, and robustness

26. Incineration is a very mature technology, and where operated properly is capable of very high destructive efficiencies. It is effective on a wide range of organic materials; consequently it is able to destroy the entire range of chemical agents, with the exception that arsenic-containing agents, such as lewisite, are not good candidates for incineration due to the potential for arsenic emissions in the flue gas. The extremely high temperatures employed and the inherent heat capacity of the system make the incineration system very stable, reliable, and robust.

Monitoring

27. The agent monitoring systems at Tooele are the same as the systems at JACADS. There are two types of analyzers: (1) the automatic continuous air monitoring system (ACAMS), which is capable of detecting agent at concentrations well below the levels that are set for stack emission criteria or present an immediate threat to plant personnel or the surrounding population, with a response time of 3–8 min; and (2) the depot area air monitoring system (DAAMS) for collecting longer, time-averaged samples for more selective subsequent analysis in the laboratory to confirm that general population monitoring criteria are being met. The ACAMS monitors in personnel areas and in the stack are set to trigger an alarm at 20 % of permissible agent levels at which point agent operations are shut down. The DAAMS samples are analyzed for the much lower permissible general population levels of 0.000003 mg/m^3 for GB and VX and 0.0001 mg/m^3 for mustard. ACAMS and DAAMS monitoring points are distributed throughout the facility at appropriate locations including the installation boundaries.

28. *ACAMS.* The ACAMS was developed in 1985. It employs a process-control gas chromatograph with a flame photometric detector that is set to monitor either phosphorus (for the nerve agents) or sulfur (for mustard). The gas chromatograph separates different compounds according to the difference in time that they require to pass through a long, thin tube (capillary column) that is packed with a material that retains them differentially.

29. In the ACAMS instrument, a sample is collected in a sorbent tube for subsequent analysis. The time for sample collection is determined by the time required to collect sufficient sample for a quantitative analysis with an agent concentration corresponding to a particular hazard level. The sample is then thermally desorbed into a carrier gas stream that passes through the chromatographic column. It exits into the flame photometric detector with a retention time characteristic of the compound.

30. The flame photometric detector provides an additional measure of selectivity, because compounds produce different light spectra when they emerge from the chromatograph tube and are burned in the detector flame. Any signal from the detector during the retention-time window of an agent is presumed to be due to that agent, though other compounds containing phosphorous or sulfur could also have a similar retention time and be potential interferents (e.g., mercaptans added to

fuels and many pesticides). Conversely, agents that do not contain either sulfur or phosphorus atoms, such as lewisite, would not be detected.

31. Currently, the ACAMS is configured to detect only one agent at a time (although work is in progress in the United States to develop an improved ACAMS that can detect more than one agent at a time) and to sound an alarm if the agent concentration exceeds a predetermined value appropriate for the location being monitored. The alarm point is currently set at 0.2 times the maximum allowed level under the appropriate standard (e.g., 0.2 times the allowable stack concentration for stack emissions).

32. With cycle times ranging from 2–10 min (the longer times being required to achieve greater sensitivity levels), the ACAMS serves as a monitor and alarm throughout the demilitarization facility, monitoring plant operations, possible worker exposure, and stack emissions.

33. When an ACAMS records an agent concentration in excess of preset values, an alarm is triggered, and a number of responses are initiated depending on the location of the instrument. In response to an alarm by a common stack ACAMS, waste feeds to all furnaces that feed that stack are automatically terminated, although the burners are kept operating with clean fuel to ensure destruction of any agent present in the furnace. Likewise, in response to a duct-monitoring ACAMS alarm, the feed to the corresponding furnace is automatically stopped. In response to an alarm by one of the work area monitors, access to that area is restricted until the nature of the alarm is determined, and a mandatory contingency response is initiated.

34. *DAAMS.* Measurements at the general population limit level and confirmation of agent presence in the event of an alarm require greater sensitivity and selectivity than the ACAMS provides. The DAAMS was designed to satisfy these needs.

35. In the DAAMS, air samples are drawn through tubes filled with a solid sorbent called Tenax. Two samples are collected in parallel to facilitate confirmation measurements in the event of a laboratory error. After sampling for a time that depends on the agent concentration of concern for the particular location, the tubes are taken to a central laboratory facility for analysis by gas chromatography (with flame photometric detection) and mass spectrometric detection. This advanced analytical instrumentation employs longer capillary columns, has more sensitive electronics, and affords greater control of the analytical procedure than does the ACAMS, allowing chromatographic peaks to be resolved much better than in the ACAMS.

Safety considerations

36. The aim of safety interlocks is to minimize the risk of human mistakes by the operators of the facility. The guiding principle throughout in the design of chemical weapon destruction facilities is as far as possible to ensure that these fail safe in the event of failure or human error.

Safety interlocks

37. The major safety concerns are in respect of agent or large amounts of the products of incomplete combustion (PICs) going up the stack. Consequently, agent flow to the burner is stopped if the temperature drops below 1400 °C in the primary combustion chamber.

38. In the event of agent release, the ACAMS monitors alarm and corrective action is initiated. For example, if agent is detected in a furnace effluent, agent feed to the furnace is stopped automatically. The DAAMS system serves the dual purpose of providing samples to confirm or refute ACAMS alarms (which are sometimes false due to interferents) and of documenting concentrations of agent at much lower levels of detection sensitivity.

Hazard inventory

39. The major hazard inventory is the liquid agent storage tank. Once the agent is pumped through the burner it is immediately destroyed in the high-temperature primary combustion chamber environment.

Materials of construction

40. Some slag produced during nerve agent destruction will form on the lower-temperature walls of the afterburner chamber. Spent decontamination fluid is also injected into the afterburner chamber to ensure destruction of any residual agent in the fluid as well as the evaporation and discharge of the water vapor. Salts contained in the fluid are deposited in the bottom of the afterburner chamber. The liquid incinerator at JACADS has had to be shut down periodically for manual removal of glass-like solidified salts from both agent and decontamination fluid disposal. A slag removal system has been developed to discharge molten salts during operations at the TOCDF, which has been reported to have been successful [63].

Environmental impact

Test runs prior to release

41. Since incineration runs are continuous and not batch, it is not possible to test the flue gas stream prior to release to the environment. Since the system does not shut down until agent is detected in the exiting gases, it is possible that some very slight traces of agent may be emitted to environment. Other process streams, such as liquid and solids, can be tested prior to release.

Environmental burden

42. Since agent trial burns have shown incinerator emissions such as trace organic substances, metals, to be extremely small, the environmental burden from incineration should be nondetectable.

B. Plasma pyrolysis

Process description

43. In plasma pyrolysis, components of chemical munitions, after disassembly, are introduced into a plasma environment generated by an electric arc, at temperatures approaching 15 000 °C, in a special furnace enclosure. Chemical agents are instantly decomposed, and metal parts are melted. The gaseous decomposition products are passed through a pollution abatement system to remove noxious constituents. Plasma pyrolysis can take several forms: plasma plants in which the plasma torch treats material fed into the plasma oven, and plasma waste converters (PWCs) in which a plasma torch is inserted into a chamber into which the material to be destroyed is introduced. Alternatively, plasmas can be created using two electrodes in which the plasma is one electrode and the material to be treated is at the bottom of the oven as an anode. When the material is introduced into the plasma oven, then very high temperatures approaching 15 000 °C are experienced. Significantly lower temperatures are measured at the surface of the treated material (slag) depending on the melting temperature of the slag. Plasma pyrolysis reactors can be designed to treat all components of chemical munitions, i.e., chemical agent, fuzes, bursters, propellant, metal casings, and packing materials. An explosion chamber can be used to deactivate explosive components by energetic intitiation (detonation or deflagration), and the resulting debris and gas from the chamber then treated in a high-temperature plasma.

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63. National Research Council. *Tooele Chemical Agent Disposal Facility: Update on National Research Council Recommendations,* p. 15, National Academy Press, Washington, DC (1999).

44. A typical plasma pyrolysis reactor as shown in Fig. 2 is a cylindrical, refractory-lined vessel with an opening in the roof through which a plasma torch is inserted; such a reactor is known as a plasma waste converter (PWC). In larger PWCs, more than one plasma torch may be inserted through more than one opening. There are no air-tight seals between the plasma torch and the vessel roof, and the PWC is operated at a slightly negative pressure to prevent gas from exiting through the opening. It follows that air is constantly leaking through this opening into the PWC. The plasma feed gas passes through the torch, and the plasma is formed in the torch between the anode and the cathode. No other materials, such as agent or energetics, are introduced into the plasma torch.

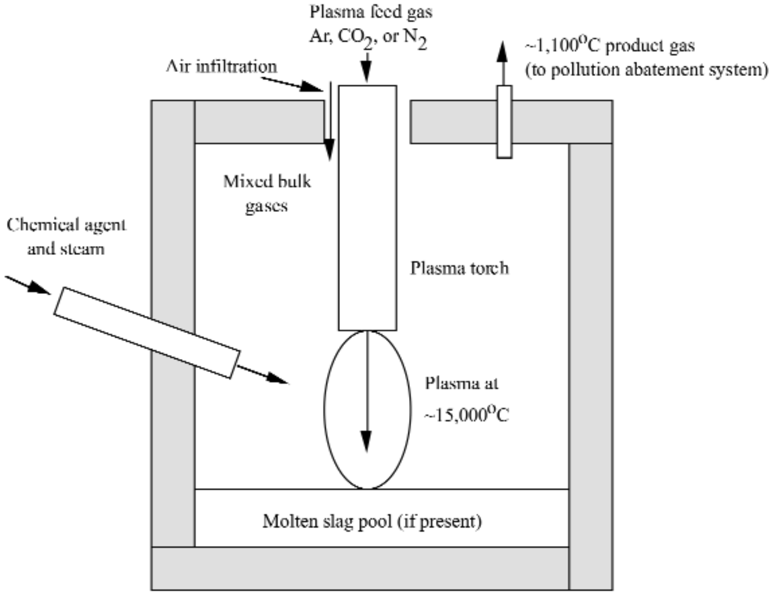

Fig. 2 Typical plasma waste converter.

45. The plasma exits the torch into the PWC chamber and impacts onto solid or liquid material such as the metal from munitions at the bottom of the chamber. In an agent-treatment PWC, agent is introduced into the hot plasma near the bottom of the PWC chamber. Steam is introduced with the agent at a controlled rate to convert elemental carbon or soot created by the dissociation of the feed stream molecules to carbon monoxide.

46. The plasma leaving the torch cools very quickly in the chamber by a combination of the following mechanisms:

- mixing with infiltration air
- heat transfer required to heat the waste feed to the PWC
- the endothermic chemistry of degradation of the agent and other organic waste materials introduced into the PWC
- decomposition of the steam introduced for soot control
- decomposition of the carbon dioxide if used as a plasma feed gas

- formation of NO_x from nitrogen in the munitions materials feed, the plasma feed gas (if nitrogen), or infiltration air
- heat losses through the PWC shell

47. Agent, after being drained from the munitions, and steam are injected into the PWC where they mix with the hot plasma. Product gas then passes through a pollution abatement system (PAS) and enters a hold-test-release system consisting of a compressor, a condenser, and storage tanks. The tank contents can then be sampled for agent and other components. If the product gas analysis is satisfactory, e.g., no agent is detected, the gas can be burned on site in a boiler or sold as a fuel. If the gas analysis is unacceptable, it can be recycled through a PWC. Other organic materials can similarly be converted to gaseous products, treated in the PAS, and sent to the hold-test-release system described above.

48. Contaminated bodies of projectiles, land mines, etc., drained of agent and with energetic materials removed, are fed to a separate PWC. Gaseous products flow through the PAS and the hold-test-release system described previously. Molten metal collects in the bottom of the PWC, which is tapped periodically, and the metal is cast into ingots.

Scientific principles

49. Electric arcs and discharges have been of interest to scientists and engineers for decades because they involve high-temperature, conductive gases (plasmas). Typically, an arc can be established between two conducting electrodes such as graphite or metal in a variety of atmospheres. The plasma is composed of molecules, atoms, ions, and electrons at temperatures of 1000 to 20 000 °C depending on the current and voltage, the gaseous environment, and the pressure of the constricting gas. Either physical or magnetic constriction can be used to increase temperatures.

50. Because plasma arcs between electrodes generally involve voltage drops of 100 V or more, chemical bonds, whose strengths range from 2–10 electron volts (eV) will be broken, and ionization processes (at 4–25 eV) will occur. Thus, material exposed to a plasma environment will be transformed into atoms, ions, and electrons with only a few molecules remaining. This makes the potential use of plasma arcs, torches, melters, and other plasma devices attractive for destroying undesirable molecules such as hazardous wastes. High-temperature plasmas can also produce endothermic neutral species, such as acetylene, cyanogens, and NO, or gaseous molecular ions, such as SiO^+ and CO^+. When the plasma is cooled to room temperature, most of the molecules are thermodynamically unstable, but some traces of metastable species that are stable at higher temperatures but unstable at lower temperatures might survive. In addition, small amounts of metastable species could be formed during cooling, which could also be present at room temperature.

Technology status

51. Research on plasma-arc technology dates back to the early 1900s, and many practical industrial applications have been developed including arc melting of metals; electric arc welding; plasma processing of ores; plasma spraying of metallic or oxide powders; and plasma generation of atomic, ionic, and molecular spectra for analytical systems. Plasma arcs have also been used for treating hazardous wastes. Wastes treated include solvents, paint, batteries, incinerator ash, and radioactive materials. Of the research initiatives by the U.S. Department of Energy and the Department of Defense over the past 10 years on plasma treatment of hazardous waste, two have reached the implementation stage: (a) a U.S. Navy project to destroy hazardous materials on shore; and (b) an ongoing asbestos destruction project at Port Clinton, Ohio. Other projects are still in the research phase. Although organic wastes have been destroyed using plasma-arc furnaces, much of the research to date has focused on the vitrification of inorganic substances within wastes (e.g., radioisotopes) rather than on the destruction of organic wastes.

52. In addition, plasma pyrolysis has been developed for the destruction of a variety of waste materials including chemical warfare agents in the PLASMOX® process. A plant is being constructed at Munster, Germany to address the disposal of viscous or solid chemical agents and, in particular, arsenicals as well as for the clean-up of arsenically contaminated soil [64]. The process involves a soil washing and flotation plant to separate contaminants from the soil. These contaminants and any arsenical chemical agents are then destroyed by thermal destruction and vitrification using the PLASMOX process to heat the feed material to temperatures of 1400 to 1600 °C in a plasma high-temperature reactor, which is a cylindrical chamber with a centrifuge at the bottom rotating at about 40 revolutions per minute into which is introduced the feed material. The plasma torches cause the rotating feed material to pyrolyze. The capacity of the centrifuge is about 1 m^3 which holds about 2 to 5 tonnes of smelt depending on its density. After 4 h, the centrifuge is stopped and the melted material is discharged into a slag cart. The quality of the smelt and of the solidified slag, respectively, can be influenced by the use of additives. In the PLASMOX process in Germany, the arsenicals are largely transferred into the gas phase because of the high temperatures and are precipitated in the PAS scrubbers as iron arsenates. This sludge is dried and put into drums for underground storage. Other heavy metals remain in the slag, which is similar to glass where they are evenly distributed and firmly bound. The EPA standard leach test in which the slag is treated in a slightly acidic environment to simulate the effect over time of acid rain on the dumped material resulted in the various elements in the slag being released in only extremely small quantities into the leach test eluate. As an inert substance, this material can be used as a filling material in civil engineering and is not required to go to a hazardous waste landfill site.

53. Very high destruction efficiencies would be expected at typical plasma pyrolysis temperatures of 15 000 °C. However, much of the agent may not be exposed to such a high temperature in the plasma pyrolysis reactor. The plasma arc is created in an enclosed torch through which only the plasma feed gas, such as argon, nitrogen, or carbon dioxide, flows. The arc heats the gas, which ionizes, dissociates, and then flows into the side of the chamber, not through the torch (see Fig. 2). Inside the chamber, the agent mixes with the plasma. The maximum temperature to which each agent molecule is exposed is unknown, but the temperature gradient within the chamber is very large, as the typical exit temperature is around 1100 °C.

54. In the United States, plasma pyrolysis reactors have not been tested with actual munitions or chemical agents. Tests conducted by Acurex Environmental Corporation at the U.S. EPA's Air Pollution Prevention and Control Division of the National Risk Management Research Laboratory showed [65] that a PWC could destroy simulants of nerve agents, blister agents, and energetics, such as thioanisole, dimethyl methylphosphate, tributylphosphate, and dinitrotoluene (DNT), to greater than 99.9999 % destruction efficiencies. Conversion data for those simulants include:

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64. H. Martens. "Recovered old arsenical and 'mustard' munitions in Germany", in *Arsenic and Old Mustard: Chemical Problems in the Destruction of Old Arsenical and 'Mustard' Munitions,* J. F. Bunnett and M. Mikolajczyk (Eds.), NATO ASI Series, 1. Disarmament Technologies, Vol. 19, pp. 68–76, Kluwer, Dordrecht (1998).
65. Burns and Roe, *Assembled Chemical Weapons Assessment Program,* proposal submitted in response to U.S. Army solicitation No. DAAMO1-97-R-0031, 15 September 1997.

Material	Destruction efficiency
Thioanisole	>99.999992
Dimethyl methylphosphate	>99.999994
Tributyl phosphate	>99.999998
Dinitrotoluene (DNT)	>99.999996

In Europe, plasma pyrolysis plants using the PLASMOX process have been used to destroy chemical agents including lewisite at rates of some 50 kg/h as follows:

- Muttenz, Switzerland, toxic waste, 1 tonne/h, 1990
- AC-Centrum, Spiez, Switzerland, chemical agent, including lewisite, 50 kg/h, 1998
- Munster, Germany, chemical warfare materiel, 700 kg/h, 1999 (trials)
- Wurenlingen, Switzerland, radioactive material, 500 kg/h, 1999 (trials)

55. Based on the many practical applications of plasma technology in the industrial sector, it can be considered a robust technology. However, robustness for destroying chemical weapons, and especially large segments of energetic rocket propellants, remains to be demonstrated. Adaptation of plasma devices of chemical weapons will require (a) special handling equipment for the safe introduction of shells, rockets, and land mines; and (b) further development of the torch and chamber designed to ensure the destruction of the agent and the production of effluents that can be scrubbed and burned or converted to slag and sent to a landfill. Meeting these requirements will require an extended development and testing program. Scale-up from the small plasma pyrolysis reactors units in existence to the very large units proposed is likely to present significant scientific and engineering challenges.

56. Monitoring of "traditional" process variables such as temperatures, liquid and gas flow rates, etc. is accomplished by using standard, off-the-shelf, chemical process equipment and instrumentation.

Safety considerations

57. The plasma pyrolysis reactors operate at very high temperatures but at slightly negative pressure. Although the plasma temperature is in the range of 15 000 °C, the interior plasma pyrolysis reactor wall temperature is expected to be much lower (1650 °C) and the temperature of the exterior reactor surface will be lower still—about 66 °C. The plasma pyrolysis reactor discharges molten metal into ladles for cooling. Although worker interactions with high-temperature equipment/material or rotating equipment should be minimized by the controls and design features, worker hazards will probably be higher in the presence of high-temperature systems than in the presence of lower-temperature systems.

58. A substantial amount of flammable product gas, such as CO, H_2, will have to be stored, whether the product gas is burned on site or shipped off site. A large explosion or deflagaration involving this gas could cause an on-site hazard, and potentially, an off-site hazard from the direct thermal effects or overpressure forces. A greater concern is the potential damage from explosions to containment structures that could lead to a release of agent. Explosion hazards are common in industry and can be minimized by good design and operation.

59. Cooling water is circulated through the plasma torch to keep it from melting at the high plasma temperatures. A leak in the cooling system could spray water into the plasma. If the leak is sud-

den, rapid vaporization could cause a pressure pulse that might overload the downstream gas-handling equipment. Untreated agent could, under such circumstances, be released into the surrounding room through the torch opening in the top of the plasma pyrolysis reactor.

Environmental impact

60. The plasma pyrolysis plant produces a combustible gaseous product that is first scrubbed to remove any residual contaminants, held and tested prior to release for burning on site or to be sold for use as fuel. The process is designed to eliminate gaseous air emissions (other than those from the burning of the product gas) and liquid discharges. The solid waste created consists of metal ingots, which may be sold as scrap, vitrified material, and possibly scrubbber salts. The vitrified material should be suitable for land disposal as it should be nonleachable, and the scrubber salts might be recycled to the plasma pyrolysis reactor and vitrified with sand to produce a very stable solid waste, although this has not yet been specifically demonstrated. Consequently, the plasma demilitarization process has the potential to have virtually no impact on the environment.

C. Molten metal technolgy

61. Molten metal, typically iron or nickel, at 1425 to 1650 °C is used to thermally decompose chemical warfare agents to simple inorganic molecules such as carbon monoxide, hydrogen, hydrogen fluoride, hydrogen chloride, nitrogen dioxide, sulfur dioxide, and phosphorus pentoxide, which can be removed by scrubbing. The molten metal process is also known as Catalytic Extraction Processing (CEP), a trademark patented by Molten Metal Technology, Inc.

Process description

62. The molten metal process has been designated by the U.S. Environmental Protection Agency as a non-incineration technology. This distinction between incineration (or combustion) and the molten metal process is based upon different reaction mechanisms and different end-products. The molten metal process is conducted mainly in a molten metal bath at high temperature and low oxygen potential so that the products are in reduced states such as carbon monoxide and hydrogen and not, as is the case with incineration in the fully oxidized state, as carbon dioxide and water.

63. For treating chemical warfare agents, two reactors are required. Each reactor is a steel pressure vessel containing a molten metal bath and an optional slag or flux cover. These reactors are typically operated in the temperature range of 1425 to 1650 °C. The vessel is lined with refractory materials selected to provide thermal insulation and resistance to corrosion, erosion, and penetration by components of the bath. An electric induction coil, embedded within the refractory lining surrounding the metal bath, provides the energy to melt the metal charge and maintain the temperature of the bath during processing. The headspace, which is several times the height of the molten metal bath, provides physical space to allow disengagement of the off-gas from the molten metal and slag. One or more tapping ports through the vessel sidewall allow recovery of metal and slag phases with minimal interruption of the destruction operation.

64. The feed material and the co-feeds of oxygen and methane can be injected into the molten metal bath either through a lance entering the top of the bath or through one or more bottom-entering *tuyeres*. Top-entering lances have been used in numerous bench-scale reactors. A *tuyere* consists of three concentric metal tubes cast into a removable refractory block that is bolted into the bottom of the reactor. The molten metal process proposes using the *tuyere* injection of liquid agent and co-feed gases for chemical weapon demilitarization.

65. Feed material, which may be liquid, gas, finely divided entrained solids, or a pumpable slurry, is metered, mixed, and pumped through the central tube of the *tuyere* at moderately high pressure,

less than 10 atm. Oxygen, in stoichiometric proportion to convert all carbon in the feed and the methane co-feed to carbon monoxide, is metered into the next annulus at high velocity to induce turbulence, mixing with the feed stream, and formation of a jet that rapidly breaks up into small bubbles. A small amount of methane is fed through the outer annulus to cool the *tuyere.*

66. An inert gas is injected automatically into each of the feed lines as necessary to make up the difference between the total flow required in each line and the flow of each feed component (agent, oxygen, and methane). During start-up and shut-down, the inert gas alone is pumped through all feed lines to prevent molten metal from entering and plugging the *tuyere.*

Scientific principles

67. The developer of the process describes the molten metal bath as a dissociation catalyst for molecular entities in feed materials, a solvent for elemental fragments, and a medium for product synthesis. The process can be regarded conceptually as stages comprising catalytic dissociation of the feed, formation of elemental intermediates with the solvent metal, product synthesis by interaction of elemental intermediates, and partitioning of products among metal, slag, and the gas phase.

68. As the NRC AltTech study [66] pointed out, this description does not address initial thermal and gas-phase reactions in the overall sequence of events between the introduction of feeds and the release of final products. A complete description of the scientific principles requires consideration of several additional phenomena including gas-phase reactions among chemical agent, oxygen, and methane in the inlet jet; interactions of these gases and intermediate products with metal vapor inside bubbles; and boundary reactions between bubble components and the surrounding metal. The AltTech study provides a more detailed description of the probable scientific principles and of the probable processes involved.

Technology status

69. As of early 1996, more than 15 000 h of molten metal test experience had been obtained on the 10 to 15 bench-scale units, which have nominal bath sizes of 4 to 9 kg. However, this experience has been on commercial waste when a wide range of materials have been processed including polystyrene with graphite, ion-exchange resins, acetone, industrial biosolid waste, chlorotoluene with heavy organic substances, chlorobenzene, fuel oil with chlorotoluene, dimethyl acetamide with heavy organic substances, benzonitrile, diazinon, diazinon with sulfur, and surplus metal components. These materials have been in various physical forms, including liquids, slurries, fine solids, and bulk solids. Injection rates comparable with commercial levels have been demonstrated at both the demonstration-scale and advanced processing units.

70. The experience of chemical warfare agent testing has been limited to evaluation in a bench-scale unit at the Battelle/Columbus Laboratory. The AltTech panel in their review of the results of these tests concluded [67] that the molten metal process can destroy chemical warfare agent to at least 99.9999 % [known as a destruction removal efficiency (DRE) of six 9s]. The specific agent processing rates used were small:

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[66] National Research Council, Panel on Review and Evaluation of Alternative Chemical Disposal Technologies. *Review and Evaluation of Alternative Chemical Disposal Technologies,* pp. 28–33, National Academy Press, Washington, DC (1996).

[67] National Research Council, Panel on Review and Evaluation of Alternative Chemical Disposal Technologies. *Review and Evaluation of Alternative Chemical Disposal Technologies,* p. 35, National Academy Press, Washington, DC (1996).

Agent tested	Bath composition	Agent processing rate (kg agent/h/1000 kg bath metal)
HD	Ni + 2 % C	7
VX	Fe + 7 % P + 7 % S + C	8

71. The molten metal technology was not recommended in the NRC AltTech study [68] for further development and implementation at the two bulk agent storage sites at Aberdeen and Newport. Subsequently, Molten Metal Technology, Inc., filed for bankruptcy, and development of the technology for chemical demilitarization has ceased.

Safety considerations

72. Process-safety risks for the molten metal process can be divided into two categories: (1) risks related to handling agent prior to its introduction into the molten metal bath and (2) risks related to the molten bath technology.

73. The risk factors inherent in the handling of agent prior to entry into the reactors include storage risk, transportation risk, and the risk from the punch-and-drain operation. These risk factors are common to all the agent-destruction technologies reviewed in this report, but they can be exacerbated or ameliorated by aspects of a specific technology. For example, how quickly a facility using the technology can reach operational status or the rate at which the agent can be processed with that technology can alter the storage risk by changing the length of time that the agent needs to be stored. The process-safety risk factors inherent in the molten metal process include issues associated with high-temperature molten baths such as the integrity of the refractory confinement, the proximity of the molten bath to water-cooling coils (raising the possibility of steam explosions), the behavior of the *tuyeres*, and the instrumentation for monitoring the refractory confinement.

Safety issues related to off-site releases

74. The following issues need to be addressed fully and clearly in a final molten metal process design:

    Integrity of the refractory. The integrity of the refractory needs to be included in the safety documentation for a molten metal design. The company has done much work to avoid gas-jet impingement on the refractory lining of the reactor and to select refractory materials for the lining that resist gas permeation, thermal degradation, corrosion, erosion, and penetration by components of the molten metal and slag.

    Integrity of components exposed to agent. Comprehensive safety and hazard analyses are needed as part of the development process. Particularly important is further exploration of scenarios involving failures of piping or components. (Failure could be caused by thermal attack by molten material, system overpressure, subtle system interactions, or other causes.)

    Cooling off-gas piping. Scenarios involving a failure to cool the off-gas piping need to be explored, as the consequences of such scenarios were not clear.

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[68] National Research Council, Panel on Review and Evaluation of Alternative Chemical Disposal Technologies. *Review and Evaluation of Alternative Chemical Disposal Technologies,* National Academy Press, Washington, DC (1996).

Buildup of combustible gases. The design as submitted for the NRC AltTech review prevents a buildup of combustible gases in the vicinity of the system by maintaining a high ventilation rate. Assurances should be made that combustible gas build-up cannot occur and that the high ventilation rate does not compromise the design capability to contain leakage of agent.

Worker safety issues

75. There are a number of worker safety issues associated with high-temperature molten baths, high-temperature corrosives in the scrubbers, and secondary containment (concerning both inadvertent leaks and maintenance activities). These risk factors need to be addressed in the design, and realistic emergency responses need to be spelled out.

Environmental impact

Test prior to release

76. Although the molten metal process is a tightly integrated continuous process, the technology provides for synthesis gas ("gaseous residuals") to be held for analytical testing prior to combustion. The products of combustion, however, are not tested prior to release to the atmosphere. Metal, sulfur, and ceramic process residuals are solids and will be tested prior to shipment off site. Recovered hydrochloric acid will also be tested prior to off-site shipment.

Environmental burden

77. The technology is designed to minimize the environmental burden by producing metal, hydrochloric acid, and elemental sulfur as by-products that can be offered on the commercial market for reuse. The technical and economic feasibility of marketing these by-products has yet to be established. The process design also includes burning the off-gas, which is rich in hydrogen and carbon monoxide, in a gas turbine to generate electricity for in-plant use. The ceramic slag will require disposal.

D. Hydrogenolysis

Process description

78. This process uses hydrogen and steam at elevated temperatures (up to 850 °C) and nominally atmospheric pressure to transform organic wastes into simpler substances that are either less toxic or convertible to less toxic materials; these simpler substances are also easier and safer to reuse or to release to the environment. The overall process requires a high-temperature reaction vessel, where the chemical reduction occurs, followed by a gas-scrubbing train to remove inorganic by-products, and thus produces a useable process gas. This process gas is burned in an on-site steam boiler to support the operation. The process also includes provisions for removing other by-products and regenerating hydrogen gas through steam reforming.

79. Chlorinated hydrocarbons, such as polychlorinated biphenyls (PCBs), are chemically broken down and reduced to methane (CH_4) and hydrogen chloride (HCl) with carbon monoxide (CO) and carbon dioxide (CO_2) as by-products. Nonchlorinated aromatic hydrocarbons such as toluene are reduced primarily to methane, with minor amounts of other light hydrocarbons. Carbon and presumably some heavier hydrocarbons are also produced.

80. The flow-through stainless steel reactor has nozzles to accelerate the vaporization or dispersion of liquid waste material inputs, which are injected directly into the reactor mix of hot gases consisting of hydrogen (H_2), water vapor (H_2O), carbon monoxide (CO), and carbon dioxide (CO_2). Within the reactor, radiant-tube heaters heat the mixture to 850 °C. The residence time in the reactor is 2 to 6 s, although reactions are expected to occur in less than 1 s.

81. The gases exiting the reactor are scrubbed to remove by-products. Water is used as a quench to decrease the gas temperature and absorb water-soluble products, including hydrogen chloride (HCl). These and other acidic products are further scrubbed by caustic scrubbers. A heavy-oil scrubber can be used in the scrubber train to remove some hydrocarbons. A standard monoethanolamine (MEA) scrubbing system removes most of the hydrogen sulfide (H_2S) (produced from sulfur-containing feeds) and carbon dioxide (CO_2) from the gas train. The separated hydrogen sulfide (H_2S) requires further treatment to convert it to elemental sulfur and water.

82. Hydrogenolysis has been under development since 1986 and has progressed from bench-scale testing through to commercial-scale operation. A number of organic feed materials, particularly chlorinated wastes, have been tested at bench scale. Several kinds of feed materials are currently being treated at commercial scale (tonnes per day), including pesticides, chlorinated hydrocarbons, and PCBs. Two full-scale plants have been operating for more than three years in Kwinana in Western Australia, and one plant was operated for a year (1996) at a General Motors of Canada facility in St. Catherine's, Ontario.

Scientific principles

83. The chemistry by which hydrogenolysis destroys organic feed material is much more complex than a simple high-temperature reduction with hydrogen of organic compounds to produce methane. The complexity results from the reduction with hydrogen being accompanied by reactions of carbonaceous intermediates, including elemental carbon, with steam to yield the final products. Although the thermodynamic principles of reducing organic substances with hydrogen to carbon and the resulting reactions of carbon with steam (carbon-steam chemistry) have been thoroughly studied and are well understood, the interplay of kinetics and thermodynamics in the hydrogenolysis reactor are less well known.

84. The chemical agents mustard, GB, and VX contain a high proportion of heteroatoms (atoms other than carbon, hydrogen, or oxygen, such as chlorine, phosphorus, sulfur, or nitrogen). The reaction products containing these heteroatoms will generate a large volume of inorganic process residuals. For example, mustard is by weight 45 % chlorine, 20 % sulfur, and 30 % carbon; VX is by weight 12 % phosphorus, 5 % nitrogen, 12 % sulfur, and 49 % carbon with the balance being made up of hydrogen and oxygen. This heteroatom content raises two uncertainties. First, what are the final heteroatom products from the reactor? Second, how are they to be scrubbed or otherwise removed? The acid gases and other inorganic products need to first be scrubbed from the reactor effluent gas and then converted to a form suitable for disposal or recycling in commerce. The reaction products or organic compounds containing heteroatoms are even more difficult to predict without the same kind of detailed experimental work that has been carried out on the feed materials currently treated successfully at the commercial facilities.

85. There is considerable operational experience treating a number of highly halogenated wastes such as PCBs, hexachlorobenzene, and 2,2-bis(4-chlorophenyl) 1,1,1-trichloroethane (DDT), which has shown empirically that a fine balance of hydrogen and steam is necessary to avoid generating substantial amounts of carbon and polyaromatics in the reactor. Empirical models have been developed to predict operating parameters that yield optimal product composition: primarily methane, with CO and CO_2.

86. For simple hydrocarbons, hydrogenolysis is a high-temperature reduction by hydrogen to produce methane. Simple thermodynamic calculations reveal, however, that considerable amounts of carbon would be expected from the initial reaction with hydrogen. Consequently, this carbon will react subsequently with H_2O to generate CO, CO_2, and, ideally, more hydrogen. Some high-molecular-weight carbon residue is also generated. This postulated reaction process is supported

by the results obtained. Steam is added to the hot feed gas to react with the carbon to form CO_2 and CO; the H_2 content of the reactant gas is maintained above 55 %, as this is a level at which experience indicates the major product will be methane.

87. Feed materials that contain heteroatoms will yield products that contain these elements in products such as acid gases [e.g., hydrogen chloride (HCl)] and reduced inorganic substances [e.g., hydrogen sulfide (H_2S)]. Chlorinated wastes yield HCl as a primary product. The clean formation of HCl under the reaction conditions can be understood in terms of simple thermodynamics, given that chlorine will probably not produce many other products under the reaction conditions.

Technology status

88. Hydrogenolysis has been used to treat organic wastes, including PCBs, other chlorocarbons, and hydrocarbons such as toluene. A significant amount of work has been conducted at laboratory, pilot, and commercial scales.

89. Pilot-scale work has been performed since 1991 at several sites in the United States and Canada. A laboratory-scale system is available for waste treatability studies and this system has been used for preliminary tests on agent surrogates, such as the organophosphorus pesticide malathion. Pilot-scale demonstrations have been performed on several materials, including polyaromatic hydrocarbons at Hamilton Harbor, Ontario, in 1991 and PCBs (PCB-contaminated soil) at Bay City, Michigan, in 1992.

90. Commercial units are currently being operated in Australia and have been operated in Canada, and others are being constructed. Hydrogenolysis is being used to treat a mixture of DDT and toluene on a commercial scale in Australia. Another system at St. Catherines, Ontario, processed PCBs both as a concentrated material and in PCB-contaminated concrete, for General Motors. For treating these feedstocks, the status of the technology is advanced, since there are commercial facilities in operation.

91. Full operational manuals, hazard and operability studies, process and instrument diagrams, and risk analyses have been developed and documented for processing DDT-toluene mixtures and PCBs.

92. The experience with organic wastes forms a basis for applying the technology to agent destruction, but further development that is specific to the chemical agents to be treated is still required. For instance, all hydrogenolysis operations to date have been carried out in the open air. Agent-destruction facilities, however, will require containment of all unit processes where agent may be present. Consequently, this need to contain hydrogen gas within a building can be hazardous. Hazardous-operation procedures for handling these conflicting safety demands need to be addressed.

93. In summary, the main uncertainty in applying this process to agent destruction centers on identifying and managing the inorganic by-products derived from the sulfur, phosphorus, and nitrogen in the agents. The primary inorganic products from the reactor need to be identified and processes developed to remove and manage them downstream.

94. The systems currently used should work well for mustard destruction after modification of the scrubber train to handle the large product load of H_2S. The status of the technology for mustard treatment is **near commercial** except for: (1) the lack of demonstrated handling of large volumes of hydrogen sulfide (H_2S), (2) the overall process demonstration on mustard itself (small-scale tests to show the process can destroy agent have been successful), and (3) the resolution of secondary containment and safety issues specific to processing chemical warfare agents and containment of hydrogen gas.

95. Because much less is known on both a fundamental and practical level about the identity and handling of phosphorus-containing residuals from hydrogenolysis, the technology for VX destruction is less mature than it is for mustard. The technology developer has little experience with phosphorus-containing materials, even at bench scale.

Safety considerations

96. The risk factors for process safety can be divided into two categories: factors related to handling agent prior to its introduction into the specific technology and factors related to the agent-destruction technology and associated system elements. The process-safety risk factors related to the handling of agent prior to entry into this technology, which are common to all the agent-destruction technologies, include storage risk, transportation risk, and the risk from the punch-and-drain operation. These factors can be exacerbated or ameliorated by unique aspects of a technology.

97. The process-safety risk factors inherent in hydrogenolysis include safety issues associated with high-temperature hydrogen, hot water and corrosives in the scrubbers, and secondary containment. Many of the risk factors that are not specific to chemical agent have been addressed in safety analyses and in hazard and operability reports.

98. No failure scenarios involving a loss of electrical power, loss of cooling, failures of pumps and valves, inadvertent overpressurization, or inadvertent temperature transients were identified in the NRC AltTech report [69] that would lead to off-site releases of agent or toxic process products. The most significant off-site risk appeared to be associated with handling agent prior to the agent-destruction process. The principal risk factors appeared to involve mishaps in the punch-and-drain operation or damage from airplane crashes or other external events to holding tanks where agent is stored before being fed to the main reactor.

99. The following subsections on process safety address risk factors specific to hydrogenolysis technology.

Hydrogen and other combustible gases

100. The process uses hydrogen. In addition to the hydrogen circulating in the process gas stream, most of which is produced in the steam reformer from methane produced in the main reactor, compressed hydrogen is stored in tube trailers and in the product gas tank. Other combustible gases (carbon monoxide, propane) are also present and need to be considered.

101. Hydrogen is commonly used in industry and can be used safely. Recent industrial accidents involving hydrogen are rare because of the care taken to handle it properly. However, because of the potential for a hydrogen explosion or fire to cause grave damage to personnel and structures if the hydrogen is not managed properly, it has to be considered. Also, a hydrogen explosion could lead to a release of chemical agent. Although leaks of flammable gases are a risk factor for worker safety, they are not currently an off-site risk factor in either of the two current commercial operations.

102. When a hydrogenolysis system is housed in secondary containment (as is required for agent-destruction facilities), the potential increases for build-up of an explosive concentration of hydrogen. The potential also increases for damage to agent-bearing structures from an explosion or fire. The containment of the system for an agent-destruction facility will need to be designed so that the hydrogen will neither stratify nor build up locally to a combustible concentration.

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[69] National Research Council, Panel on Review and Evaluation of Alternative Chemical Disposal Technologies. *Review and Evaluation of Alternative Chemical Disposal Technologies,* National Academy Press, Washington, DC (1996).

103. A large detonation or burn near the containers that store the agent could damage containment structures and cause a release of agent. This risk factor needs to be considered when designing component locations and shielding. The hydrogen tube trailer, product gas tank, or any other combustible storage area should be located a safe distance away from the agent-containing components (holding tank, reactor).

Gas-phase chemical reduction

104. Another risk factor that needs to be considered is from combustible mixtures of air and hydrogen inside the circulating-gas system, which could result from air leaking into the system combined with flow imbalances. The current industrial systems have design features and controls in place that appropriately address this risk.

Environmental impact

Test prior to release

105. The process gas stream that goes to the steam boiler for combustion is held in tanks and tested prior to combustion, although the products of combustion are not tested prior to release through the stack. Solid and liquid residuals are tested prior to release.

Environmental burden

106. Aside from the uncertainties about phosphorus, all the inorganic substances derived from the heteroatoms present in the agent are ultimately converted to common salts, salt solutions, or elemental sulfur. These will require proper landfill disposal. The steam boiler, which burns a mixture of process gas and propane, discharges combustion products through a stack to the atmosphere. The issues typically raised about trace products of inorganic combustion and the release of combustion products to the environment need to be addressed if this technology approach is to be implemented.

E. Destruction of arsenicals

Although chemical weapon agents containing arsenic can be destroyed by both high-temperature and low-temperature destruction technologies, the destruction of arsenicals is addressed in this report under high-temperature destruction technologies as this approach is continuing to be used in Germany.

Introduction

107. A number of chemical warfare agents based on organic compounds containing arsenic were developed during World War I and were stockpiled both then, during the interwar years and in World War II. Initially, some organoarsenic compounds could penetrate the filters in early gas masks, which were designed to absorb chlorine and phosgene, and because the organoarsenic agents (Clark agents) were vomiting agents they caused the wearers to remove the masks. Another advantage was that the addition of organic arsenical compounds to mustard reduced the freezing point of mustard from 14 °C, making the mustard/arsenical agent easier to use under cold weather conditions. Mustard-lewisite mixtures had freezing points ranging from –24 to –42 °C

depending on the ratio of the mixture. The most important agents containing arsenic are shown in the table below [70]:

Agent	Chemical name	Symbol	Agent type
Lewisite	2-chlorovinyldichloroarsine	L	Vesicant and systemic poison
Mustard/lewisite	Mixture of mustard and lewisite	HL	Vesicant
Phenyldichloroarsine	Phenyldichloroarsine	PD	Vomiting and vesicant properties
Ethyldichloroarsine	Ethyldichloroarsine	ED	Vomiting and vesicant properties
Methyldichloroarsine	Methyldichloroarsine	MD	Vomiting and vesicant properties
Diphenylchloroarsine	Diphenylchloroarsine	DA, Clark I	Vomiting agent
Adamsite	10-chloro-5,10-dihydrophenarsine	DM	Vomiting agent
Diphenylcyanoarsine	Diphenylcyanoarsine	DC, Clark II	Vomiting agent

In addition, a number of mixtures containing arsenic compounds, such as arsenic trichloride, were also produced and deployed in World War I munitions.

108. Arsenic-containing chemical weapon agents were produced and stockpiled by a number of countries during the period 1930–1945 [71]:

Country	Lewisite L	Diphenyl chloroarsine DA	Diphenyl cyanooarsine DC	Adamsite DM
France	Yes		Yes	
Germany		Yes		Yes
Italy	Yes	Yes		Yes
Japan	Yes	Yes	Yes	
UK	Yes	Yes	Yes	Yes
USA	Yes		Yes	
USSR	Yes		Yes	

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70. Developed from Table 2.1 in K. Lohs and T. Stock, "Characteristics of chemical warfare agents and toxic armament wastes", in *The Challenge of Old Chemical Munitions and Toxic Armament Wastes*, T. Stock and K. Lohs (Eds.), SIPRI Chemical and Biological Warfare Studies, No. 16, Oxford University Press (1997) and from Table 2 in R. G. Manley, "The problem of old chemical weapons which contain "mustard gas" or organoarsenic compounds: An overview", in *Arsenic and Old Mustard: Chemical Problems in the Destruction of Old Arsenical and 'Mustard' Munitions,* J. F. Bunnett and M. Mikolajczyk (Eds.), NATO ASI Series, 1. Disarmament Technologies, Vol. 19, Kluwer, Dordrecht (1998).
71. Based on Table 4 in R. G. Manley, "The problem of old chemical weapons which contain "mustard gas" or organoarsenic compounds: An overview", in *Arsenic and Old Mustard: Chemical Problems in the Destruction of Old Arsenical and 'Mustard' Munitions,* J. F. Bunnett and M. Mikolajczyk (Eds.), NATO ASI Series, 1. Disarmament Technologies, Vol. 19, Kluwer, Dordrecht (1998).

Today, the proportion of the U.S. stockpile of chemical weapons and agents that contain arsenical agents is limited to 10 one-ton containers of lewisite at Tooele Army Depot corresponding to around 0.03 % of the total U.S. stockpile. Russia has the world's largest stockpile of lewisite with about 7000 tonnes of lewisite in both containers and filled into weapons [72]. It is also known that Japan produced quantities of lewisite and DC (Clark II) [73] during World War II. In Europe, old chemical weapons containing any of the arsenical agents are found from time to time.

Scientific principles

109. Insofar as the arsenicals that were produced and stockpiled during the period 1930 to 1945 are concerned, their behavior in water provides some insight into ways in which they may be destroyed [74]. The hydrolysis of diphenylchloroarsine (DA, Clark I) produces diphenylarsenious acid and hydrochloric acid, while diphenylcyanoarsine (DC, Clark II) produces diphenylarsinous oxide and hydrocyanic acid. Both diphenylarsenious acid and hydrocyanic acid are toxic but quickly detoxify in water. The organoarsenic compounds may later decompose to toxic inorganic arsenic compounds. Adamsite (DM) hydrolyses very slowly in water and is almost insoluble. Its reaction products are diphenylarsinous acid and hydrochloric acid. It can, however, be hydrolyzed by phosphorous acid yielding arsenic, diphenylamine, hydrochloric acid, and phosphates. It is also hydrolyzed by concentrated hydrochloric acid yielding arsenic trichloride and diphenylamine hydrochloride [75]. Lewisite is only slightly soluble, but when it dissolves it hydrolyzes rapidly into 2-chlorvinylarsine oxide. The real problem that has to be faced in addressing the destruction of arsenicals is that the products of destruction will themselves still contain arsenic in some form or another and thus still be toxic. The technology status is considered first for lewisite and then for Adamsite.

Technology status—lewisite

110. Most attention has been given to the destruction of lewisite, as this is the arsenical that has been most widely stockpiled and still has to be destroyed today. Various alternative

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72. S. V. Petrov, V. I. Kholstov, V. P. Zoubrilin, N. V. Zavialova. "Practical actions of Russia on preparations for destruction of stockpiled Lewisite and 'mustard'", in *Arsenic and Old Mustard: Chemical Problems in the Destruction of Old Arsenical and 'Mustard' Munitions,* J. F. Bunnett and M. Mikolajczyk (Eds.), NATO ASI Series, 1. Disarmament Technologies, Vol. 19, Kluwer, Dordrecht (1998).
73. R. G. Manley. "The problem of old chemical weapons which contain "mustard gas" or organoarsenic compounds: An overview", in *Arsenic and Old Mustard: Chemical Problems in the Destruction of Old Arsenical and 'Mustard' Munitions,* J. F. Bunnett and M. Mikolajczyk (Eds.), NATO ASI Series, 1. Disarmament Technologies, Vol. 19, p. 8, Kluwer, Dordrecht (1998). See also information available at http://www.tcp-ip.or.jp/~e-ogawa/BRIEFING.HTM#faq9
74. K. Lohs and T. Stock. "Characteristics of chemical warfare agents and toxic armament wastes", in *The Challenge of Old Chemical Munitions and Toxic Armament Wastes*, T. Stock and K. Lohs (Eds.), SIPRI Chemical and Biological Warfare Studies, No. 16, p. 47, Oxford University Press (1997).
75. Z. Wertejuk, M. Koch, W. Marciniak. *Recovered Old Arsenical and 'Mustard' munitions in Poland,* in *Arsenic and Old Mustard: Chemical Problems in the Destruction of Old Arsenical and 'Mustard' Munitions,* J. F. Bunnett and M. Mikolajczyk (Eds.), NATO ASI Series, 1. Disarmament Technologies, Vol. 19, Kluwer, Dordrecht (1998).

approaches for the destruction of lewisite in the Russian stockpile have been identified [76]. These include:

a. Treatment with sulfur at temperatures of 160–180 °C using a lewisite/sulfur mass ratio of 1/3 with a reaction time of 30–40 min producing a tough polymeric mass which can be buried in special burial grounds. The main disadvantage is the mass of polymeric material produced and the need to bury it away from underground aquifers.

b. Reaction with ethyleneglycol monomethacrylate ester and its subsequent polymerization at 60–90 °C. However, as with the sulfur treatment, the main disadvantage relates to the burial and prevention of aquifer contamination.

c. Chlorination with gaseous chlorine at 110–130 °C produces arsenic trichloride and a mixture of chlorinated hydrocarbons. The main shortcomings are that the conversion of lewisite is not complete and the chlorinated hydrocarbons are toxic.

d. Alkaline hydrolysis for 1 h at 103–110 °C using aqueous alkali can achieve full decomposition of the lewisite. Subsequent electrolysis yields metallic arsenic.

e. Alcoholysis using alcoholic solutions of sodium alkoxides at 50–80 °C for 2–3 h produces acetylene, sodium chloride, and a trialkyl arsenite. However, the treatment is regarded as being unsuitable, as the trialkyl arsenite is toxic and flammable.

f. High-temperature oxidation in which lewisite is completely oxidized in the flame of a gas burner at over 600 °C. Although the method is regarded as being reliable for destruction of lewisite and it is possible to recover and store the arsenic oxide, it is suggested that the burning of lewisite can produce toxic chemicals such as dioxins [77].

g. Hydrogenolysis in which lewisite is destroyed at 800–1000 °C by treatment with hydrogen diluted with nitrogen. The disadvantage is the presence of toxic agents at high temperatures together with hydrogen and hydrogen chloride. There is also the possibility that toxic arsine, AsH_3, may be produced.

h. Ammonia reduction at 1000–1100 °C producing elemental arsenic. The disadvatage is the high temperature and the large quantity of ammonia.

The approach reported in the late 1990s as having been selected as the preferred technology in Russia for the destruction of lewisite is that of alkaline hydrolysis by hot sodium hydroxide followed by subsequent electrolysis.

$$ClCH{=}CHAsCl_2 + 6NaOH = Na_3AsO_3 + C_2H_2 + 3NaCl + 3H_2O$$

$$Na_3AsO_3 + 3H^+ + 3\,e^- = As + 3NaOH$$

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76. S. V. Petrov, V. I. Kholstov, V. P. Zoubrilin, N. V. Zavialova. “Practical actions of Russia on preparations for destruction of stockpiled Lewisite and ‘mustard’”, in *Arsenic and Old Mustard: Chemical Problems in the Destruction of Old Arsenical and ‘Mustard’ Munitions,* J. F. Bunnett and M. Mikolajczyk (Eds.), NATO ASI Series, 1. Disarmament Technologies, Vol. 19, p. 79, Kluwer, Dordrecht (1998).
77. S. V. Petrov, V. I. Kholstov, V. P. Zoubrilin, N. V. Zavialova. “Practical actions of Russia on preparations for destruction of stockpiled Lewisite and ‘mustard’”, in *Arsenic and Old Mustard: Chemical Problems in the Destruction of Old Arsenical and ‘Mustard’ Munitions,* J. F. Bunnett and M. Mikolajczyk (Eds.), NATO ASI Series, 1. Disarmament Technologies, Vol. 19, p. 79, Kluwer, Dordrecht (1998).

111. Canada in the early 1990s carried out the destruction of 1.5 tonnes of lewisite [78]. A three-step neutralization process was used [79]:

a. Oxidation of lewisite to 2-chlorovinylarsonic acid by addition of lewisite to aqueous caustic hydrogen peroxide under controlled pH conditions:

$ClCH{=}CHAsCl_2 + H_2O_2 + 2\ NaOH = ClCH{=}CHAsO_3H_2 + 2NaCl + H_2O$

b. Removal of excess hydrogen peroxide by circulating through a catalyst bed containing manganese dioxide, thereby causing decomposition to water and oxygen

$2H_2O_2 = 2H_2O + O_2$

c. Conversion of the 2-chlorovinylarsonic acid to sodium arsenate and sodium chloride and free acetylene by the addition of sodium hydroxide. This step was carried out under nitrogen while bleeding off the acetylene to atmosphere.

$ClCH{=}CHAsO_3H_2 + 2HCl + 6NaOH = Na_3AsO_4 + C_2H_2 + 3NaCl + 5H_2O$

This stage is important to ensure that no hydrogen peroxide remains in the third stage when acetylene is produced.

After analysis to verify the efficiency of lewisite destruction, batches of the arsenic salt solution were mixed with sodium silicate and cement to produce a concrete stabilized final product, which was cured in 210 L polyethylene barrels which then went to a landfill site. The United States in the late 1990s is examining this process for the destruction of its 13 ton (11.8 tonne) stockpile of lewisite held at Tooele.

Technology status—mixtures containing arsenic compounds

112. In Germany, an incineration plant at Munster has been used to destroy several arsenicals including Clark agent and mustard-containing various arsenical compounds [80]. Prior to incineration, the chemicals to be destroyed are analyzed for the presence of arsenicals and batches for destruction are made up on the basis of this analysis. In the Munster incineration process, agent is first evaporated and subjected to partial pyrolysis at 300 °C for up to 12 h. The vaporized agent is then passed through the main combustion chamber at temperatures of 1000 to 1200 °C with a residence time of 2 s. The product gas is then cooled rapidly to 80 °C by the injection of cooling water and then passed through two scrubbing towers washed with aqueous sodium hydroxide to neutralize the sulfur dioxide and hydrogen chloride as well as arsenic oxide (As_2O_3). The flue gas passes through an aerosol separator, which removes any remaining liquid or solid particles such as arsenic oxide (As_2O_3) before it is discharged through the stack. If the material to be destroyed contains arsenic, then the wastewater has to be subjected to supplementary treatment, as the incineration of the organic arsenic compounds produces arsenic trioxide which is then scrubbed into

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78. R. G. Sutherland. "The destruction of old and obsolete chemical weapons: Past experience", in *The Challenge of Old Chemical Munitions and Toxic Armament Wastes*, T. Stock and K. Lohs (Eds.), SIPRI Chemical and Biological Warfare Studies, No. 16, p. 150, Oxford University Press (1997).
79. J. M. McAndless, V. Fedor, T. Kinderwater. *Destruction and Waste Treatment Methods used in a Chemical Agent Disposal Project,* DRES Suffield Memorandum No. 1392, October 1992.
80. Hermann Martens. "The German programme for the disposal of old chemical weapons", in *The Challenge of Old Chemical Munitions and Toxic Armament Wastes*, T. Stock and K. Lohs (Eds.), SIPRI Chemical and Biological Warfare Studies, No. 16, pp. 171–175, Oxford University Press (1997).

the aqueous sodium hydroxide as trivalent arsenite. Conversion of these compounds into insoluble arsenic compounds requires oxidation using potassium permanganate or hydrogen peroxide in order to produce pentavalent arsenates. When ferric chloride is added, precipitation of insoluble iron arsenate occurs. The resulting sludge material is dehydrated in a filter press and then filled into drums for final deposit in an underground waste dump. The waste air and wastewater data for the Munster facility in 1993 were approximately 0.2 mg/m^3 for arsenic in the waste air emission compared to the allowable level of 1.0 mg/m^3 and adjusted to less than the limit of 1 mg/L in wastewater.

113. A second incineration plant was recently constructed at Munster to address the disposal of viscous or solid chemical agents and, in particular, arsenicals as well as for the clean up of arsenically contaminated soil [81]. The process involves a soil-washing and flotation plant to separate contaminants from the soil. These contaminants and any arsenical chemical agents are then destroyed by thermal destruction and vitrification using high-temperature plasma technology, which is described in the section above on plasma pyrolysis (Section VI.B). This high-temperature plasma technology (PLASMOX process) is used to heat the organic chemical feed material to temperatures of 1400 to 1600 °C in a plasma high-temperature reactor which is a cylindrical chamber with a centrifuge at the bottom into which is introduced the feed material. The plasma torches cause the rotating organic chemical feed material to pyrolyze. After 4 h, the centrifuge is stopped and the melted material is discharged into a slag cart. Heavy metals such as arsenic remain in the slag, which is similar to glass where they are evenly distributed and firmly bound. The EPA standard leach test in which the slag is treated in a slightly acidic environment to simulate the effect over time of acid rain on the dumped material resulted in the various elements in the slag being released in only extremely small quantities into the leach test eluate. As an inert substance, this material can be used as a filling material in civil engineering and is not required to go to a hazardous waste dumping site. In Germany, two important aspects have to be taken into account in regard to the possible disposal of slag: (a) leachability and (b) the amount of toxic material per kg of slag. Slag with an arsenic content of more than 2 % would have to be set aside for underground storage.

114. As already noted in section VI.B on plasma pyrolysis, the PLASMOX process has been used in Europe to treat toxic waste, radioactive materials, and chemical agent as follows:

    - Muttenz, Switzerland, toxic waste, 1 tonne/h, 1990
    - AC-Centrum, Spiez, Switzerland, chemical agent, including lewisite, 50kg/h, 1998
    - Munster, Germany, chemical warfare materiel, 700kg/h, 1999 (trials)
    - Wurenlingen, Switzerland, radioactive material, 500kg/h, 1999 (trials)

Technology status—Adamsite

115. Adamsite can be reduced [82] using phosphorous acid, according to the following equation:

$$2C_6H_4{\cdot}NH{\cdot}AsCl{\cdot}C_6H_4 + 3H_3PO_3 \rightarrow 2Ph_2NH_2Cl + 2As + 3HPO_3$$

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81. Hermann Martens. "Recovered old arsenical and 'mustard' munitions in Germany", in *Arsenic and Old Mustard: Chemical Problems in the Destruction of Old Arsenical and 'Mustard' Munitions,* J. F. Bunnett and M, Mikolajczyk (Eds.), NATO ASI Series, 1. Disarmament Technologies, Vol. 19, pp. 68–76, Kluwer, Dordrecht (1998).

82. S. Neffe. "Polish Experience in Safe Disposal of Arsenic Containing Chemical Warfare Agents", in *Proceedings of the International CW Destruction Symposium,* V. Starrock and A. Krippendorf (Eds.), Munster, Germany, 22–25 March 1998.

In this reaction, the actual reducing agent is phosphine (PH_3), which is formed through the disproportionation of phosphorous acid:

$$4H_3PO_3 \rightarrow PH_3 + 3H_3PO_4$$

$$2H_3PO_4 \rightarrow H_2O + H_4P_2O_7$$

116. The reagents for the destruction of Adamsite are phosphorous and phosphoric acid, sodium hydroxide, sodium hypochlorite, and water. The process is irreversible and produces high-purity, dispersed metallic arsenic, diphenylamine (DPA), hydrochloric acid, and phosphates. The speed of the reduction reaction can be increased by increasing the temperature of reacting mixture.

117. This technology has been recently used in Poland by Chemical Rescue, Ltd. and has been found to be very effective, safe for workers and environment. The reaction was carried out using batches of about 150 kg of Adamsite in 3 h, under atmospheric pressure and at the temperature in the vicinity of 180 °C. Using this method, about 9300 kg of Adamsite have been successfully destroyed. The reaction products have been separated and reused or neutralized. The resulting metallic arsenic has been separated by filtration and the wastewater has been treated by biodegradation in which the organic substances (diphenylamine) and inorganic compounds (H_3PO_4) formed during the Adamsite reduction provide nutrition to the microorganisms in the biotreatment process. The biotreatment process oxidizes the diphenylamine and any other organic matter to produce CO_2, nitrogen, and water. Gaseous hydrogen chloride, and other possible volatile acidic side-products, are absorbed in solution of sodium hydroxide and sodium hypochlorite. The metallic arsenic was obtained in the form of powder, and has been disposed of by vitrification. Only a small amount of solid hazardous wastes (organic pitch containing some metallic As) needs to be stored or disposed of.

Safety considerations

118. The safety considerations are the same as those identified for in section VI.B on plasma pyrolysis. Plasma torches operate at very high temperatures but at slightly negative pressure. Although the plasma temperature is in the range of 15 000 °C, the interior plasma reactor temperature is expected to be much lower (1400–1600 °C), and the temperature of the exterior PWC surface will be lower still—about 66 °C. The PWC discharges molten slag for cooling. Although worker interactions with high-temperature equipment/material or rotating equipment should be minimized by the controls and design features, worker hazards will probably be higher in the presence of high-temperature systems than in the presence of lower-temperature systems.

119. Cooling water is circulated through the plasma torch to keep it from melting at the high plasma temperatures. A leak in the cooling system could inject water into the plasma. If the leak is sudden, rapid vaporization could cause a pressure pulse that might overload the downstream gas-handling equipment. Untreated agent could, under such circumstances, be released into the surrounding room through the torch opening in the top of the plasma torch. Similar conditions relate to the water-cooling systems of the rotating cylinder and the wall of the plasma chamber.

Environmental impact

120. The major concern is to reduce the level of arsenic compounds in the gaseous and liquid waste streams to levels that do not present a risk to public health or the environment, and to ensure that solids going to landfills will not leach arsenic compounds in quantities that would have a negative impact on groundwater.

VII. LOW-TEMPERATURE DESTRUCTION OF CHEMICAL AGENTS

A. Hydrolysis of mustard agent HD

Process description

1. Neutralization [83] employs process conditions that are specific for each type of agent. Thus, a neutralization process for destroying a specific agent or class of agents would not be suitable for treating a wide range of other wastes (e.g., commercial hazardous wastes). There may need to be variations in the process when treating different types of the same agent such as H, HD, and HT. A particular benefit from neutralization is that it detoxifies mustard agent rapidly at low temperature and low pressure. Batch or semibatch processing allows retention of the products from neutralization until testing can verify destruction of the chemical agent.

2. The U.S. Army, along with several other countries [84], has evaluated many different approaches [85] to the neutralization of HD. Intensive testing using HD during 1994 and 1995 led the United States to choose direct hydrolysis with hot water followed by biodegradation of the hydrolysis product as the best candidate for scale-up to a pilot plant demonstration. The U.S. Army focused its testing on HD because the technology is being considered for use at a storage site that only has HD.

3. Although neutralization of HD detoxifies the agent, the resulting hydrolysate needs further treatment prior to final disposal. Treatment of the hydrolysate has to destroy both thiodiglycol, which is the major residual in the hydrolysate, and any chlorinated volatile organic compounds (VOCs), which result from impurities in the HD. Management of hydrolysate from HD neutralization may be either on site, through additional treatment following the neutralization process, or off site, by shipping the hydrolysate to a permitted waste-management facility.

4. On-site treatment of the hydrolysate requires substantially more complex processing than does the neutralization process alone. The primary process considered for on-site treatment of hydrolysate is biodegradation. Aqueous effluent from an on-site biodegradation process potentially could be discharged to the existing publicly or federally owned treatment works or alternatively the water recycled if zero liquid effluent discharge is desired.

5. Various neutralization process configurations are possible, depending on the options selected [86]. Figure 3 shows the configuration involving on-site biodegradation and water recycling that is being considered for the Aberdeen Chemical Disposal Facility [87].

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[83] In the context of this report, *neutralization* refers to reaction of agents with water, which may be catalyzed by acidic or basic conditions, and with reagents such as alkoxides and amines, often called nucleophiles, which convert the agents into other substances generally of much lower toxicity. *Hydrolysate* refers to the effluent from a neutralization process.

[84] See several articles in T. Stock and K. Lohs (Eds.), *The Challenge of Old Chemical Weapons and Toxic Armament Wastes,* Stockholm International Peace Research Institute, Oxford University Press (1997).

[85] National Research Council, Committee on Alternative Chemical Demilitarization Technologies. *Alternative Technologies for the Destruction of Chemical Agents and Munitions,* National Academy Press, Washington, DC (1993).

[86] National Research Council, Panel on Review and Evaluation of Alternative Chemical Disposal Technologies. *Review and Evaluation of Alternative Chemical Disposal Technologies,* National Academy Press, Washington, DC (1996).

[87] National Research Council, Committee on Review and Evaluation of the Army Chemical Stockpile Disposal Program. *Integrated Design of Alternative Technologies for Bulk-Only Chemical Agent Disposal Facilities,* National Academy Press, Washington, DC (2000).

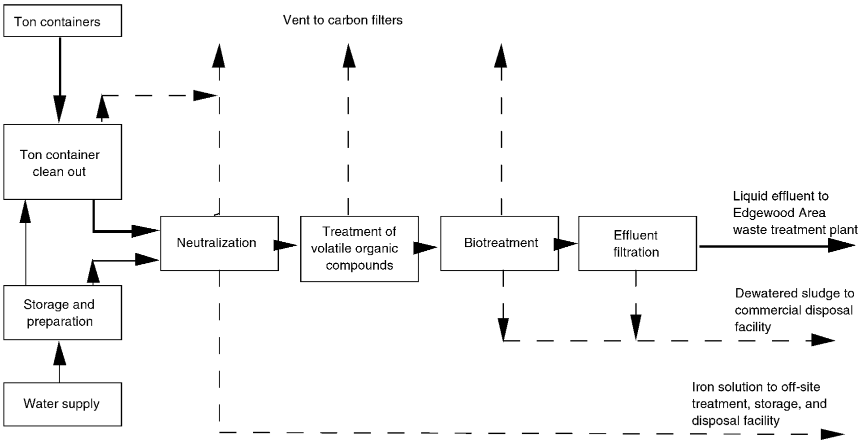

Fig. 3 Configuration for mustard hydrolysis and on-site biotreatment for Aberdeen Chemical Disposal Facility.

Scientific principles

6. The neutralization process for the disposal of HD is, in principle, a simple hydrolysis, that is, a reaction with water to form thiodiglycol [bis(2-hydroxyethyl)sulfide] and hydrochloric acid:

$$S(CH_2CH_2Cl)_2 + 2H_2O = S(CH_2CH_2OH)_2 + 2HCl$$

Even though HD is only slightly soluble in water, the C–Cl bonds, which are associated with mustard's toxicity, react readily in hot water to produce the relatively innocuous thiodiglycol. Pure agent reacts with neutral or acidic water predominantly as shown in the equation above, although the detailed reaction mechanism is more complex. The reaction is carried out in hot water, with the final hydrolysate being a dilute aqueous solution (e.g., less than 10 wt % hydrolyzed agent) to minimize the production of unwanted by-products such as sulfonium ions (R_3S^+ where R is an organic constituent). The hydrolysis reactions are exothermic, releasing about 15 kilocalories per mole of HD in the neutral-to-acidic hydrolysis. Under alkaline conditions, much the same chemistry occurs, but it is accompanied by side-reactions that give rise to many minor products, some of which are undesirable. Consequently, sodium hydroxide is not added until after the initial reaction, when it is used to neutralize the hydrochloric acid present in the hydrolysate from the reaction of mustard with water and to react with any remaining sulfonium ions. As implied by the equation, the hydrolysis is, in principle, reversible although at high dilution, the equilibrium lies on the side of the hydrolysis products. However, the reformation of mustard agent is prevented by adding sodium hydroxide to make the hydrolysate alkaline.

7. Munitions-grade mustard agent contains several impurities that are formed during manufacture. Several significant impurities—dithiane (1,4-dithiacyclohexane) and chlorinated ethanes—do not react extensively with water under standard hydrolysis conditions, and they remain in the hydrolysate. While the chemistry of the hydrolysis of the distilled mustard (HD) and its impurities in storage in bulk containers at Aberdeen, Maryland has been extensively studied and is well known, this is not the case for other munitions grade mustard (H or HT).

Technology status

Hydrolysis of HD

8. Alkaline hydrolysis has been used extensively to detoxify mustard agents. Munitions-grade mustard agents have been hydrolyzed with methanolic NaOH on a pilot scale in Poland [88]. This procedure was effective for liquid agent and for solids that remained in the storage containers. The methanol solutions of hydrolyzed agent were incinerated. In Canada in the mid-1970s, mustard agent was hydrolyzed on a production scale (8-tonne batches) with hot lime water prior to incineration [89]. Recent laboratory evaluations of the alkaline hydrolysis of HD by the U.S. Army have not shown any particular advantages in using lime instead of the more soluble sodium hydroxide. Lime was probably used in the Canadian hydrolysis process to avoid high concentrations of sodium in the hydrolysate during subsequent incineration, because sodium attacks common refractories.

9. Simple hydrolysis of mustard with hot water is not as extensively documented as alkaline hydrolysis, but it has apparently been used in France and is the basis for the long-used method of steam cleaning and decontaminating storage containers. Although undisturbed mustard can co-exist with still cold water for long periods because the solubility of mustard in cold water is so low, hydrolysis in stirred water at 90 °C is reasonably fast because the rate of solution under these conditions is much greater. With vigorous agitation and temperatures of 75 to 90 °C, the reaction is essentially complete in 1 h. Extensive U.S. Army testing at laboratory and bench-scale (up to 114-L reactors) have provided valuable operating experience and engineering data on a scale that can be readily extrapolated for designing production-scale reactors.

10. These large-scale tests showed that the reaction proceeds cleanly with thiodiglycol as the primary reaction product. The overall reaction scheme is as indicated below (Fig. 4):

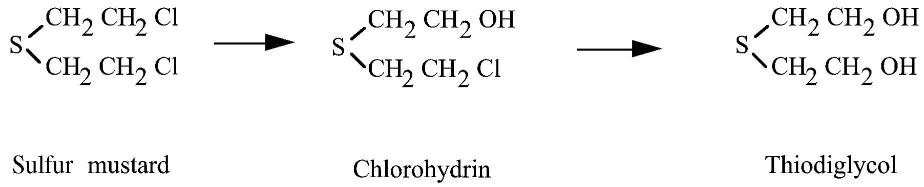

Fig. 4 Reaction scheme for hydrolysis of mustard.

Although side-reactions take place [90] between intermediates and the thiodiglycol product, these are minimized by keeping the mustard as a dilute component in water during the reaction. The residual HD concentrations in the hydrolysate from these experiments dropped below 200 ppb in

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88. Z. Wertejuk, M. Koch, W. Marciniak. "Recovered old arsenical and 'mustard' munitions in Poland", in *Arsenic and Old Mustard: Chemical Problems in the Destruction of Old Arsenical and 'Mustard' Munitions,* J. F. Bunnett and M, Mikolajczyk (Eds.), NATO ASI Series, 1. Disarmament Technologies, Vol. 19, pp. 91–104, Kluwer, Dordrecht (1998).
89. National Research Council, Committee on Alternative Chemical Demilitarization Technologies. *Alternative Technologies for the Destruction of Chemical Agents and Munitions,* p. 63, National Academy Press, Washington, DC (1993).
90. These side reactions are shown in the reaction schematic on p. 126 of National Research Council, Panel on Review and Evaluation of Alternative Chemical Disposal Technologies, *Review and Evaluation of Alternative Chemical Disposal Technologies,* National Academy Press, Washington, DC (1996).

less than 20 min, and the toxicity was dramatically reduced. Processing at bench scale also has demonstrated the successful destruction of HD present in the residue removed from a ton container. Overall, 161 kg of HD were destroyed in the laboratory and bench-scale studies [91].

Stability, reliability, and robustness

11. The neutralization of HD is simple and easily controlled. Because the equipment is standard for the chemical industry, it should be reliable. The semibatch process operates at the relatively low temperature of 75 to 90 °C and atmospheric pressure, and the energy content of the reaction mixture is low. These characteristics preclude uncontrollable or runaway reactions.

Monitoring

12. The process is monitored by analyzing for residual agent before the effluent (hydrolysate) is released from the neutralization reactor.

Safety considerations

Safety interlocks

13. The unit processes, such as neutralization and biodegradation, operate independently of each other with interstage storage of the aqueous process stream. Therefore, only minimal interlocks are required.

Hazard inventory

14. The inherent hazard potential, apart from the hazards associated with handling agent, is limited because the aqueous streams are nonflammable and at relatively low temperature (90 °C) and pressure (1 atm gauge). The process does, however, require that workers handle sodium hydroxide at concentrations in the range of 18 to 50 %.

Materials of construction

15. When agent is first hydrolyzed, the solution in the reaction vessel becomes acidic. This solution is moving at a relatively high velocity because it is being vigorously mixed. Depending on how much oxygen is available, corrosion of the reactor and components at the vapor–liquid interface may be accelerated. The extent of these combined effects is uncertain because sulfur and chloride in the solution may also influence the corrosion rate. The possibility of accelerated corrosion resulting from the combination of these conditions needs to be considered. In addition, the contents of the neutralization reactor go from a low pH near the end of hot-water hydrolysis to an alkaline pH from the addition of sodium hydroxide just prior to discharge to the bioreactor system. This pH change necessitates that the reactors be made from a versatile metal or one lined with glass or a plastic-like polyvinylidenefluoride (Kynar), but these are not unusual materials of construction. Most other systems in a mustard hydrolysis plant are standard or have already been developed for the baseline incineration technology.

Environmental impact

Test prior to release

16. The hydrolysate from the neutralization reactor is readily tested for the presence of residual agent before release from the toxic control area. Similarly, the process vapors can be scrubbed through a sodium hydroxide solution and passed through multiple carbon filters before release.

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[91] National Research Council, Panel on Review and Evaluation of Alternative Chemical Disposal Technologies. *Review and Evaluation of Alternative Chemical Disposal Technologies*, p. 127, National Academy Press, Washington, DC (1996).

Environmental burden

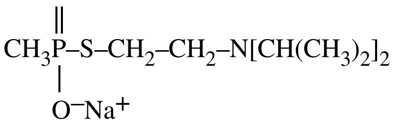
17. The only process residuals from the process configuration are waste salts, which need to be landfilled, and biomass in the form of bacterial cell material that resembles municipal sewage solid, which also will require disposal and may require special testing. If water recycle is not used then a major liquid process residual after biotreatment is a large volume of dilute aqueous solution of sodium chloride, sodium sulfate, and unbiodegraded organic compounds, which can be discharged to a publicly or federally owned treatment plant.

B. Hydrolysis of mustard and nerve agents using aqueous sodium hydroxide

Process description

18. The neutralization of nerve agents (GB, VX) and mustard (H, HD, HT) can be carried out under mild conditions, using alkaline reagents such as aqueous sodium hydroxide (NaOH), to yield products with greatly reduced toxicity. Hydrolysis of HD with aqueous NaOH results in a largely similar set of reaction products to those from hydrolysis with water, although with aqueous NaOH small amounts of ethers are formed which are more resistant to the action of the biodegradation microorganisms, thus requiring different subsequent treatment prior to disposal. The situation with the nerve agents GB and VX is similar in that the neutralizing reagent (neutral water, aqueous NaOH) chosen determines the reaction products and the subsequent treatment requirements. The reactions can be carried out in commercially available chemical reactors at temperatures below 100 °C and near atmospheric pressure.

19. Neutralization of chemical agent with aqueous NaOH is similar to the first part of the HD hydrolysis with water treatment described in the previous section. The agent needs to first be removed from the munition/container (usually by punch-and-drain process), transferred to a holding tank, and then fed slowly into a vigorously stirred reactor containing hot aqueous sodium hydroxide solution. Significant quantities of GB have been destroyed by hydrolysis using aqueous NaOH at ambient temperature since the late 1960s, first in the United Kingdom, then in the United States and, more recently, in Iraq. Currently, the only large-scale destruction of chemical agent planned using aqueous NaOH is that in the United States for the destruction of VX at Newport, Indiana. The following discussion is accordingly focused on VX neutralization. For VX hydrolysis, the U.S. Army has selected 20 % aqueous sodium hydroxide solution at 90 °C (20.6 wt %) [92]. The mixture is heated for approximately 6 h to destroy both the agent VX and a hydrolysis by-product with similar toxicity to VX that is present in trace amounts, known as EA-2192:



$$\mathrm{CH_3\underset{\underset{O^-Na^+}{|}}{\overset{\overset{O}{\|}}{P}}{-}S{-}CH_2{-}CH_2{-}N[CH(CH_3)_2]_2}$$

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92. National Research Council, Panel on Review and Evaluation of Alternative Chemical Disposal Technologies. *Review and Evaluation of Alternative Chemical Disposal Technologies*, p. 143, National Academy Press, Washington, DC (1996).

Scientific principles

20. The neutralization processes evaluated for disposal of VX involve hydrolysis of the P–S bond [93], which is essential to the toxicity of this nerve agent. Figure 5 shows the reaction scheme for hydrolysis mediated by sodium hydroxide. The reaction with sodium hydroxide produces the relatively nontoxic ethyl methyl-phosphonic acid (EMPA), which is present as its sodium salt, and an aminothiol compound. The aminothiol, which has a very unpleasant odor but low toxicity, is often referred to as "thiol", and should not to be confused with methylmercaptan, which is also known as "thiol". Much the same reaction occurs during hydrolysis with neutral water, when the resulting EMPA is then present as the corresponding acid rather than the sodium salt.

21. A major advantage of the alkaline hydrolysis process became evident during neutralization studies on impure munitions-grade VX that contained small amounts of a compound containing two P–S bonds. This material (known as "VX-bis") reacts with water to form EA-2192 (which is present as the sodium salt under alkaline conditions). EA-2192 is almost as toxic as VX itself and is resistant to further hydrolysis by water alone. The concentration of EA-2192 is low, but it contributes significantly to the toxicity of the hydrolysate. During hydrolysis mediated by sodium hydroxide, EA-2192 is also hydrolyzed by an analogous reaction to form aminothiol and the sodium salt of methylphosphonic acid (MPA), which has low toxicity. At low temperatures (20 to 25 °C), small quantities of EA-2192 may be present for a prolonged period owing to slow reaction rates. At higher temperatures (75 to 90 °C), both VX and EA-2192 hydrolyze at acceptable rates to form relatively nontoxic products. The alkaline hydrolysis of VX is exothermic, releasing 32.3 kcal/mole.

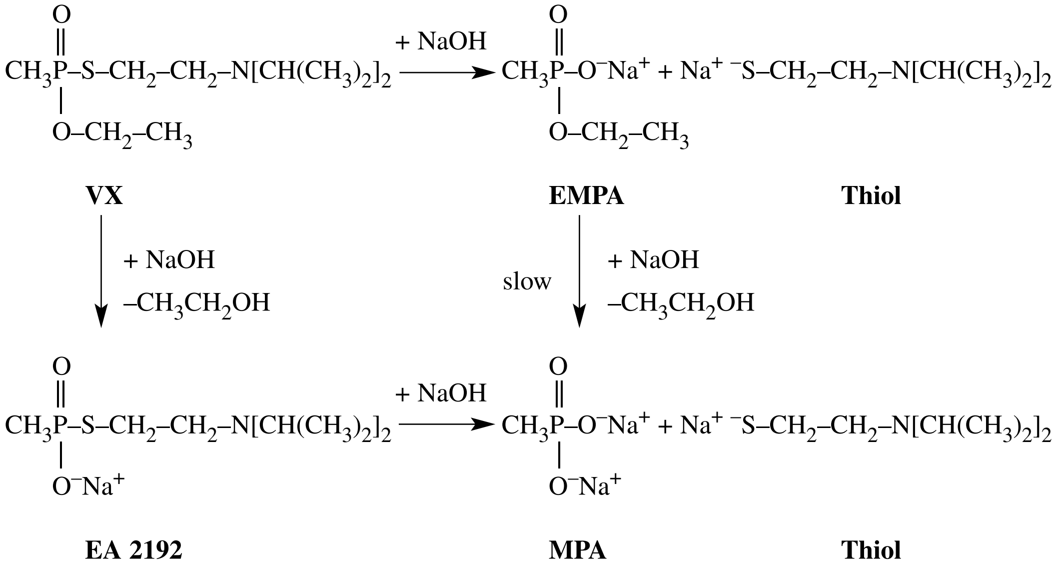

Fig. 5 Reaction scheme for neutralization of VX with sodium hydroxide.

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93. For further information on the chemistry associated with the detoxification of VX see Yu-Chu Yang, "Chemical detoxification of nerve agent VX", *Acc. Chem. Res.* **32**, 109–115 (1999).

Technology status

Alkaline hydrolysis

22. The neutralization technology chosen for destroying VX agent described above was developed by the U.S. Army on the basis of previous experience and ongoing research. Although not much has been reported about the alkaline hydrolysis of VX, sodium hydroxide has been used to destroy GB (sarin) nerve agent on a substantial scale. The experience gained from those operations facilitated the development of a VX hydrolysis process in U.S. Army research carried out since 1993.

23. The VX neutralization process was developed utilizing a series of laboratory-scale reactors and through bench-scale testing in a 114-L (30-gal) stirred reactor. The bench-scale studies in Mettler reactors yielded reliable data on heats of reaction and reaction rates. The tests monitored the disappearance of VX and of secondary products, such as EA-2192, as well as enabling the optimum conditions to be determined for the 114-L reactor. Five tests using the 114-L reactor each destroyed 25 to 30 kg of VX in a typical run, and neutralization of as much as 39.4 kg was demonstrated. More important, the effects of reaction times and mixing (e.g., stirring rate and the effect of adding a static mixer) were evaluated on a large enough scale to extrapolate to pilot- or production-scale reactors.

Stability, reliability, and robustness

24. The low-temperature, low-pressure, semibatch processing should be stable and reliable. The hydrolysis reaction is mildly exothermic (heat-releasing), but the relatively low energy content of the hydrolysis mixture precludes uncontrolled or runaway reactions. The simple unit processes and standard equipment closely resemble well-tested counterparts in the chemical industry.

Monitoring

25. The hydrolysate from neutralization is analyzed for residual agent before it is released from the toxics control area. Under current rules, a second step will be necessary to break the C–P bond before the waste can be considered as meeting the CWC requirements.

Safety considerations

Safety interlocks

26. The unit processes, such as ton-container processing and agent neutralization, operate independently with interstage storage of the aqueous process stream. Therefore, only minimal interlocks are required.

Hazard inventory

27. The inherent hazard potential, except for the hazards associated with handling agent, is limited because the aqueous streams are nonflammable and at low temperature and pressure. The hydrolysate retains some non-agent toxicity. The process requires handling caustic sodium hydroxide solutions, but the procedures for doing this are standard in the chemical industry.

Materials of construction

28. Materials of construction concerns should be similar to hydrolysis with neutral water and their selection should not present serious problems.

Environmental impact

Test prior to release

29. The hydrolysate from the neutralization reactor can be tested for the presence of residual agent and for any toxic by-product (EA-2192) before release from the toxic control area. Process vapors, which are monitored for agent, can be scrubbed through a sodium hydroxide solution and

passed through carbon filters before release. Emptied munitions or storage containers can be steam-cleaned and tested for the presence of agent vapor before being shipped off site for disposal or reclamation.

Environmental burden

30. The hydrolysate from the neutralization reactor will require further treatment prior to discharge to the environment. The major residuals are likely to include a liquid process stream and waste salts.

C. Reaction of mustard and nerve agents using amines and other reagents

Process description

31. Mustard and nerve agents can be reacted with monoethanolamine, or in the case of VX with potassium isobutylate (potassium 2-methyl-1-propoxide), at 100 °C under atmospheric pressure for about an hour. The resulting reaction products then need to be disposed of in the second stage of the process. The second phase can involve incineration of the reaction products, or bitumenization (mixing the reaction products with hot bitumen to produce monolithic bitumen blocks for burial).

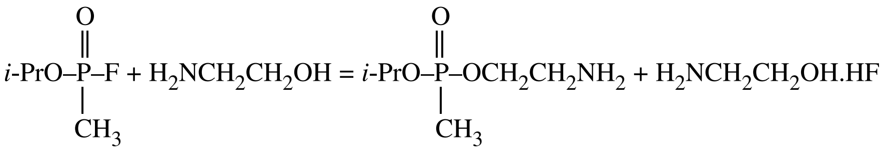
Scientific principles

32. Mustard is neutralized by monoethanolamine at 100 °C under atmospheric pressure to yield products that include chloroethanol, monoethanolamine hydrochloride, water, and more complicated organic molecules.

$$S(CH_2CH_2Cl)_2 + 3H_2NCH_2CH_2OH = S(CH_2CH_2)_2NCH_2CH_2OH + 2H_2NCH_2CH_2OH.HCl$$

The reaction mass can then be incinerated or reacted with calcium hydroxide and bitumen to produce insoluble calcium salts in the bitumen reaction mass.

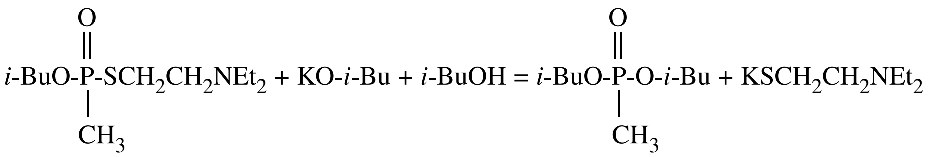
33. The nerve agents GB or GD are neutralized by monoethanolamine at 100 °C under atmospheric pressure to yield, in the case of GB, isopropyl methylphosphonic acid and 2-aminoethylisopropyl methylphosphonate and, in the case of GD, the corresponding products.



$$i\text{-PrO–}\underset{\underset{\displaystyle CH_3}{|}}{\overset{\overset{\displaystyle O}{\|}}{P}}\text{–F} + H_2NCH_2CH_2OH = i\text{-PrO–}\underset{\underset{\displaystyle CH_3}{|}}{\overset{\overset{\displaystyle O}{\|}}{P}}\text{–}OCH_2CH_2NH_2 + H_2NCH_2CH_2OH.HF$$

In the second stage, the reaction mass can then be incinerated or reacted with calcium hydroxide and bitumen at 200 °C under reduced pressure to form insoluble calcium methylphosphonate and other salts in the bitumen mass and to release ethanolamine and isopropyl alcohol in the case of GB and the corresponding materials for GD.

34. The nerve agent VR (Russian VX) is neutralized using a decontamination solution known as RD-4, which contains potassium isobutylate dissolved in isobutanol and *N*-methylpyrrolidinone, at 90–95 °C under atmospheric pressure to break the P–S bond and yield diisobutyl methylphosphonate and other products.



$$i\text{-BuO-}\underset{\underset{\displaystyle CH_3}{|}}{\overset{\overset{\displaystyle O}{\|}}{P}}\text{-}SCH_2CH_2NEt_2 + KO\text{-}i\text{-Bu} + i\text{-BuOH} = i\text{-BuO-}\underset{\underset{\displaystyle CH_3}{|}}{\overset{\overset{\displaystyle O}{\|}}{P}}\text{-O-}i\text{-Bu} + KSCH_2CH_2NEt_2$$

In the second stage, the reaction mass can be incinerated or reacted with bitumen (without calcium hydroxide) at a temperature which is increased from 130–140 °C to about 180 °C under reduced pressure to form potassium methylphosphonate and other salts in the bitumen mass and to release isobutanol and *N*-methylpyrrolidinone.

Technology status

35. Neutralization of mustard and nerve agents using monoethanolamine has been used by Russia for several years in chemical weapon destruction applications. The KUASI mobile system is designed to destroy chemical munitions filled with GB, GD, and VR (Russian VX) but without explosives. KUASI uses monoethanolamine (MEA) to neutralize GB, GD, and VR by heating to 100 °C for 30 to 45 min followed by dilution with equal volume of water or alkali solution prior to transfer to a liquid-waste incinerator. The system has been used to destroy more than 4000 munitions during the period 1980–1990 [94].

36. In a meeting in 1991, Russia reported [95] that it preferred a two-stage process in which GB, GD, and mustard are reacted with ethanolamine to produce a detoxified product which is then incinerated. VR (Russian VX) is reacted with a 1:1 mixture of ethylene glycol and orthophosphoric acid before incineration. The processes are discontinuous with 1 h for reaction followed by a further 1.5 h for analysis to confirm the absence of any agent in the material to be incinerated.

37. The Russian preferred mustard destruction process involves the reaction of mustard with an equal weight of reagent, which is a 9:1 mixture of monoethanolamine and ethylene glycol [96]. Reaction temperature is 100–110 °C for 1 h. The original intentions were to incinerate the reaction products, but incineration might produce dioxins and an alternative to incineration was therefore sought. This led to the bitumenization solution in which tough road bitumen with a softening temperature of 65–70 °C was used. The reaction products are processed in bitumen with calcium hydroxide at 170 °C for 45 min producing bitumen masses with a softening temperature of 81.5 °C, which enabled the masses to be formed into monolithic blocks for subsequent burial.

38. The preferred process for destruction of nerve agents consists of reacting GB and GD with a mixture of monoethanolamine and water followed by a second stage in which the reaction products are combined with calcium hydroxide and bitumen [97]. The GB or GD is dissolved in industrial

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[94] R. G. Sutherland. "The destruction of old and obsolete chemical weapons: Past experience", in *The Challenge of Old Chemical Munitions and Toxic Armament Wastes*, T. Stock and K. Lohs (Eds.), SIPRI Chemical and Biological Warfare Studies, No. 16, p. 151, Oxford University Press (1997).

[95] As described in R. G. Sutherland, "The destruction of old and obsolete chemical weapons: Past experience", in *The Challenge of Old Chemical Munitions and Toxic Armament Wastes*, T. Stock and K. Lohs (Eds.), SIPRI Chemical and Biological Warfare Studies, No. 16, p. 151, Oxford University Press (1997).

[96] S. V. Petrov, V. I. Kholstov, V. P. Zoubrilin, N. V. Zavialova. "Practical actions of Russia on preparations for destruction of stockpiled Lewisite and 'mustard'", in *Arsenic and Old Mustard: Chemical Problems in the Destruction of Old Arsenical and 'Mustard' Munitions,* J. F. Bunnett and M. Mikolajczyk (Eds.), NATO ASI Series, 1. Disarmament Technologies, Vol. 19, Kluwer, Dordrecht (1998).

[97] Bonn International Center for Conversion & Stockholm International Peace Research Institute. *Chemical Weapons Destruction in Russia (1996–97).* Available at http://projects.sipri.se/cbw/research/sipri-bicc-cw-mainpage.html

grade ethanolamine, which contains around 20 % water, and the mixture heated to 110 °C for 1 h at atmospheric pressure. This treatment achieves a destruction removal efficiency of greater than 99.9999 % with both GB and GD resulting in a reaction mass with a toxicity slightly greater than that of monoethanolamine. In the second stage, the reaction masses are combined with calcium hydroxide and bitumen and heated to about 200 °C under reduced pressure for 1 h. Under these conditions, chemical reactions are expected to destroy any traces of GB or GD that remained after the monoethanolamine treatment. The alcohols released and any excess solvent ethanolamine are distilled out of the bitumenization reaction mixture and are collected by condensers. At the end of the process, the liquid bitumen-salt mass is drained from the reactor and allowed to solidify.

39. For VR (Russian VX), the first step is to react the agent with a decontamination solution known as RD-4, which contains potassium isobutylate dissolved in isobutanol and *N*-methylpyrrolidinone, and the mixture heated at 90–95 °C for 30 min at atmospheric pressure. This treatment achieves a destruction removal efficiency of greater than 99.9999 % resulting in a reaction mass with a toxicity comparable to that of the solvent isobutanol. In the second stage, bitumen, but in this case without calcium hydroxide, is added to the reaction products. Over a period of 45 min, the reactor temperature is gradually increased from 130–140 °C to about 180 °C as the pressure above the hot bitumen is slowly reduced to about 150 torr. Volatile constituents emitted are recovered in condensers and include isobutanol and *N*-methylpyrrolidinone.

40. The bitumenization product in both cases include methylphosphonate products which may be leached over time from the bitumen-salt mass, and will need to be taken into account in considering disposal of the bitumen-salt masses. The amount of waste generated during the destruction process for GB and GD was 4 to 7 times the original amount destroyed while that generated during the VR destruction was approximately three times greater.

Safety considerations

41. The neutralization is carried out at about 100 °C under atmospheric pressure using monoethanolamine or decontamination solution RD-4, which does not present any unusual safety concerns. The second stage of bitumenization, although at slightly higher temperatures and reduced pressure, also does not present any unusual safety concerns.

Environmental impact

42. The principal concern relates to the bitumen mass produced from the reaction products of the neutralization and the extent to which some of the salts may be leached over time. This will need to be considered in considering disposal of the bitumen mass.

D. Electrochemical oxidation

Process description

43. This is a patented process, known as Silver II, which was originally developed for destroying solid and liquid radioactive organic waste streams from a fast-reactor development program. The process takes place in two separate 180-kW electrochemical cells which are connected in parallel through a 360-kW power cell. At the start of operation, the composition of the anolyte is an aqueous solution that is approximately 8 molar in nitric acid, 0.5 molar in silver nitrate, and 0.02 to 0.03 molar in agent. The catholyte is an aqueous solution of 4 molar nitric acid.

44. When power is applied to the cell, Ag(I) ions are oxidized at the anode to the highly reactive Ag(II). The Ag(II) species have been shown to exist in the form of $AgNO_3^+$ ions, which impart a brown color to the solution in the absence of organic materials. In the presence of organic substances, $AgNO_3^+$ ions oxidize water into intermediates such as hydroxyl radicals that rapidly oxi-

dize the organic species. Simultaneously, Ag(II) is reduced back to Ag(I), which migrates back to the anode surface where it is reoxidized to Ag(II). Silver therefore serves as an electron-transfer intermediate that is not consumed in the process. However, when chloride ions or organic chlorides are present, as in HD, Ag(I) precipitates as AgCl.

45. Some CO will form as well, by analogous reactions, but laboratory tests have shown that carbon is converted primarily to CO_2. Hydrated protons (hydronium ions, H_3O^+) move across the membrane toward the cathode, where the primary reaction is reduction of nitric acid to nitrous acid:

$$HNO_3 + 2H^+ + 2e \Rightarrow HNO_2 + H_2O$$

The nitrous acid will partially decompose to NO gas, nitric acid, and water. In laboratory tests, the gas leaving the cathode compartment had the characteristic red-brown color of NO_2, which can form by oxidation of NO in the gas phase when O_2 is present. The reaction products are subsequently treated outside the electrochemical cell in order to reoxidize HNO_2 to HNO_3 and to neutralize the acids containing the sulfur, phosphorus, nitrogen, and chlorine components of the agent to their corresponding sodium salts (sodium sulfate, sodium phosphate, sodium nitrate, and sodium chloride).

46. The overall reactions are similar to the overall reactions for incineration of VX and HD, but they occur at low temperature (less than 90 °C) and close to atmospheric pressure. In the electrochemical process, with both agents, carbon is released to the gas phase primarily as CO_2, and the sulfur, phosphorus, and chlorine components of the agent appear in the final effluent as hydrated anions in aqueous solution with sodium being the principal cation. This solution can be analyzed and treated further, if necessary, prior to release.

47. Three additional reactions that can occur will affect the energy efficiency of the process. First, Ag(II) can react directly with water in the anode compartment to form oxygen gas (O_2). Second, the Ag(I) can migrate across the membrane to the cathode compartment. Third, cationic impurities, such as iron, copper, or mercury, in the agent can migrate across the membrane to the cathode compartment.

48. The process reactions involving agent cannot be reversed. Therefore, once agent is destroyed, it cannot reform. However, agent destruction is likely to proceed in several steps, some of which may produce volatile organic intermediates that will enter the gas phase and require further treatment. In laboratory tests, varying levels of alkyl nitrates were identified in the anolyte off-gas, which was mainly CO_2. Nonvolatile organic intermediates that may also form will remain in the anode compartment and will ultimately undergo complete conversion to simpler inorganic products, such as sulfate, phosphate, chloride, and CO_2/CO.

Scientific principles

49. Ag(II) in an acidic medium is one of the most powerful oxidizing agents known. The standard reduction potential of the Ag(II)/Ag(I) couple is 1.98 V, whereas the standard reduction potential of the O_2/H_2O couple is only 1.23 V in nitric acid. Several published studies [98] report on the use of anodically generated Ag(II) to oxidize organic substances in an acid solution.

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[98] See references cited on p. 78 of National Research Council, Panel on Review and Evaluation of Alternative Chemical Disposal Technologies, *Review and Evaluation of Alternative Chemical Disposal Technologies,* National Academy Press, Washington, DC (1996).

50. The basic half cell reactions for the Silver II process are as follows:

$$\begin{array}{lll} \text{Anode:} & 2Ag^+ \Rightarrow 2Ag^{++} + 2e & E° = -1.98\text{ V} \\ \text{Cathode:} & HNO3 + 2H^+ + 2e \Rightarrow HNO_2 + H_2O & E° = +0.94\text{ V} \end{array}$$

The net reaction is therefore:

$$2Ag^+ + HNO_3 + 2H^+ \Rightarrow 2Ag^{++} + HNO_2 + H_2O \quad E° = -1.04\text{ V}$$

In these equations, E° is the standard equilibrium potential at zero current flow when all reactants and products are at unit activity. In practice, the required potential is larger than the standard equilibrium potential owing to ohmic heating and other effects. An applied potential of 2 V is typically used.

51. Oxidation of Ag(I) to Ag(II) at the surface of a platinum anode is rapid, and the required overpotential is low: 120 mV at 5 kA/m^2. The principal Ag(II) species formed is $AgNO_3{}^+$, which has a dark brown color. The color disappears almost instantaneously in the presence of organic substances due to several complex reaction steps that result in the complete oxidation of the organic substances and the reduction of Ag(II) back to Ag(I). Silver is not consumed in the process but functions as a mediator between the electric power fed into the cell and the organic compounds being destroyed.

52. The reaction mechanisms in silver-mediated electrochemical oxidation are not well understood, but are believed to involve highly reactive, short-lived species, including hydroxyl and other radicals. In a study [99] of the electrochemical oxidation of ethylene glycol and benzene by Ag(II), several relatively long-lived reaction intermediates were identified, but with sufficient time complete oxidation was achieved as evidenced by measurement of stoichiometric quantities of CO_2 in the final product.

Technology status

53. The Silver II process has yet to be operated on a commercial scale although the electrochemical cell in the Silver II process is used commercially in the chlorine-alkali industry. The largest-scale pilot tests of the Silver II process have been conducted with 4-kW cells consisting of a single anode-cathode pair. The most extensive tests have been conducted with spent tributyl phosphate dissolved in kerosene as the feed material. These tests, which were run continuously, 24 h per day for up to 14 days, destroyed a total of 150 L of the feed material. Laboratory tests have been successfully completed on 10-g batches of agent in a pilot plant constructed at DERA, Porton Down, UK, that is suitable for tests on 15-L batches of agent. All of the tests prior to start-up of the Porton Down plant had been conducted with only the electrochemical cell component of the agent-destruction system. The Porton Down facility also includes anolyte and catholyte feed circuits, an anolyte off-gas condenser, a NO_x reformer system, and a modified version of the combined off-gas treatment circuit, which culminates in a sodium hydroxide scrubber.

54. The NRC AltTech report [100] summarizes the results of a test conducted at Porton Down on 14.62 kg of “as supplied VX”, which contained 12.7 kg of agent. The test consisted of a single continuous run of 6.5 days. At the end of the run, no agent was detected in the catholyte or in the process residuals. The lower detection limits for VX were 7.6 mg/m^3 in the anolyte, 9.2 mg/m^3

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99. J. C. Farmer *et al.* J. Electrochem. Soc. **139** (3), 654–662 (1992).

100. National Research Council, Panel on Review and Evaluation of Alternative Chemical Disposal Technologies. *Review and Evaluation of Alternative Chemical Disposal Technologies,* p. 79, National Academy Press, Washington, DC (1996).

in the catholyte, and 1.7 mg/m^3 in the residuals discharged during the trial. The corresponding volumes were 0.0724 m^3 of anolyte, 0.0854 m^3 of catholyte, and 0.0929 m^3 of process residuals. The total residual VX was therefore less than 1.5 mg out of an input of 12.7 kg of VX, corresponding to an agent destruction efficiency of greater than 99.99998 %. The destruction efficiency for conversion of organic carbon to CO_2 and CO was 88.7 %.

55. Additional bench-scale tests (1/35 full-scale) involved the treatment of 100 g of GB [101]. A 60-W cell was used, and small batches of material were added. The reaction time was 17 h, after which the destruction efficiency was greater than 99.9999 % based on detection limits. The oxidation efficiency based on CO/CO_2 in the off-gas as compared to the carbon feed was relatively poor (70 %). There was no measure of total hydrocarbons in the off-gas. Energetic materials were tested in an isolation laboratory with a 20 % slurry of energetic material in water. Separate runs were conducted with 100 g of TNT in the form of fine particles, 100 g of RDX, 100 g of tetryl, and 100 g of double-base propellant. In two tests, the TNT slurry was run for 42 h, after which TNT was below detection limits, corresponding to a destruction efficiency of greater than 99.9999 %.

Stability, reliability, and robustness

56. The agent destruction process operates at low temperatures and atmospheric pressure. The processes in the unit operations of the system are not sensitive to small excursions in composition or temperature. Rapid or runaway changes that might create emergency conditions are highly unlikely. Therefore, the response time required for control instrumentation is not very demanding. However, the reaction rates and processes are sensitive to temperature, which can be difficult to control at larger scales, and it may be difficult to control to prevent localized boiling in the cells. The design temperature for the process is 90 °C. Portions of the process are exposed to high electric currents that can raise temperatures, however, and any blockage that restricts flow could result in localized boiling. This difficulty would add complexity to scale-up.

57. The NRC report [102] indicated several concerns about the ability of the process to handle nonoptimal feed streams and especially (1) the potential for plugging caused by the accumulation of solids; (2) the effects of metals on the electrolytic reaction efficiency; and (3) the reaction of nitric acid with organic substances in the feed. Until these issues have been thoroughly investigated, the robustness of the process was considered questionable.

Monitoring and control

58. The monitoring and control system involves a relatively straightforward application of normal industrial techniques. The transducers for temperature, pressure, flow, and liquid level are commercially available. A centralized computer is used to achieve automatic closed-loop control via control algorithms and operator interface. The complexity of the control systems is consistent with the chemical process plants in general. There is, however, some uncertainty as to how holes in cell membranes might be detected.

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101. National Research Council, Committee on Review and Evaluation of Alternative Technologies for Demilitarization of Assembled Chemical Weapons. *Review and Evaluation of Alternative Technologies for Demilitarization of Assembled Chemical Weapons,* pp. 50–51, National Academy Press, Washington, DC (1999).
102. National Research Council, Committee on Review and Evaluation of Alternative Technologies for Demilitarization of Assembled Chemical Weapons, *Review and Evaluation of Alternative Technologies for Demilitarization of Assembled Chemical Weapons,* pp. 51–52, National Academy Press, Washington, DC (1999).

Safety considerations

Safety interlocks

59. The electrochemical oxidation process consists of several unit operations, but these do not have to be tightly integrated. Temperature, pressure, and chemical concentrations are monitored closely. If the monitoring data signal a malfunction, the cell current can be rapidly shut down. Once the problem causing the malfunction has been found and corrected, restarting the process is straightforward.

Hazard inventory

60. The Silver II processes operate at the relatively low temperature of 90 °C and low pressure (essentially atmospheric pressure), this minimizing stored energy and reducing process hazards. Nitric acid concentrations are expected to be within safe operating ranges of 4 to 12 molar for anolyte and 2 to 6 molar for catholyte.

61. The agent feed rate of about 0.01 m^3/h for each 180-kW cell implies that 12.7 kg/h of mustard is added to each cell or 10 kg/h of VX. Because the agent will be rapidly hydrolyzed by the concentrated nitric acid, the inventory of agent in the anolyte circuit at any given time would be far less than 12.5 kg (equivalent to 5000 ppm in a 2.5 m^3 anolyte volume).

62. The process requires the handling of highly corrosive or reactive materials such as nitric acid, concentrated sodium hydroxide solutions, hydrogen peroxide, and 90 % oxygen gas. Nitric acid has been described as the common chemical most frequently involved in reactive incidents owing to its exceptional ability to function as an effective oxidant even when fairly dilute or at ambient pressure. Many reported incidents have involved closed or nearly closed vessels that have failed from internal gas pressure created either by oxidation of organic compounds to CO_2 or autodecomposition of nitric acid to NO_X fumes and oxygen. Such incidents are unlikely in the Silver II process because the system is essentially open and the concentration of organic substances in contact with nitric acid is low. Worker-safety training and chemical containment are therefore particular concerns, but harmful releases to the surrounding community are unlikely.

Environmental impact

Test runs prior to release

63. All liquid and solid reaction products can be tested prior to release. Gaseous products are not tested prior to release but are treated extensively to ensure the removal of any agent and of volatile organic contaminants formed in the electrochemical cell. Moreover, reaction conditions such as temperature, pressure, and the basic reaction mechanism ensure very low concentrations of agent and other organic substances in the feed to the gas cleaning system. The off-gas circuit can be modified to accommodate hold-and-test prior to release, if that is required.

Environmental burden

64. The major liquid process residual is an aqueous solution of common salts: sodium chloride, sodium sulfate, sodium phosphate, and sodium nitrate. The solution will contain silver at a concentration below the applicable regulatory standards in many countries.

65. Gaseous effluents are anticipated to be primarily CO_2, O_2, and N_2.

E. Solvated electron technology (SET)

66. Solvated electron technology (SET) can be used to destroy chemical agents, deactivate energetic materials, and decontaminate metal parts and dunnage. SET solutions of metallic sodium in anhydrous liquid ammonia are highly reducing and are characterized by an intense blue color from the presence of partially solvated (i.e., ammoniated) electrons. The blue color provides a visual indicator of the reactivity of the solution for destroying agents and energetics. The solid and liquid residuals of the SET process are hydrated with water to destroy the excess sodium. The hydration products from agent and energetics destruction is further treated by oxidation with sodium persulfate or hydrogen peroxide. Teledyne Commodore has proposed a technology package for the destruction of assembled chemical weapons based on SET [103].

Process description

67. The proposed disassembly processes differ significantly from the U.S. Army baseline incineration system as used at JACADS and TOCDF principally in the use of ammonia-jet cutting and ammonia wash-out. In both the cutting and wash-out operations, ammonia is pressurized to 2720 atm by an intensifier pump and delivered to the work area through a 0.25-mm-diameter orifice at velocities of about 1000 m/s. Pre-intensifier boost pumps are used to ensure adequate pressure and volume of ammonia and prevent flashing of the liquid into gas during the suction stroke of the intensifier. For the cutting operation, 180-micron abrasive particles, normally of garnet, are added to the pressurized ammonia stream through a stainless steel venturi mixing section. A pressure vessel surrounds the cutting and wash-out processing equipment, providing an intermediate chamber that is maintained at 10.5 atm inside a U.S. Army baseline explosion-containment room. The pressurized fluid from the intensifier pump is passed through a chiller to reduce the temperature of the liquid significantly below room temperature because prechilling is reported to enhance the jet cutting properties of the liquid ammonia.

68. An SET solution is generated by mixing liquid sodium and liquid ammonia to form a 4 % solution of sodium in liquid ammonia. The sodium is transferred at its melting point of 97.5 °C; the liquid ammonia is transferred at room temperature and 10.5 atm (saturated conditions) and the two reagents combined in an in-line static mixer. The prepared SET solution is fed to a static reactor mixer, and agent from the feed vessel is introduced below the liquid surface. The reaction is carried out at temperatures of 19 to 23 °C and pressures of 8.5 to 12.4 atm. The agent destruction reactions are exothermic, and temperature is controlled by evaporation of ammonia. The evaporated ammonia and off-gases from the SET reaction are collected in holding tanks for testing prior to venting to the gas-treatment train. The slurry from the SET reaction, still at elevated pressure, is treated with water to destroy the excess sodium. The resultant suspension is transferred at elevated pressure to a centrifuge where liquids and solids are separated. The solids are transferred to a carbon steel vessel and mixed with water. The solution is then oxidized with sodium persulfate. The liquids remaining in the centrifuge are mixed with water and fed to the bottom of an ammonia-recovery tower.

69. The slurry produced from the wash-out of energetic material is collected in a carbon steel vessel, diluted with ammonia to a standard composition and mixed with a solution of sodium in liquid ammonia in a reaction vessel. Munitions metals are shredded and transferred to a metal SET reactor for treatment. Agent-contaminated dunnage is decontaminated in SET solution. The technology approach is summarized in the table.

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[103] National Research Council, *Review and Evaluation of Alternative Technologies for Demilitarization of Assembled Chemical Weapons,* National Academy Press, Washington, DC (1999).

Major demilitarization operation	Approach(es)
Disassembly of munitions	High-pressure ammonia fluidized jet cutting and ammonia-jet wash-out.
Treatment of chemical agent	SET reduction; hydration of the condensed-phase products; oxidation of the hydrolysate with sodium persulfate or hydrogen peroxide.
Treatment of energetics	SET reduction; hydration of the condensed-phase products; oxidation of the hydrolysate with sodium persulfate or hydrogen peroxide.
Treatment of metal parts	Agitation of shredded parts in SET solution to a 3X condition[a]
Treatment of dunnage	Grinding or shredding; mixing with SET solution to destroy agent.
Disposal of waste	**Solids.** Product from process and decontaminated dunnage sent to a suitable permitted landfill; metal parts shipped to Rock Island Arsenal for 5X treatment. **Liquids.** Stabilized with cement and shipped to appropriately permitted landfill; oil and hydraulic fluids sent to a TSDF (treatment, storage, or disposal facility). **Gases.** Off-gases from process and vaporized hydrocarbon residuals burned in boiler.

[a] At the 3X decontamination level, solids are decontaminated to the point that the agent concentration in the head space above the encapsulated solid does not exceed the health-based, 8-h, time-weighted average limit for worker exposure. Materials classified as 3X may be handled by qualified plant workers using appropriate procedures but are not releasable to the environment or for general public reuse. In specific cases in which approval has been granted, a 3X material may be shipped to an approved hazardous waste treatment facility for disposal in a landfill or for further treatment.

Scientific principles

70. Although reactions of organic substances with solutions of metallic sodium in liquid ammonia have been studied since 1865, the reaction products depend on the type of organic substance being reacted. In general, the solvated electrons are attracted to the polar bond between carbon and a more electronegative species such as chlorine, fluorine, phosphorus, sulfur, or oxygen. The result is cleavage of the covalent bond. The strongly electronegative species leaves as an anion. The complementary site on the less electronegative atom, usually carbon, may capture a second electron, thereby becoming negative; or the bonds in the remaining carbon skeleton may rearrange themselves and release a gaseous alkane or alkene. Further reaction occurs when the condensed phase products of the SET reaction are hydrolyzed.

71. The experimental results from treating chemical agents in the laboratory are described below:

Agent HD (mustard). The expected initial reaction of mustard in the SET process is cleavage of the carbon–chlorine and of the carbon–sulfur bond by a solvated electron to form sodium chloride and sodium sulfide. Gaseous ammonia released in the SET reaction results from evaporation, which is used to control the temperature of the liquid mixture. Teledyne-Commodore, who was developing the technology, was unable to determine the molecular composition of the slurry from the SET reaction prior to hydration because of analytical difficulties.

Agent GB. The expected initial reaction of GB in the SET process is cleavage of the phosphorus–fluorine bond by a solvated electron to form sodium fluoride. Release of ammonia gas in the SET reaction again results from evaporation used for temperature control. The composition of the slurry from the SET reaction was not analyzed prior to hydration. In small-scale tests, GB was not detectable in any of the reaction products.

Agent VX. Unlike mustard and GB, the VX molecule does not have strongly polar bond for the solvated electrons to attack. Teledyne-Commodore postulates that cleavage occurs initially at the phosphorus–sulfur bond, the carbon–sulfur bond, or at both simultaneously. Ammonia is vaporized during the SET reaction. The composition of the slurry from the SET reaction was not analyzed prior to hydration.

Technology status

72. Teledyne-Commodore proposes a disassembly process based on ammonia-jet cutting. They suggest several advantages of ammonia over water as many of the hazardous materials that are washed out of munitions have very low solubility in water and contain surfactants that aid in the formation of stable aqueous emulsions which present serious safety and maintenance problems in full-scale conventional-munition disassembly facilities. Anhydrous ammonia, in contrast, dissolves most of the explosive materials and forms nondetonable solutions. Teledyne-Commodore have successfully demonstrated ammonia-jet cutting at Redstone Arsenal on M60 (inert) and M61 (live) rockets, a 4.2-inch inert mortar, and a 105-mm M60 inert projective. Successful wash-out of Comp B high explosive and M28 propellant was demonstrated during the M61 test series. Teledyne-Commodore claims that ammonia-jet cutting is 25 % faster than water-jet cutting.

73. Chemical agent destruction tests using SET have been conducted by Teledyne-Commodore. The largest quantities of agent tested in a single batch were 0.64 kg of HD, 0.45 kg of HT, 0.45 kg of VX, and 0.59 kg of GB. The concentration of agent in the SET solution after completion of the laboratory tests was below detection limits in all cases (less than 200 ppb for HD and HT; and less than 20 ppb for VX and GB). This has demonstrated that the SET process, followed by hydration, can destroy chemical agents to a destruction efficiency of at least 99.9999 %. However, considerably more testing and analysis will be required to determine the exact molecular composition, phase distribution, and quantity of reaction products. This lack of information compounds the difficulty of developing optimum conditions for the final oxidation step.

74. The capacity of the SET process, followed by hydration, to decompose the energetic materials has yet to be demonstrated. In laboratory experiments, the condensed-phase products were generally pasty, difficult to handle, of unknown polymeric composition, and sensitive to electrostatic ignition. Moreover, the reaction products identified represented less than 1 wt % of the material treated. In several instances, apparently spontaneous exothermic reactions occurred and the root causes of the exotherms have yet to be identified.

75. The SET/hydration products from the treatment of GB and VX include Schedule 2 chemicals that must be further treated. Teledyne-Commodore has tested sodium persulfate oxidation as the method of secondary treatment, but only on a laboratory scale. A substantial amount of additional testing will be needed to validate the process and determine optimum conditions for full-scale operation. In the few laboratory tests that were completed, the reactions were highly exothermic and led to bubbling and rapid rises in temperature. To maintain the temperature in the range of 90 to 100 °C, the sodium persulfate solution had to be added in extremely small increments, which increased the reaction time.

76. No standard generally acceptable sampling and analysis methods are available for systems based on liquid ammonia. The condensed phase products of SET can only be analyzed for specific chemical components after hydration. The hydration process changes the composition of the SET products, in addition to converting excess sodium to sodium hydroxide and producing hydrogen gas.

77. There have been no full-scale applications of the technology package discussed above. The system is complex and has never been operated as a totally integrated package that includes oxidation. The system involves at least 16 unit operations. Five are for SET treatment of agents, energetics, shredded dunnage, metal parts and fuzes; the other eleven are for hydration of agents and energetics, fluid-jet cutting, oxidation of energetic residue, oxidation of agent residue, evapora-

tion of oxidized residues, recovery of ammonia, stabilization of oxidized residues in cement, detonation of fuzes, decontamination of abrasives, and stabilization of fuzes/abrasives.

78. The SET process appears to be capable of destroying agents with a wide range of feedstock compositions, temperature, and pressures. The reaction seems to be most sensitive to the sodium/feedstock ratio, which must be high enough to ensure complete reaction. However, the capability of the SET/hydration process to deactivate energetics does not appear to be satisfactory, and optimum operating conditions have not been established. Teledyne-Commodore uses conductivity as the main indicator that the reaction is complete. However, because some of the products of the SET reaction contribute to conductivity, additional control algorithms are being developed that incorporate temperature, pressure, and feed composition.

Safety considerations

79. The SET process operates at ambient temperatures, using evaporation of ammonia to remove heat from the mildly exothermic reactions between the SET solution and the agent and energetics in their respective reactors. Pressures as high as 2720 atm are used for the ammonia-jet cutting solution during disassembly operations. With the exception of the small section of piping and the intensifier pump for the fluid-cutting solution, most of the systems operate at near atmospheric pressure to 10.5 atm. Where liquid ammonia is used, vessels will be operated at approximately 10.5 atm pressure which is the vapor pressure of ammonia at typical ambient temperatures.

80. The Teledyne-Commodore technology package is basically an adaptation of existing technologies used for the destruction of conventional munitions and other hazardous chemicals. Assuming careful design and operation, the general technology of fluid-cutting and fluid wash-out should achieve acceptable worker-safety levels.

81. A particular aspect of the technology from the standpoint of worker safety is the hazard associated with the primary chemicals used to destroy the agent and energetics. Liquid anhydrous ammonia boils at –33.4 °C and becomes a toxic gas capable of burning in air. Liquid sodium (melting point 98 °C) is a reactive and pyrophoric metal that burns violently upon exposure to air or other oxidizing media and requires special firefighting methods and materials. Sodium persulfate and hydrogen peroxide solutions are reactive chemical oxidizers as well as health hazards.

82. Although all of these chemicals are widely used in industry and releases and accidents are infrequent, because of the hazardous and reactive nature of these chemicals, the SET systems must be carefully designed to ensure worker safety from, for example, toxic gas exposures and fires. This includes minimizing the occasion when workers are in contact with the areas in which these hazardous chemicals may be present.

Environmental impact

83. Teledyne-Commodore has not characterized the effluents from their total system in sufficient detail to assess the potential impacts on human health and the environment. The chemical composition of the products of final oxidation is unknown, and the oxidation processes themselves are still under development. It has been demonstrated that agent is unlikely to be present in any of the process effluents but the absence of other chemical compounds of concern has not been shown. In addition, the persulfate oxidation process results in a heavy burden of sodium sulfate arising from the sodium persulfate and this may be difficult to stabilize for disposal [104].

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[104] U.S. Army Non-Stockpile Chemical Materiel Project. *Technology Evaluation Panel Report: Evaluation of Neutralent Post-Treatment Technologies for the Non-Stockpile Chemical Materiel Program,* 18 September 2000, pp. 9–4. Available at http://www-pmcd.apgea.army.mil/nscmp/ip/r/tepoct00/index.asp

VIII. EFFLUENT TREATMENT

1. All the technologies used for chemical weapon destruction result in effluent streams—gas, liquid, and solid—which need to be treated to ensure that any toxic chemicals that are formed as a result of the agent destruction process are destroyed and any remaining trace contaminants are at acceptable levels, which comply with national standards for release of the effluent stream into the environment, for recycling, for commercial use, or to a landfill. Attention is given in this section to treatment of gas, liquid, and solid effluent.

A. Gas

2. The appropriate approach to be taken for air pollution control depends on the nature of the destruction process, the nature of the effluent, and the national regulations governing release to the atmosphere. The principal air pollution control devices currently being used in waste destruction facilities include liquid scrubbers using packed towers, spray dryers, dry scrubbers for gaseous pollutant control, wet or dry electrostatic precipitators, HEPA filters for particulate control, and reactive carbon filters.
3. As chemical weapons are organic chemicals containing various heteroatoms such as chlorine, fluorine, sulfur, oxygen, phosphorus, and nitrogen, their destruction through incineration results primarily in carbon dioxide and water along with products containing the heteroatoms as well as products of incomplete reaction. The efficiency of the agent destruction process is designed to be very high and to exceed a destruction efficiency of greater than 99.9999 %; the residual amount of the original agent will be very small. Nevertheless, the effluent treatment scheme is designed to remove any trace amounts of agent remaining after the destruction process, along with the products of destruction.
4. The approaches to be taken to treat effluent are designed to meet the national standards and regulations governing emissions, which initially were introduced because of widespread international concerns about emissions of dioxins and acid gases. As national standards and regulations vary widely, this report considers, as an example, the standards required in the United States, as there has been more work carried out in the United States than anywhere else to dispose of chemical weapons [105]. The key regulatory provisions in the United States are the following:
    - Resource Conservation and Recovery Act (RCRA), 1976
    - Toxic Substances Control Act (TSCA), 1976
    - Clean Air Act, 1977
    - Clean Water Act, 1977
    - Regulations covering boilers and industrial furnaces that burn industrial waste, 1991

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105. National Research Council, Committee on Demilitarizing Chemical Munitions and Agents. *Disposal of Chemical Munitions and Agents,* Appendix E, pp. 185–189, National Academy Press, Washington, DC (1984); National Research Council, Committee on Review and Evaluation of the Army Chemical Stockpile Disposal Program. *Recommendations for the Disposal of Chemical Agents and Munitions,* pp. 58–60, National Academy Press, Washington, DC (1994); National Research Council, Committee on Review and Evaluation of the Army Chemical Stockpile Disposal Program. *Carbon Filtration for Reducing Emissions from Chemical Agent Incineration,* pp. 11–12, National Academy Press, Washington, DC (1999).

The U.S. Environmental Protection Agency (EPA) under the RCRA establishes limits on the quantity of agent that may be permitted in an emission; stricter limits may be imposed by some State regulations. In addition, RCRA regulates more typical products of combustion which can be monitored on a more or less continuous basis, such as carbon monoxide (CO), that may contribute to general pollution or be indicative of incomplete agent destruction. It also sets detailed limits on operating conditions and metal emissions as well as requiring a program to reduce the volume or quantity and toxicity of the hazardous waste generated and shipped off site. TSCA regulates the incineration of PCBs. The Clean Air Act requires U.S. plants to obtain permits for regulated air emissions. More recently, regulations covering boilers and industrial furnaces that burn hazardous waste were adopted in 1991, which set maximum allowable concentrations for a wide range of trace organic and inorganic compounds in ambient air. In 1995, the Clean Air Act set standards for maximum achievable emissions control technology for municipal waste combustors that incinerate more than 250 tons a day. These standards apply to dioxin emissions and to emissions of mercury, lead, cadmium, arsenic, beryllium, and chromium. These controls are intended to limit emissions to levels that are unlikely to harm human health or the environment. It should be noted, however, that public perceptions sometimes cause regulatory agencies to adopt even lower emission standards. Shortly, the United States will require all incinerators to employ the Maximum Achievable Control Technology (MACT).

5. Within the European Union, the approach has been to adopt the Best Available Techniques Not Entailing Excessive Cost (BATNEEC) and the Best Practical Environmental Option (BPEO) as the principles upon which the environmental standards are being based [106]. Whereas targets are set for major pollutants, the operators of plants producing such pollutants are required to employ the BATNEEC principle. They also have to consider the impact of their processes across the entire environmental spectrum—air, water, and land—and apply the BPEO principle to determine the best overall environmental option.

Acid scrubber

6. Packed towers are usually used to remove acid vapors such as hydrogen chloride. Typically, the packed towers are vertical columns that have been filled with packing to provide a large surface area. The absorbing liquid is distributed over and trickles down through the packed bed, thus exposing a large liquid surface area. The gas stream, containing pollutants such as hydrogen chloride, moves upward through the packed bed countercurrent to the absorbing liquid. Although the absorbing liquid is usually water, other aqueous chemical solutions such as caustic soda or lime slurry may be used, thereby enhancing the absorption as the pollutants then react chemically with the absorbing solution. For example, hydrogen chloride would react with caustic soda to produce sodium chloride. The resulting liquid stream containing the absorbed pollutant then needs to be treated as a liquid effluent.

7. Dry and semidry scrubbers are also being introduced as flue-gas cleaning systems. Dry scrubbing involves the injection of a solid powder absorbent, such as lime or sodium bicarbonate, into the flue gas. Acid gas removal occurs in the dust collector as absorbent and ash particles and condensed volatile matter are captured. In semidry processes, also known as spray drying, the absorbent enters the flue gas with sufficient moisture to promote rapid absorption of acid gases, yet can be rapidly evaporated leaving solid particles prior to entering the collection system. Spray

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[106] R. G. Manley. "Chemical weapon agent and historic chemical munitions disposal: The British experience", in *The Challenge of Old Chemical Weapons and Toxic Armament Wastes,* T. Stock and K. Lohs (Eds.), Stockholm International Peace Research Institute, Oxford University Press (1997).

dryer absorbers are large cylindrical chambers into which a finely atomized absorbent, typically a lime slurry, is sprayed into the gas stream containing acid gases. The acid gases react with atomized slurry droplets and form solid reaction products, such as calcium chloride. The emerging gas stream is usually sent to a high-efficiency particulate collector such as a fabric filter or dry electrostatic precipitator.

Particulate removal

8. Particulate removal is usually accomplished by wet scrubbers, electrostatic precipitators, or fabric filters. A small droplet diameter and high relative velocity between the particle and water droplet are required in conventional wet scrubbers in order to achieve a high-particulate collection efficiency. In a venturi scrubber, this is achieved by introducing the scrubbing liquid at an angle to a high-velocity gas flow in the venturi throat. Water is typically injected into the venturi in quantities ranging from 22 to 55 L per 285 hL of gas. Very small water droplets are formed, and high relative velocities maintained until the droplets are accelerated to their terminal velocity. Gas velocities through the venturi throat typically range from 60 to 160 m/s. The velocity of the gases causes atomization of the liquid, and the particulate is encapsulated by the droplets. The energy expended in the scrubber is accounted for by the pressure drop of the gas stream in the scrubber. Particulate collection efficiency is directly proportional to this gas stream pressure drop. The venturi itself needs to be followed by a separating section for the elimination of entrained droplets from the flue gas.

9. An electrostatic precipitator requires that an electric charge be induced on the particulates by means of a discharge electrode system, thereby forcing the charged particles to accumulate on the oppositely charged collection plate system. From time to time, the collected particles must be shaken or knocked off the plates in a dry electrostatic precipitator. In a wet system, the collected particulate matter is washed continuously off the plates by a thin film of water flowing over the plates.

10. Fabric filter dust collectors are among the oldest and most widely applied high-efficiency particulate emission control devices. The universal principle of operation is the removal of particulates from particulate-laden gas by passing the gas through a filtration medium, normally a fabric. The cleaned gas emerges from one side of the filtration medium, while the particulate is collected onto the other side. Subsequently, the collected particulates are removed from the fabric. The fabric filter is often used as a particulate control device with spray dryer acid scrubbers, although electrostatic precipitators can also be used either instead of or in series with the fabric filter.

Activated carbon filters

11. Activated carbon bed filters are widely used in the chemical industry to recover low-concentration chemicals from dilute gas streams and are also used to control volatile organic emissions from production processes. In the mid-1980s, carbon bed filters were used to clean up effluent-gas streams from coal-fired utility boilers, hazardous waste incinerators, and municipal waste incinerators [107]. Carbon bed filters not only remove gaseous pollutants, they also act as a filter to remove particulates. The available data from carbon bed filters used on incinerators in Europe has shown that emissions of particulates, acid gases (hydrogen chloride and sulfur dioxide), mercury, and dioxins and furans were reduced to levels near or below detection limits.

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[107] National Research Council, Committee on Review and Evaluation of the Army Chemical Stockpile Disposal Program. *Carbon Filtration for reducing Emissions from Chemical Agent Incineration,* Appendix C, pp. 70–71, National Academy Press, Washington, DC (1999).

Pollution abatement system

12. It is useful to consider how the gaseous effluent may be treated prior to release by considering the U.S. baseline incineration process. In this, the effluent from the liquid incinerator, the deactivation furnace system, and the metal parts furnace goes to identical and dedicated separate pollution abatement systems for the removal of gaseous pollutants and particles to meet emission standards. Each pollution abatement system (see Fig. 6) consists of a quench tower, a venturi scrubber, a packed-bed scrubber, a mist-eliminator vessel, and an induced draft blower [108].

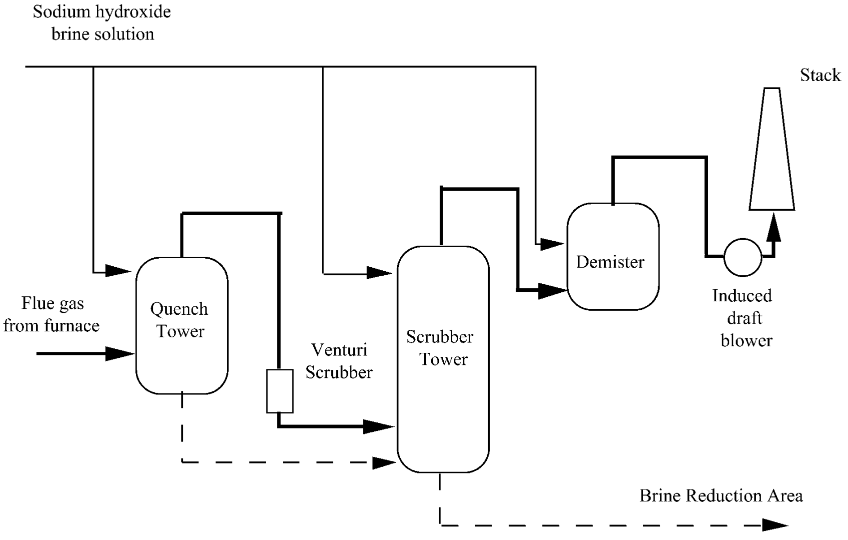

Fig. 6 Pollution abatement system.

The exhaust gas enters the quench tower near the bottom, where it is cooled by contact with a countercurrent spray of caustic brine containing sodium hydroxide with a pH at above 8 or 9 pumped from the packed-bed scrubber pump. Acidic gases (such as hydrogen chloride, hydrogen fluoride, nitrogen oxides, carbon dioxide, and sulfur dioxide, depending on the chemical agent being destroyed) in the exhaust gas react with caustic brine to form salts, which remain in solution in the brine. The cooled gas stream exits from the top of the quench tower and enters a variable-throat venturi where it is scrubbed to remove particulates. The venturi uses a variable throat to maintain a constant pressure drop independent of the flow of exhaust gases. The brine streams from the quench and the venturi scrubber are returned to the scrubber tower sump. An 18 % sodium hydroxide solution is added as necessary to maintain the brine pH at above 8 or 9.

13. The exhaust gas stream from the venturi scrubber enters the packed-bed scrubber tower below the clear liquor reservoir tray, moves upward through the packed-bed section, and exits at the top of the tower, after passing through a mist-eliminator pad. In the packed-bed section, the gas stream comes in contact with a brine solution flowing concurrently through the bed. Acidic gases in the exhaust gas stream are further scrubbed with caustic brine. The brine solution from the packed-

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108. National Research Council, Committee on Review and Evaluation of the Army Chemical Stockpile Disposal Program. *Review of Systemization of the Tooele Chemical Agent Disposal Facility,* pp. 93–94, National Academy Press, Washington, DC (1996).

bed section falls back into the reservoir tray and is recycled back to the top of the packed-bed section. Excess brine overflows into the tower sump.

14. The scrubbed gases then enter a candle mist-eliminator vessel. Mist-eliminator candles—candle-shaped fabric filters—remove very fine mist and submicron particulate matter that was not removed in the venturi scrubber. The cooled and cleaned exhaust gases are pulled through an induced draft blower located upstream of the stack shared by the three pollution abatement systems. In tests carried out at JACADS, particulate emissions from the three disposal furnaces were consistently low. The mean particulate concentration for all trial burns was less than 5mg/m^3—well below the permitted level of 180 mg/m^3. In a later report [109], it is stated that the JACADS and TOCDF incineration systems have been extensively tested, and the results have consistently shown that emissions regulated under the Clean Air Act, as well as trace emittants, are either the lowest or among the lowest in the EPA's Hazardous Combustor Waste Emissions Database.

B. Liquid

15. Agent oxidation produces water along with other products. In addition, water is used in various stages in the baseline process, as well as in the pollution abatement system in the U.S. baseline incineration technology. Designs for zero liquid water discharge are increasingly being adopted for industrial plants that work with hazardous chemicals. This is also the case in the baseline incineration technology where water discharge as vapor in the flue gas makes liquid water recycling unnecessary. In some of the alternative technologies, such as neutralization, there are significant quantities of water used necessitating treatment. There are three such techniques considered here:

    I. Supercritical water oxidation (SCWO)
    II. Biodegradation
    III. Advanced oxidation processes (AOP)

    Each is considered in turn.

I. Supercritical water oxidation (SCWO)

Process description

16. Chemical agents can be disposed of with technologies based on chemical neutralization. This destruction process results in the production of a solution called "hydrolysate" that retains some undesirable characteristics and requires further treatment in order to comply fully with the requirements of the CWC. The composition and potentially viable treatment alternatives for each hydrolysate varies based on the type of agent and the neutralization process selected. Supercritical water oxidation (SCWO), while technically viable for the destruction of neat agent, is also appropriate for the further treatment of hydrolysate to meet the requirements for safe aid environmentally acceptable disposal. SCWO has been selected for the treatment of the hydrolysate from the nerve agent VX stored at the Newport, Indiana storage site [110]. The SCWO system is a hydrothermal process for the oxidation of hydrolysate that yields a wastewater stream and salts.

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[109] National Research Council, Committee on Review and Evaluation of the Army Chemical Stockpile Disposal Program. *Carbon Filtration for reducing Emissions from Chemical Agent Incineration,* Appendix C, p. 16, National Academy Press, Washington, DC (1999).

[110] National Research Council, Committee on Review and Evaluation of the Army Chemical Stockpile Disposal Program. *Using Supercritical Water Oxidation to Treat Hydrolysate from VX Neutralization*, p. 7, National Academy Press, Washington, DC (1998).

17. In a typical chemical agent destruction process, agent would be drained from the weapon or container, hydrolyzed in a well-stirred reactor, tested to verify agent destruction, and then released to the SCWO process unit. The hydrolyzate is heated and pumped into an SCWO reactor along with an oxidizing agent (air or oxygen), and the heat of reaction increases the temperature to 600 to 650 °C under about 275 bar pressure. In the course of about 30 s, the organic components are largely (about 99.99 %) oxidized to water and sodium salts, as well as gaseous nitrogen-containing products (e.g., N_2 and NO_x). This mixture of materials is cooled by adding quench water and through heat exchange and then released from the SCWO reactor through a pressure reduction system. The resulting effluent is a mixture gases (O_2, N_2, CO_2), a concentrated aqueous salt solution, and entrained solid salts. Trace concentrations of partially oxidized organic constituents may also be present.

18. The aqueous products from the SCWO reactor, including entrained solids, are then fed to the evaporation unit, where the mixture is heated to distill excess water. At this point, the salts that have crystallized from solution are filtered and packaged for disposal in a secure landfill. A large portion of the water distilled from the SCWO effluent is recycled back to the process. All gases reduced during the SCWO treatment step are filtered prior to release using activated carbon to remove any residual volatile organic contaminants.

Scientific principles

19. SCWO technology involves operations above the critical temperature and pressure of pure water (Tc = 374 °C, Pc = 221 bar), which significantly alters the properties of water. At supercritical conditions, organic compounds that are insoluble at ordinary temperatures usually become more soluble, whereas salts that are soluble at ordinary temperatures become much less soluble. Thus, organic materials in supercritical water can be rapidly oxidized using air or oxygen to produce fully oxidized species, with the salts precipitating out.

20. The reaction mechanisms for the destruction of organic compounds by SCWO generally involve free-radical chain reactions with oxidative radicals, mostly OH and OOH. Thermal bond cleavage and polar or ionic reactions, including hydrolysis, also occur under these severe conditions. With residence times of seconds to minutes at temperatures of 400 to 650 °C, very high destruction efficiencies (>99 to 99.9999 %) have been reported for the destruction of a large number of organic compounds. Aqueous organic wastes with sufficient fuel value can be self-sustaining in that they can maintain the necessary reaction temperatures for extensive oxidation without supplemental fuel.

Technology status

21. In the last two decades, SCWO technology has evolved from the bench-scale treatment of certain organic hazardous wastes to limited, modest-sized commercial operation. However, using this technology to treat chemical agent hydrolysate raises several challenges. These include the reaction kinetics, full-scale reactor design, the management of the large volumes of salts generated, and corrosion problems associated with the fluid streams and salt deposits.

22. SCWO technology has matured to one current and several pending full-scale operations. Although it has been tested on a laboratory scale for treatment of a wide variety of wastes ranging from hazardous waste to sewage sludge, pilot-scale testing for the treatment of more complex wastes (e.g., heterogeneous wastes, wastes containing high concentration of heteroatoms that generate salts, and corrosive wastes) has been limited. Wastes characterized by high salt or salt-producing content and corrosivity during treatment have presented major technological challenges.

23. The implementation of SCWO technology has evolved into three basic reactor configurations and two approaches to temperature and pressure reduction after reaction at supercritical conditions. The three basic reactor configurations are tubular, vertical cylindrical, and transpiring wall. All three configurations mix the reactants [waste, supplementary fuel (if necessary), and oxidant] at the entrance or in the uppermost zone of the reactor.

24. Both the vertical cylindrical and the transpiring wall configurations have been demonstrated at pilot-scale for the treatment of chemical agent hydrolysate and similar wastes. Tubular reactors utilize relatively small-diameter, high-pressure tubing with long lengths (about 3 cm diameter × 36 m) to achieve the required residence times for reaction. The relatively high flow velocities (e.g., 1 m/s) could be helpful for moving precipitated salts along. However, the long reactor lengths are usually oriented horizontally with several passes (i.e., U-bends) or spirals. The narrow inner diameter and the bends in these configurations make them less desirable for systems at pressures of approximately 400 bar and with high-salt loadings because of the presence of a solid salt phase and the possibility of salt deposition and plugging. The vertical tubular reactor has a larger diameter and much shorter length (9 to 25 cm diameter × 2 to 5 m length) to achieve the residence time required for reaction.

25. The inner wall of a transpiring wall reactor is formed of layers of porous platelets that allow the continuous transpiration of deionized water at 315 °C, below the critical temperature, through an exterior plenum and then through the inside wall of the reactor during the SCWO reaction. This inner transpiring wall is contained within a conventional outer wall. The injection of transpiration water during operation is intended to separate the SCWO working fluid, at 780 °C and 238 atm from the inside surface of the reactor, which is kept at the transpiration water temperature of 315 °C. This reactor technology is believed to have the following advantages over conventional-wall SCWO reactors:

    - Contact between the working fluid and the reactor wall is reduced, thereby minimizing corrosion.
    - Deposition of salt on the reactor wall is essentially eliminated.
    - The cooled reactor wall allows higher working-fluid reaction temperatures, reducing the residence time necessary for complete oxidation.

    The cooler transpiration water (315 °C vs. 780 °C for the working fluid) is intended to dissolve any inorganic salts that reach the reactor wall and carry them to the bottom of the reactor, where, together with other reactor contents, the reaction mixture is quenched and collected. The design is intended to prevent the deposition of inorganic salts and plugging.

26. Using SCWO to treat chemical agent hydrolysate raises many challenges. The operating conditions (temperature, pressure, and residence time) for the destruction of key bonds, e.g., carbon–phosphorus bond, combined with the transition from alkaline to acidic composition during oxidation of the hydrolysate components, creates severe requirements for the materials of construction to prevent corrosion. In addition, the large amount of inorganic salt-producing elements present in the original agent and added during the neutralization process (sodium as sodium hydroxide) require that a high solids content fluid be managed in and downstream of the SCWO reactor. Experience has shown that salts that are insoluble in the SCWO reactor fluid phase have a propensity to adhere to the reactor walls, which can cause reactor plugging, and to erode the components of pressure let-down systems. These problems have been overcome for the treatment of other wastes. However, the composition of chemical agent hydrolysate is significantly different from other wastes treated by SCWO technology. Pilot-scale testing of SCWO technology specifically for the treatment of chemical agent hydrolysate has been carried out using a vertical

cylindrical reactor both with surrogates for the hydrolysate and with actual chemical agent hydrolysate. Active research, development, and testing programs are currently underway with the intention of enabling SCWO to be scaled up for corrosive, high-salt, full-scale applications

Stability, reliability, and robustness

27. Because a fundamental understanding of the fluid dynamics, mixing processes, and reaction kinetics occurring in a SCWO reactor does not exist, process scale-up has been based on reactor residence time, engineering judgement, and significant pilot-scale testing. This empirical approach to scale-up is especially important for complex systems, like chemical agent hydrolysate, that contain large quantities of salt and may have several phases. For example, mixing of materials in the reactor is important; cold feed needs to mix with hot product to bring the material to reaction temperature; solids condensed from the gas will impinge on, and may stick to, the reactor walls or other surfaces. There is no good way to extrapolate these complex flow effects from smaller to larger scale.

28. The key areas of concern for scale-up application of SCWO to chemical agent hydrolysate are: (1) salts management and solids handling; (2) the impact of the oxidant (e.g., air vs. oxygen) on mixing and heat balance; (3) corrosion of the materials of construction; and (4) reliability of pressure let-down systems. A better understanding of the design, engineering, and operational implications of these issues is also critical for demonstrating the stability and reliability of the full-scale process.

Monitoring

29. The use of a new technology, such as SCWO, as the final step for the destruction of agent hydrolysate requires the development of process monitoring and control strategies that are tailored for the new system. While not all of the monitoring requirements have been fully defined, continuous monitoring of reactor temperature and pressure profiles, salt removal, as well as of flow rates (which determine residence times), will clearly be necessary for SCWO process until pilot-scale SCWO demonstration studies on chemical agent hydrolysate have clearly shown that failure to maintain design pressure and temperature will result in decreased destructive removal efficiency.

Safety considerations

30. Process safety requirements are based on the nature of process reagents and products and the potential for process failure modes that could result in harm to workers or the surrounding population.

31. The primary process hazard is associated with high-pressure fluids in the SCWO system. Failure of the pressure containment system (piping, SCWO reactor, postreactor air cooler, or pressure let-down system) could result in rapid depressurization and the dispersal of hot fluids and debris at high velocities. Similarly, failure of the pressure let-down system could result in a large pressure surge that could rupture equipment downstream. Protection from the failure of the pressure-containment systems is provided by (1) an adequate safety margin in system specifications (e.g., piping and pressure vessels); (2) rupture disks or pressure-relief valves to prevent overpressurization of the SCWO reactor and high-pressure components; (3) rupture disks or pressure-relief valves immediately downstream of the pressure let-down system; and (4) depressurization capacity in the secondary containment, in the event of a sudden release of pressure through relief valves on high-pressure components.

Materials of construction

32. Materials of construction that can withstand the extreme pressures, temperatures, and often corrosive conditions within a SCWO reactor remain one of the key challenges for the broad imple-

mentation of SCWO technology. This is particularly true for the treatment of wastes that contain heteroatoms and generate significant quantities of oxyacids or their salts depending on the cations present in the system. Numerous studies have demonstrated that streams that contain chloride are especially corrosive. In general, it is believed (and some test results have corroborated) that salt solutions at intermediate temperatures (e.g., during pressure let-down or during heat-up, or near inlet or exit areas) can be much more corrosive than the supercritical fluid in the reactor. Erosion from precipitated salts at high velocities could also be an important issue. Materials of construction are an important consideration for the reactor inlet system, the reactor itself, and all hardware and plumbing downstream of the reactor (e.g., pressure let-down equipment and reactor exit plumbing).

Environmental impact

33. Process effluents from the neutralization/SCWO facility include: vent gases from the neutralization, SCWO, and evaporator units; liquid effluent from the SCWO; and crystallized salts from the evaporator/crystallization unit. These streams need to meet regulatory requirements for disposal.

34. Gaseous effluents from the SCWO unit can be filtered and released; solid wastes from the evaporator can be disposed of in a licensed disposal facility. Most evaporator condensate can be recycled within the facility, but some may be discharged periodically to a sanitary sewer system.

II. Biodegradation

35. Biodegradation exploits the ability of certain microorganisms—bacteria or fungi—to degrade hazardous organic materials to innocuous materials such as carbon dioxide, methane, water, inorganic salts, and biomass. Microorganisms can derive the carbon and energy required for growth through biodegradation of organic contaminants.

Process description

36. Bioreactor design for aerobic treatment needs to solve two problems. First, the bacteria must be in contact with the contaminants for extended periods of time to complete the biochemical reactions. Secondly, the design needs to ensure oxygen transfer to the bacteria. Energy requirements for oxygen transfer are usually the main operating cost of a bioreactor, other than manpower costs.

37. Available designs for biological treatment of organic constituents in agent destruction process streams, such as hydrolysate, are based on systems designed to treat wastewater. Bioreactors for treating contaminated water can be separated into several main types:

    - *Suspended-growth reactors.* The bacteria are grown in the water and intimately mixed with the organic contaminants in the water. Sequencing batch bioreactors fall into this category. Oxygen is supplied through a surface aerator or air diffusers.
    - *Fixed-film reactors.* The bacteria are grown on an inert support medium within the reactor. The contaminated water passes over the attached bacteria and forms a thin water film into which the contaminants and oxygen diffuse. The bacteria degrade the organic contaminants and the waste by-products such as carbon dioxide and water, diffuse into the water stream.
    - *Submerged fixed-film reactors.* In this version of the fixed-film reactor, the support medium is submerged in the water in the reactor tank. The water is in constant contact with the bacterial film, as opposed to passing through in thin water films.
    - *Reactors based on activated carbon.* The combination of powdered activated carbon and active bacteria increases the removal capabilities of the treatment system. The activated car-

bon adsorbs organic contaminants and acts as an attachment site for bacteria. Another design, a fluidized-bed reactor, is basically a submerged fixed-film system. The support medium consists of small-diameter particles. As water and air flow upwards through the medium, the bed is fluidized. Recently, activated carbon has been the main medium used in these systems.

The biodegradation of organic constituents in agent destruction process streams can be carried out either on site in coordination with the agent destruction process or off site at a commercial TSDF (treatment, storage, or disposal facility).

Scientific principles

38. Biodegradation is the use of microorganisms to destroy organic compounds in solution. Aerobic processes can result in the partial or total oxidation of the products from neutralization of chemical agents, although the structures of some organic compounds render them highly resistant. Oxygen is supplied, usually as air that is introduced into the reactor. Nutrients, such as nitrogen in the form of an ammonium salt, and a carbon source, such as glucose, are often added. The key requirement is to match the microorganisms used in the biodegradation to the constituents of the waste stream.

Technology status

39. Sequencing batch reactors (SBRs) have been used for full-scale treatment of industrial wastewater streams for several years. An SBR is a large tank that has piping for the injection of air, feedstock (the hydrolysate), and inorganic nutrients; a manifold for the withdrawal of settled sludge; a floating intake on an articulated arm, which is used to withdraw clear supernatant liquid; and a circulating pump to agitate the contents of the reactor.

40. SBRs have been selected by the U.S. Army for biodegradation of the mustard hydrolysate, which primarily contains thiodiglycol, at Aberdeen, Maryland [111]. After neutralization, the hydrolysate would first be passed through an air stripper used to remove volatile organic compounds prior to biotreatment and then, after adding nutrients (including aqueous ammonia, phosphoric acid, potassium chloride), adding 18 % sodium hydroxide to raise the pH, thereby increasing the biodegradability, and dilution, fed into an SBR.

41. SBRs are semibatch biological reactors that operate in several different states during a complete reaction cycle. During start-up, a bacterial culture that has either been adapted to grow on thiodiglycol, the principal hydrolysate constituent, or that comes from a wastewater treatment facility is added to the reactor tank. During the first step in the reaction cycle, the hydrolysate diluted with additional water and supplemented with inorganic nutrients and sodium bicarbonate for pH control is pumped into the reactor tank. The filling process is carried out in the presence of air over a period of about 5 h. Mixing and the addition of air initiates microbial oxidation of the thiodiglycol and other organic compounds in the hydrolysate. The major products are water, carbon dioxide, and bacterial cell mass; traces of methane may be evolved. During this aerobic phase, the sulfur in the thiodiglycol is oxidized to sulfate. The air injection is continued for about 17 h at which point greater than 99 % of the thiodiglycol and 90 % of the total organic carbon in the hydrolysate have been oxidized. The air injection and circulation are then stopped, and the solids in the reactor are allowed to settle. The clear liquid at the top is decanted, and some of the

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[111] National Research Council, Committee on Review and Evaluation of the Army Chemical Stockpile Disposal Program. *Integrated Design of Alternative Technologies for Bulk-Only Chemical Agent Disposal Facilities,* National Academy Press, Washington, DC (2000).

settled sludge is pumped out through the manifold at the bottom of the tank. The residual liquid and sludge are left in the tank for a fresh cycle of reactions. The cycle of filling, reacting, and decanting is repeated every 24 h. The residence time for the liquid contents in the SBR is about 10 days; the residence time of the solids is about 15 days.

42. The relatively clear liquid decanted from each SBR is sent to a water recycling facility. The sludge withdrawn from the bottom of the SBR is sent to a pair of aerobic digesters for further biotreatment. Polymers to facilitate dewatering are added to the digested sludge in a drum thickener, after which the sludge is dewatered in a filter press. Water exuded from the press is either sent for recycling or discharged. The solid residue from the filter press, the filter cake, is disposed of in accordance with standard disposal practices for dewatered sludges from biological wastewater treatment. The filter cake from hydrolysate treatment may be disposed of at a TSDF, probably in a landfill, or it could be delisted and disposed of as a nonhazardous solid waste. In the past, the hydrolysate from bench-scale neutralization and the aqueous effluent from bench-scale bioreactors treating the hydrolysate have been delisted, i.e., allowed to be disposed of as a nonhazardous waste.

Stability, reliability, and robustness

43. Bioreactors have proven to be stable when properly operated. Possible improper operations include an upset in a feed (air, nutrients, or hydrolysate) or improper mixing. Because several SBRs are used in parallel, a failed reactor could be readily restarted with biomass from another operating SBR.

44. The SBRs can be filled and started up using either the hydrolysate or a surrogate material to establish an equilibrium composition and distribution of microorganisms, and to stabilize functioning support systems such as the various nutrient feed streams. Tests have shown that no further acclimatization of the microbial population is required prior to introducing the hydrolysate for biodegradation.

45. Although the bioreactors must continue to operate to maintain their active microbial populations, several SBRs will be operating in different phases, providing flexibility in operational modes. Further, the feed to each SBR can be shut off for a short time without significantly harming the microbial population. Alternative feeds can be provided to maintain the population during more extended shutdowns.

Safety considerations

46. Biodegradation is generally perceived to be a publicly acceptable approach to the destruction of wastes. The operating temperature is near ambient, precluding the formation of chlorinated dioxins and furans. Biodegradation is used to treat sewage in many countries, and the safety and reliability of this technology are taken for granted.

Environmental impact

47. The principal uncertainty in respect of biodegradation relates to the ability of the microorganisms in the bioreactor to degrade all the organic materials in the hydrolysate. The nature of these may change from time to time as a result of variations in the composition of the agent being destroyed. The filter cake will need to be disposed of at a TSDF or delisted and disposed of as a nonhazardous solid waste.

III. Advanced oxidation processes (AOPs)

Process description

48. Advanced oxidation processes (AOPs) represent a relatively new class of industrial wastewater treatment technologies that permanently destroy organic contaminants in the waste stream. AOP,

also referred to as ultraviolet (UV) oxidation or photochemical oxidation, combines ultraviolet light with an oxidant such as hydrogen peroxide and/or ozone to form hydroxyl radicals, powerful oxidizers capable of increasing rates of reaction by several orders of magnitude over UV light or peroxide/ozone alone.

49. AOPs that combine hydrogen peroxide with UV light to produce hydroxyl radicals generally consist of a reaction vessel that houses one or more oxidation chambers, and a hydrogen peroxide feed unit. Oxidation chambers are configured in a shell- and tube-type arrangement, incorporating a UV lamp encased in a quartz tube at the center of the chamber. Contaminated water is passed through the chamber in the annular space between the quartz tube and the chamber wall, while hydrogen peroxide is either metered into the waste stream ahead of the unit or is combined with small amounts of treated water from the reactor effluent and split into each of the oxidation chambers.

50. In UV/ozone and UV/ozone/peroxide AOP systems, ozone gas is first generated in an off-line unit, typically by transmission of an electrical current through either air or oxygen gas. The resulting ozone is introduced to the waste stream through diffusers located in the oxidation chamber. The process by which hydroxyl radicals are generated in UV/ozone/peroxide systems is more complex than that of systems incorporating UV/peroxide alone, as excess ozone reacts with intermediates formed by the reaction of hydrogen peroxide and water and with the hydroxyl radicals. Unlike UV/peroxide systems, UV/ozone/peroxide systems rely more heavily on these intermediate chemical reactions to effect hydroxyl radical formation than by direct photolytic reaction with UV light.

51. The ozonized gas-to-liquid flow rate is a critical operating variable in UV/ozone and UV/ozone/peroxide systems, as it will impact the mixing regime within the reactor and can thereby affect reaction kinetics. Furthermore, excess turbulence caused by excessive gas-to-liquid ratios can result in stripping of volatile organic contaminants to the gas stream, defeating the benefits of the destruction process. Although catalytic ozone decomposition units are used on UV/ozone and UV/ozone/peroxide units to remove excess ozone released from the reactor, this equipment is not necessarily effective for treatment of residual contaminants.

Scientific principles

52. In advanced oxidation processes, the primary treatment mechanism involves the reaction of UV light with hydrogen peroxide or ozone to generate highly reactive hydroxyl radicals (OH) as shown below:

$$H_2O_2 + \text{UV light} \Rightarrow 2OH$$

The UV light also serves as an “activator” by initiating destruction of robust organic molecules to less-stable forms that are more amenable to oxidation. The hydroxyl radicals then effect a series of contaminant-specific oxidation-reduction reactions, which when carried to completion result in conversion of the contaminant molecules to carbon dioxide and water, as well as ions (such as halides) previously bonded to the contaminants, a portion of which may recombine with free hydrogen ions in the form of the conjugate acid. This oxidation can be greatly enhanced by the additive of catalysts, which increase the efficiency of the UV light reactors.

53. The technology is applicable to treatment of a range of organic contaminates such as chlorinated alkenes, phenols, *N*-containing organic substances, aromatics, ketones, alcohols, and alkanes. As indicated, chlorinated alkenes, phenols, and *N*-containing organic substances react faster principally due to the presence of double bonds within the molecular chain and other characteristics that make these compounds susceptible to oxidation. In contrast, the chlorinated alkanes are straight-chained, single-bonded molecules and react more slowly.

Technology status

54. UV-oxidation treatment alternatives are currently available in the environmental market. Processes are patented and marketed under strict adherence to specific operating conditions and equipment requirements.

55. As a sole treatment technology, AOP has been used primarily in the treatment of groundwater containing volatile organic contaminants (VOCs), a function of the large number of sites exhibiting this type of contamination as well as the benefits of AOP treatment over other VOC remediation alternatives. Treatment of PCB-contaminated waters is another area in which AOP has distinct advantages over other remediation processes. As regulators frequently limit discharge concentrations of PCBs in the final effluent to part-per-trillion levels, conventional methods of PCB treatment such as with granular activated carbon (GAC) may require long residence times, necessitating large and costly carbon beds. In addition, GAC cannot be regenerated through conventional steam stripping, requiring incineration or disposal of the spent carbon.

56. A common complaint about AOPs is the high capital cost associated with the equipment. Implementation of advanced oxidation treatment can be made more cost-effective when the process is combined with other forms of treatment to effect the contaminant removal goals than when it is used as a sole treatment technology. For example, installation of AOP as a polishing step to remove low concentrations of organic substances to regulate discharge levels following chemical hydrolysis or other primary treatment technologies generally require shorter reaction times and less oxidant than an AOP system designed to remove the full organic load, reducing the capital cost for the AOP treatment unit and the operational costs for power and oxidant supply.

Stability, reliability, and robustness

57. Inorganic materials associated with scale formation can adversely impact treatment efficiency. Metals such as iron, manganese, and calcium may precipitate out of solution and coat the quartz sleeve housing the UV lamp, reducing ultraviolet light transmission and treatment efficiency. Similarly, high turbidity levels caused by suspended metals in the influent waters will also impede UV light transmission, and can react with hydroxyl radicals to decrease treatment efficiency. The temperature of the influent water can be an issue for ozone-based systems, as ozone will decompose to oxygen gas to temperatures above 50 °C, reducing hydroxyl radical formation efficiency [112].

Monitoring

58. Both types of systems—systems using only UV/hydrogen peroxide and systems using UV with ozone or ozone and peroxide—incorporate control panels to monitor and/or regulate key operating variables such as flow rate, UV lamp intensity, temperature, and oxidant feed rate. In addition, some systems provide automatic tub cleaners consisting of scrubbers that periodically wipe the quartz tubes clean of precipitated solids, films, etc., so that UV light transmission is not impeded.

Safety considerations

59. Regulatory and safety issues to consider when designing an AOP system extend to both the reactor equipment and the oxidant. Aside from regulations governing clean-up goals and discharge

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112. U.S. Army Corps of Engineers. *Design Considerations for Ultraviolet/Chemical Oxidation Engineering Technical Manual*, Contract No. DACW45-93-D-0025. USACOE, Omaha, NE, October 1994.

requirements, certain States enforce chemical bulk storage regulations that may require peroxide tank registration, secondary containment, leak detection monitoring, etc. Additionally, in the United States, for example, concentrated hydrogen peroxide is considered hazardous by OSHA definition and is therefore subject to employee notification and training requirements and, if stored in quantities greater than 10 000 lb, emergency planning and reporting requirements. Systems using ozone may also require an air emissions permit.

60. Engineering controls and contingency measures that needs to be considered when designing and implementing AOP systems include: the need for adequate ventilation of the process enclosure, particularly for UV/ozone and UV/ozone/peroxide systems; installation of the equipment in an area suitable for high-voltage equipment and specification of safety interlocks on the main power panel of the unit; and provisions for an eyewash station and safety shower for systems using hydrogen peroxide. The manufacturer should also equip the unit with safety interlocks on the UV lamp enclosures to de-energize the system when the enclosure door is opened as well as UV light filters on all oxidation chamber reaction ports to minimize the potential for accidental exposure to UV radiation.

Environmental impact

61. Effluent goals are dictated by several factors, including regulatory requirements for discharge and/or the need to achieve specific contaminant concentrations prior to post-treatment in a downstream treatment unit. In addition, other effluent qualities may also need to be addressed, such as limitations on peroxide concentrations or temperature limitations. Some residual hydrogen peroxide should be measured in the reactor effluent from UV/peroxide AOP units to ensure that the destruction reaction is not being limited by insufficient hydroxyl radical formation. This can lead to elevated dissolved oxygen concentrations in the receiving waters, which may be problematic in some situations. Furthermore, the UV lamps generate significant heat and can add several degrees of temperature to the water as it passes through the reactor, a potential drawback where thermal discharge limitations are a concern. Fortunately, all these are readily manageable by designing the system in a batch mode and employing a test-prior-to-release step.

C. Solid

62. The composition of chemical agents is such that some processes, e.g., incineration, SCWO, will have residual salts in the effluent steams. In general, this will require evaporation (drying) to concentrate the salts into a manageable waste stream. In biological treatment processes, biomass filter cake will result. In many proposed processes, granulated activated carbon (GAC) is used to scrub vent-gas steams. Thus, GAC, potentially contaminated with agent, needs to also be managed. Finally, some neutralization approaches employ reaction of the chemical agent with an organic reagent and subsequent incorporation of the products into a bitumen mass. In all cases, the resultant solid needs to be landfilled, or in the case of GAC, burned. Since frequently the salts and biomass may also contain heavy metals and trace organic substances, proper disposal of this solid waste to protect public health and the environment is essential. Depending on the nature of the solid and its leaching characteristics, additional treatment prior to disposal may be required. This treatment is likely to involve stabilization and solidification.

63. Stabilization and solidification are generic names applied to a wide range of discrete technologies. These technologies, i.e., stabilization and solidification, are closely related in that both use chemical, physical, and/or thermal processes to reduce potential adverse impacts on the environment from the disposal of hazardous waste. But, they are distinct technologies.

64. Stabilization refers to techniques that reduce the hazard potential of a waste by converting the contaminants into less-soluble, mobile, or toxic forms. The physical nature and handling characteristics of the waste are not necessarily changed by stabilization.

65. Solidification refers to techniques that encapsulate the waste, forming a solid material. The product of solidification, often known as the waste form, may be a monolithic block, a clay-like material, a granular particulate, or some other physical form commonly considered "solid". Solidification as applied to fine waste particles is termed microencapsulation, and that which applies to a large block or container of wastes is termed macroencapsulation. Solidification can be accomplished by a chemical reaction between the waste and solidifying reagents or by mechanical processes. Contaminant migration is often restricted by decreasing the surface area exposed to leaching and/or by coating the wastes with low-permeability materials.

66. Stabilization chemistry is similar to wastewater treatment, but the waste to be treated is usually soil, sludge, or similar material. Stabilization processes can treat wastes containing metals (and occasionally, other inorganic species such as cyanides) or organic contaminants, and often both in the same waste. The chemistry involved is, however, different for the two contaminant types.

67. Cementitious stabilization and solidification technologies use inorganic reagents to react with certain waste components; they also react among themselves to form chemically and mechanically stable solids. Cementitious binders and other additives react in a controlled manner to produce a solid matrix. The matrix itself often is or becomes, a pseudo-mineral. This type of structure is stable and has a rigid, friable structure similar to many soils and rocks.

68. A number of stabilization and solidification commercial processes are available to treat residual solid-waste streams. The process best suited to a specific solid-waste stream needs to be determined following evaluation of leaching characteristics from treatability studies. An excellent resource for guidance in selecting stabilization and solidification processes was recently published by the American Academy of Environmental Engineers [113].

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113. P. D. Kalb, J. R. Conner, J. L. Mayberry, B. R. Patel, J. M. Perez Jr. *Innovative Site Remedation Technology: Design and Application: Stabilization/Solidification*, Vol. 4, American Academy of Environmental Engineers, Annapolis, MD (1997).

IX. DEALING WITH OLD RECOVERED MUNITIONS

1. The large number of incidents that have resulted from the finding of old munitions, sometimes resulting in injuries or death, that have occurred since the end of World War II have amply demonstrated the risk that old chemical weapons pose to humans and the environment. Many European countries must deal continuously with newly discovered chemical weapons from World War I, the inter-war period, or World War II. For this reason, there is much more experience in dealing with old recovered chemical weapons in Europe than in the United States or elsewhere. A particular problem regarding the destruction of old recovered chemical weapons that is currently receiving considerable attention is in relation to the 700 000 or so chemical weapons abandoned by Japan in China. Following World War II and in the early 1950s, old chemical weapons were routinely disposed of by open-pit burning, burial, or dumping at sea. In 1972, the Oslo Convention for the Prevention of Marine Pollution by Dumping of Wastes and Other Matter dated 29 December 1972 [114] and amended on 12 October 1978 and 1 December 1980 prohibited sea dumping. Under the CWC, all of these methods of disposal are prohibited.

2. In the CWC, "*old chemical weapons and abandoned chemical weapons*" are defined as:

> *"Old Chemical Weapons" means:*
>
> *(a) Chemical weapons which were produced before 1925; or*
> *(b) Chemical weapons produced in the period between 1925 and 1946 that have deteriorated to such an extent that they can no longer be used as chemical weapons."*
>
> *"Abandoned Chemical Weapons" means:*
>
> *Chemical weapons, including old chemical weapons, abandoned by a State after 1 January 1925 on the territory of another State without the consent of the latter.* [115]

3. Part IV (B) of the Verification Annex sets out the requirements for the destruction of both old and abandoned chemical weapons. In respect of **old chemical weapons produced before 1925**, the significant requirement is that

> *6. A State Party shall treat old chemical weapons that have been confirmed by the Technical Secretariat as meeting the definition in Article II, paragraph 5 (a), as toxic waste. It shall inform the Technical Secretariat of the steps being taken to destroy or otherwise dispose of such old chemical weapons as toxic waste in accordance with its national legislation.* [116]

The logic in regarding these particular old chemical weapons as toxic waste will be apparent when it is recalled that the wide range of toxic chemicals used in World War I were generally available toxic chemicals or industrial chemicals which were used as chemical weapons and were not made expressly for this purpose.

4. In regard to **old chemical weapons produced between 1925 and 1946**, the principal consideration is whether or not they can still be used as chemical weapons. If the Technical Secretariat con-

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114. Oslo Convention for the Prevention of Marine Pollution by Dumping of Wastes and Other Matter, dated 29 December 1972 and amended on 12 October 1978 and 1 December 1980. Available at http://sedac.ciesin.org/entri/texts/marine.pollution.dumping.of.wastes.1972.html
115. CWC, Article II, paras. 5 and 6.
116. CWC, Verification Annex, Part IV (B), para. 6.

firms that they meet the definition in Article II, paragraph 5(b)—namely that they **have deteriorated to such an extent that they can no longer be used as chemical weapons**—then the requirement in the CWC is that

> *7. ...a State Party shall destroy old chemical weapons that have been confirmed by the Technical Secretariat as meeting the defintion in Article II, paragraph 5 (b), in accordance with Article IV and Part IV (A) of this Annex. Upon the request of the State Party, the Executive Council may, however, modify the provisions on time-limit and order of destruction of these old chemical weapons, if it determines that doing so would not pose a risk to the object and purpose of this Convention. The request shall contain specific proposals for modification of the provisions and a detailed explanation of the reasons for the proposed modifications.*

Other chemical weapons produced between 1925 and 1946 which do not meet the definition in Article II, paragraph 5(b) shall be destroyed in the same way as chemical weapons produced from 1 January 1946 onwards—in accordance with Article IV and Annex IV (A) of the Verification Annex.

5. For **abandoned chemical weapons**, the requirement is that these be destroyed. These will be treated in the same way as declared chemical weapons unless the Executive Council of the CWC agrees that the abandoned chemical weapons also meet the definition of old chemical weapons when the provisions for destruction may be modified so long as doing so "*would not pose a risk to the object and purpose of this Convention.*" [117]

6. Consequently, under the CWC there are essentially two principal categories of chemical weapons:

   a. Those declared by States Parties which are essentially chemical weapons or chemical warfare agents in the stockpile of that State, and which have to be destroyed during the period commencing two years after entry into force of the CWC for that State and being completed not later than 10 years after entry into force of the CWC, i.e., by 29 April 2007.

   b. Old chemical weapons that have been produced before 1925 which shall be destroyed as toxic waste.

7. Abandoned chemical weapons form an intermediate group which may be destroyed in the same way as stockpiled chemical weapons or possibly, with the agreement of the Executive Council, destroyed in the same way as old chemical weapons, as toxic waste. In effect, chemical weapons are either **stockpile** munitions or agents which are still in storage or **non-stockpile** munitions or agent which are buried often on battlefields, on present and past military bases, along transportation routes or dumped at sea. Insofar as **non-stockpile** munitions or agent are concerned, Article IV of the CWC also states that:

> *17. The provisions of this Article and the relevant provisions of Part IV of the Verification Annex shall not, at the discretion of a State Party, apply to chemical weapons buried on its territory, before 1 January 1977 and which remain buried, or which had been dumped at sea before 1 January 1985.*

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[117] CWC, Verification Annex, Part IV (B), para. 17.

Consequently, there is no requirement for States Parties to recover such buried or dumped chemical weapons, but should a State Party decide to recover them then they have to be destroyed in accordance with the requirements specified in the CWC.

8. A particular area in which chemical weapons have been dumped has been in the Baltic. During the 1990s, particular attention was given to these weapons by the Ad Hoc Working Group on Dumped Chemical Munition of the Baltic Marine Environment Commisssion of the Helsinki Commission (HELCOM CHEMU). A useful summary is provided in the Third Periodic Assessment of the State of the Marine Environment of the Baltic Sea, 1989–1993 [118], which states that around 40 000 tonnes of chemical munitions have been dumped in the Baltic Sea and that it has been estimated that these contained no more than 13 000 tonnes of chemical warfare agent. The assessment is made that "*Based on present knowledge, a widespread risk to the marine environment from dissolved warfare agents can be ruled out.... No detrimental effects on the marine environment due to warfare agents have been so far observed.*" More recently, the conclusions of the Fourth Periodic Assessment [119] make a general statement that "*concentrations of most of the hazardous substances monitored have decreased over the past 30 years in the whole of the Baltic marine area, although many of these still cause concern*", and in respect of chemical munitions say that "*dumped chemical warfare agents are not considered a widespread risk to the marine environment. However, a group at risk could be the crews of fishing vessels. Although the dumping areas are clearly marked on nautical charts, chemical munitions are occasionally caught in bottom trawls and hauled on board.*" As noted above, there is no requirement for States Parties to recover such dumped chemical weapons, but should a State Party decide to recover them, then they have to be destroyed in accordance with the requirements specified in the CWC.

9. In this section, attention is first given to how to deal with recovered chemical weapons—transportation, identification, removal of chemical warfare agents, destruction (including mobile destruction facilities), and transportation of toxic waste. The situation regarding the chemical weapons abandoned by Japan in China is then outlined, and a final section addresses the U.S. Army Non-Stockpile Chemical Materiel Project.

10. The technical approach that needs to be followed when dealing with old chemical weapons is different from that taken when dealing with stockpiled chemical weapons. It is not easy with old weapons to distinguish chemical munitions from high explosive (HE) munitions of the same time period. In addition, in some instances, the explosive charge train may still be active and not easy to remove. Finally, the contents of the chemical weapon are sometimes complex mixtures that have undergone partial decomposition.

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118. Baltic Marine Environment Protection Commission, Helsinki Commission. *Third Periodic Assessment of the State of the Marine Environment of the Baltic Sea, 1989–1993,* HELCOM, Helsinki (1996). Executive Summary available at http://www.baltic.vtt.fi/pdfs/bsep64a.pdf. Chapter 8.3, which addresses dumping of chemical munitions, is available at http://www.baltic.vtt.fi/
119. Baltic Marine Environment Protection Commission, Helsinki Commission, Fourth Periodic Assessment of the State of the Marine Environment of theBaltic Sea, 1994–1998, HELCOM, Helsinki, 2001. Executive Summary available athttp://baltic.vtt.fi/pdfs/bsep82a.pdf See also http://www.helcom.fi/

A. Transportation of old chemical weapons

11. In Germany, such chemical weapons are found scattered over a wide area. Transport from the location where the chemical weapon has been found to an interim storage area prior to destruction is carried out using sturdy, gas-tight containers that are coated to withstand subsequent aggressive decontamination, should that be necessary. Such containers need to be approved by the German Federal Authority that regulates the transport of dangerous goods and explosives. When old chemical weapons are moved to the temporary storage area, detailed arrangements are made with the federal police and environmental agencies about the route to be taken. Personnel trained in detection and decontamination, as well as medical support, accompany such transports.

12. More recently, in Germany, an explosive-proof vessel is regularly used for transportation of items that have an increased risk of explosion. Such a mobile explosion containment chamber (MECC) (Dynasafe, Sweden) is a medium-to-heavyweight vehicle with a high explosion containment capacity of 5 to 15 kg TNT, depending on the model. The MECC is mounted on a trailer/truck and has been developed for the safe transport of an explosive device from one place to another. The chamber is gas-tight, which means that in the event of a detonation, the detonation gases are retained within the MECC. A valve system can be used for the sampling of the gases inside the MECC or for connection to a waste-gas treatment unit.

13. Dynasafe explosion-containment vessels are designed as cylinders with flat or curved ends depending on the type of the chamber. For maximum safety, the chambers are designed as a double containment system with double steel walls. The space between the walls can be filled with a suitable liquid or gas. The chambers are also fitted with double doors where the inner door is designed to withstand the blast wave and the outer door designed as a gas-tight door. In the standard design, there are also double valves for gas sampling, drainage of the chamber, connection to a waste-gas treatment unit, release of gases to the atmosphere, and connections for decontamination liquids. Opening and closing of the doors and valves is controlled from the control panel, which has an interlocking system to ensure safety during operation. There are also systems to indicate whether there is a pressure within the chamber as well as video systems enabling the interior of the chamber to be monitored during transport. Loading and unloading of munitions into the chamber can be carried out manually or by remote control depending on the particular requirements. The size of the chamber is such that a considerable number of munitions can be transported simultaneously. The explosion-containment chamber, weighing from 10 to 45 tons, is mounted either directly on a heavy truck or on a trailer towed by a heavy truck.

14. In Belgium, unexploded fuzed chemical weapons are found on former battlefields (almost exclusively WWI) or test firing sites. Such chemical weapons are occasionally discovered during road or foundation works, but mainly in farm fields during normal farm activities. Sometimes shells are simply surfacing probably due to the freeze-thaw cycle and the related changes in the groundwater level in autumn or spring. In many countries such as Belgium, there is no active search program. Usually, the finding of such items is reported very much on a case-by-case basis to local authorities, who inform the EOD squad.

15. Transportation from the location in Belgium where the chemical weapon has been found to an interim storage area prior to destruction is carried out using light trucks or pick-up vehicles. Shells are immobilized on wooden box pallets using sandbags. The shell axis is perpendicular to the driving direction to avoid accidental functioning of the fuzes system by gravity forces, due to acceleration or braking of the vehicle. Personnel trained in detection and decontamination, as well as medical support, accompany such transportation.

16. In the United Kingdom, the routine recovery and disposal of old munitions is undertaken by explosive ordnance disposal (EOD) teams of the British Army. Should a suspected chemcial munition be discovered, these are suitably over-packed (placed in a steel container with an absorbent such as charcoal) and transported to the CBD Sector at Porton Down. On arrival, the munitions are carefully unpacked by personnel dressed in full protective clothing, including respiratory protection. After detailed examination, the munitions are placed in a special well-isolated storage area to await disposal.

B. Identification

17. Frequently, the unearthed munitions are corroded and covered with dirt. They have to be cleaned at the site where they are found prior to identification. If there is suspicion that the munitions are leaking, then a procedure is carried out to confirm whether this is so. Cleaning is done either manually by gently tapping with a small hammer or with CO_2 pellets under high pressure. To distinguish between chemical and high-explosive (HE) munitions, X-raying is a necessary step. A 400-kVA-powered system is usually sufficient for imaging the internal structure. This image is then compared with a database of old CW shells. Modern image processing systems enable the operator to compare the X-ray image with various images from the database on the screen and thereby decide whether 100 % identification as a chemical shell has been made. Frequently, further classification of the nature of the chemical warfare agent is possible: tilting the shell indicates whether or not the actual chemical fill is liquid or liquefied; the presence of an internal bottle indicates Clark I (diphenyl chloroarsine) or Clark II (diphenyl cyanoarsine), both solid agents, which are found in WWI shells.

18. Neutron activation analysis (NAA) techniques may provide further information on the elemental composition of shell contents; however, the decision as to whether to use NAA techniques is decided on a case-by-case basis. A type of decision tree also has to be developed in order to interpret the NAA spectra and thereby identify the chemical contents.

C. Removal of chemical warfare agents from munitions

19. Disassembly of old chemical weapons involves separation of the fuse and explosive charge from the rest of the shell. The chemical can then be drained or otherwise removed. This process has been carried out on a routine basis in Germany and in the United Kingdom since the early 1980s and in Belgium since 1998. The necessary equipment consists of drilling, milling, or sawing machines. These are contained in a bunker structure protecting the personnel from the effects of blast, fragments, toxic aerosol, or vapors, should an explosion occur during these operations.

20. In addition, in some countries, the compartments in which the dismantlement operations are carried out are maintained under a lower atmospheric pressure (ca. 50 Pa). The air from these compartments is filtered through a set of activated charcoal filters before being released to the atmosphere. Dismantling operations are constantly monitored and recorded on videotape for later evaluation of possible incidents. Drilling, milling, or sawing is done under remote control; however, the draining or otherwise removing of chemical agents, is carried out manually by operators. If shells contain gas under pressure (phosgene or hydrogen cyanide), then the gas is released through an aqueous solution containing caustic soda. Thereafter, the shell is milled to separate the fuse and burster from the rest. Shells containing liquid or solid agents are milled directly. After cutting the shell, the fuse and burster charge are removed, soaked in butanol for at least 24 h, and stored for disposal by detonation. In Germany, these components are decontaminated with calcium hypochlorite emulsion prior to demolition.

21. A literature search [120] indicated some 60 possible combinations of chemical agents that were used in World War I. At the old chemical weapons dismantlement facility in Poelkapelle (near Ypres, Belgium), some chemical agents are neutralized before intermittent storage prior to incineration at a waste incineration plant INDAVER near Antwerp in accordance with European standards [121]. This is a general-purpose incinerator that is used from time to time to incinerate chemical agents. It consists of a rotary kiln, kept at a minimum mean temperature of 1100 °C, and a post-combustion chamber for complete burning out of hazardous waste, at temperatures up to 1200 °C. The combustion gases then flow to a steam boiler where the heat, which is produced, is recovered and converted into electricity by means of a turbo-alternator. Next, dust is removed from the gases in an electrostatic filter, washed in a four-step gas-washing unit with various streams of chemicals to remove acid gases, and the gases are finally led through a dioxin filter and discharged through a chimney. The exhaust is continuously monitored for dust, CO, NO_x, SO_2, O_2, total organic carbon, and hydrogen chloride.

22. Mustard gas is neutralized and hydrolyzed using an aqueous ethanolic caustic solution whereas diphosgene (sometimes containing phosgene in solution) or chloropicrin are treated with an aqueous sodium hydroxide solution. These agents, together with Clark agents, are those most frequently found in the recovered old chemical munitions found in Belgium.

23. Agents other than mustard, phosgene, diphosgene, and chloropicrin are currently dissolved in about the same amount of butanol, which serves as combustible solvent for later incineration as toxic waste. Alternative methods are being developed to enable the toxic chemical content to be systematically neutralized.

24. Dismantlement and, in particular, the draining of chemical agents are operations that involve a high risk of contamination. Consequently, workers are required to wear protective suits. Two types of suits are used in Belgium: (1) a fully encapsulating suit comprising of underwear and an impermeable overgarment consisting of 14 layers of laminate [122] and (2) the NBC-protective suit. Both suits are worn with butyl rubber boots and butyl gloves and used with closed-circuit breathing apparatus with a compressed-air canister carried on the operator's back. Under normal working circumstances the NBC suit is worn, except when an incident has occurred or when the automated chemical alarm indicates mustard gas or Clark concentrations higher than 200 mg/cm^3. In that case, the operators are replaced by colleagues wearing the impermeable suit, however, at the expense of considerable heat stress. A 2-h limit is imposed for working in the multi-suit including the time taken for donning and doffing the multi-suit, which takes more than half an hour.

25. In addition to a short-term automated chemical alarm that triggers at 200 mg/cm^3, workers are also monitored for their long-term exposure to carcinogenic agents such as mustard. The long-

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[120] Coppee-Courtoy. "Studieovereenkomst inzake de vernietiging van toxische chemische afval opgestapeld in de installaties van de ontmijningsdienst van de Landmacht te Poelkapelle", Revisie A, 3 Augustus 1992, Ministeries van Volksgezondheid en Leefmilieu. (Coppee-Courtoy. "Study agreement on the destruction of toxic waste stored in the facilities of the explosive ordnance disposal units of the Army at Poelkapelle", Revision A, 3 August 1992, Ministry of Health and Environment).

[121] European Community Directive. *Directive 2000/76/EC of the European Parliament and of the Council of 4 December 2000 on the Incineration of Waste,* Official Journal, L 332/91, 28 December 2000. Available at http://www.europa.int.

[122] Chemrel Max GT, Chemron Inc., USA.

term exposure level for mustard is set at 0.2 μg/cm^3 (unprotected workers—exposure during normal work life) and is monitored by tenax tube sampling using portable air pumps.

26. In the United Kingdom, the most frequent filling found in the recovered chemical munitions is sulfur mustard, which is destroyed by incineration in a licensed hazardous waste incinerator at Porton Down [123].

D. Destruction including mobile destruction facilities

27. As noted above, destruction in Belgium, Germany, and the United Kingdom is carried out at licensed hazardous waste incinerators. In addition, attention has also been given in some countries to the use of mobile destruction facilities.

28. The mobile PLASMOX facility consists of three transportable containers (7.15 m long, 2.5 m wide, and 2.72 m high) which can be moved by road. The system has been tested for the destruction of small amounts (kg quantities) of CW agents showing that mustard, Clark, and lewisite are destroyed at a rate of 40 g/min.

29. The major components of this mobile system are as follows: the first of the three transportable containers has two feeding devices, a plasma melting and combustion chamber, a secondary combustion chamber, and a slag removal chamber; the second transportable container has an off-gas treatment, a dust-measuring device, and an off-gas emission control measurement system; and the third transportable container has the command and control unit.

30. The plasma torch uses the “transferred arc” system (much like an electric arc) using nitrogen as plasma gas and a power of 200 kW with typical voltages of 250–450 V and currents from 250 to 450 A; plasma torch temperatures as high as 15 000 °C are reached. In the hearth of the plasma system, vitrification of added sandy or glassy material occurs; in this smelt at temperatures between 1200 and 1400 °C, thermal decomposition occurs. To ensure full oxidation, oxygen is added during the feeding of the incinerables. The secondary combustion chamber is equipped with a propane-fired burner and is temperature-controlled. The combustion gases are kept at temperatures above 1200 °C for more than 2 s to ensure complete combustion/oxidation.

31. The off-gases are quenched by circulated cooling water and cleaned in an acid wet scrubber, followed by a basic wet scrubber. The off-gas stream is exhausted by a fan through a HEPA and a charcoal filter; this fan maintains a negative pressure in the whole system.

E. Transportation of toxic waste

32. Transportation of toxic waste from the contents of the shells and from the dismantlement operations is carried out in accordance with the requirement of the European Agreement Concerning the International Carriage of Dangerous Goods by Road (ADR) [124] (commonly abbreviated to

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[123] R. G. Manley. “Chemical weapon agent and historic chemical munitions disposal: the British experience”, in *The Challenge of Old Chemical Weapons and Toxic Armament Wastes,* T. Stock and K. Lohs (Eds.), Stockholm International Peace Research Institute, Oxford University Press (1997).

[124] European Agreement concerning the International Carriage of Dangerous Goods by Road (ADR), 30 September 1957. Available at http://www.unece.org/trans/danger/publi/adr/ADRagree_e.pdf. See also Restructured ADR applicable as from 1 July 2001 available at http://www.unece.org/trans/danger/publi/adr/adr2001/English/ContentsE.html

the ADR Convention). Each waste container is provided with an ADR-label indicating the hazardous chemical, pictograms showing the nature of the hazard, and information on the identity of the sender. A second label is added as required by the general national Rules for the Protection of Workers [125], which also contains information on the chemicals present and their hazard as shown by pictograms. Appropriate risk and safety warnings are also added.

F. Chemical weapons abandoned by Japan in China

33. Japan and China have been working together on these abandoned chemical weapons since China made a formal request to Japan in 1990 that Japan should dispose of these weapons. A Memorandum of Understanding was signed on 30 July 1999 between Japan and China on the destruction of abandoned chemical weapons in China [126]. The main points of the Memorandum include confirmation that huge amounts of abandoned chemical weapons that were owned by the former Japanese Army exist in China, that Japan will provide all necessary financial, technical, expert, facility, and other resources for the destruction of these chemical weapons and for the destruction of any chemical weapons that are confirmed to be of Japanese origin in the future and that Japan and China will consult together on the destruction of these abandoned chemical weapons. In addition,

> *The two governments will select mature destruction technology which is fully reliable in terms of destruction efficiency, safety and environment. Concrete types of destruction technology will be finally decided upon after being discussed and thoroughly examined by experts on both sides of the Japan-China Joint Working Group meeting, by methods of assured transparency and impartiality.*

It is also noted that "*utmost priority will be given to preventing the ecological environment of the People's Republic of China from being contaminated and to securing the safety of the personnel at work.*" Furthermore, it is stated that the two governments "*will adopt in principle the Chinese standards with regard to the environmental standards to be kept during the destruction operation, and have decided to conduct environmental-impact assessment and monitoring.*"

34. There appear to be some 20 sites in China at which chemical weapons were abandoned by Japanese troops when they returned to Japan in 1945. Some 14 sites have been excavated, and 6 are sites which have yet to be excavated. Another account [127] divides the abandoned chemical weapons sites into three categories:

- Group 1, in which 729 munitions are stored at 10 sites
- Group 2, in which over 4000 munitions are buried at 6 sites

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125. Algemeen Reglement op de Arbeidsbescherming. A series of leaflets issued by the Belgian Ministry of Labour and constantly being updated.
126. The Ministry of Foreign Affairs of Japan. *Signing of the Memorandum of Understanding between Japan and China on the Destruction of Abandoned Chemical Weapons in China,* 30 July 1999. Available at hyyp://www.mofa.go.jp/announce/annouce/1999/7/730.html
127. S. Hinata, Director-General, Cabinet Coordination Office for ACW, Japan. *ACW Destruction Project in China,* Proceedings of the CW Destruction Conference, Bournemouth, pp. 269–302, June 1998.

- Group 3, in which more than 674 000 munitions are estimated to be buried at 3 sites, including a site at Haerbaling estimated to contain 674 000 munitions with as yet unknown quantities at the other two sites

The biggest site is in the Haerbaling area, which is estimated, on the basis of excavations of two pits, as containing some 674 000 buried munitions. The other sites are widely dispersed with as much as 2000 km between two site locations. Further burial sites may be discovered in the future. The Japanese government has estimated that there are some 700 000 chemical weapons abandoned in China; a Chinese estimate is that the total number may be some 2 million chemical munitions. There are also indications that as many as 300 000 chemical munitions and 120 tons of bulk chemical agents have been recovered from these sites and destroyed or given preliminary treatment by China [128]. The types of chemical agent in the abandoned chemical weapons are shown in Table 9.

Table 9 Color coding of Japanese abandoned chemical munitions in China.

Color coding	Chemical agent
Yellow	Mustard H and mustard/lewisite
Red	Diphenylcyanoarsine (Clark I) DA Diphenylchloroarsine (Clark II) DC
Blue	Phosgene CG
White	Arsenic trichloride
Brown	Hydrogen cyanide AC
Green	Chloroacetophenone CN

35. An overall plan has been developed by the Japanese government in consultation with China [129], which is aimed at completing destruction by April 2007. Work has commenced on the excavation of sites: some 20 000 smoke canisters were recovered from Nanjing site in May 2000 and a further few thousand canisters await excavation at that site; some 3000 munitions were excavated from a site in Bei'an City (about 900 were chemical munitions); and plans are being made for the excavation at Haerbaling. Studies are being made into destruction technologies, which are focusing on destruction of yellow (mustard and mustard/lewisite) and red (Clark I and Clark II agents) munitions as these make up the majority of the abandoned chemical weapons.

36. Technical activities include development of a remote operation system for excavation, evaluation of the potential explosion risks from picric acid and picrates contained in the abandoned chemical weapons, and the examination of various elements of destruction technologies, including:

    - water-jet cutting to obtain data on efficiency and on safety in respect of picric acid/picrates;
    - cryogenic fragmentation to obtain data on efficiency and effectiveness and on safety in respect of picric acid/picrates;

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128. See, for example, information available at http://www.tcp-ip.or.jp/~e-ogawa/BRIEFING.HTM#faq9.

129. A report considering how the technologies for destruction of these chemical weapons might be addressed has been issued by the Science Council of Japan. Science Council of Japan, Japan National Committee for Restoration of Devastated Living Environment by Advanced Technology, *Safe Destruction Technology for Abandoned Chemical Weapons,* 23 July 2001.

- hydrolysis and oxidation to verify data on effectiveness and efficiency for mustard, lewisite, Clark I, Clark II, and explosives; and
- incineration to verify data on effectiveness and efficiency for mustard, lewisite, Clark I, Clark II, and explosives.

Initial studies are examining the hydrolysis of mixtures of mustard and lewisite using aqueous sodium hydroxide at 20 °C and 90 °C. Other studies are being made into the direct oxidation of mixtures of mustard and lewisite suspended in hydrochloric acid to which is added 30 % hydrogen peroxide solution. In addition, studies are being made into the removal of arsenic compounds from chemical treatment and incineration processes and into the stabilization of arsenic compounds removed from the treatment process.

G. U.S. Army Non-Stockpile Chemical Materiel Project

37. U.S. law has divided chemical weapons materiel in the United States into two categories: stockpile and non-stockpile materiel. Stockpile materiel includes all chemical agents available for use on the battlefield and includes chemical agent assembled into weapons and chemical agents stored in bulk containers. Stockpile materiel is stored at nine locations; eight in the continental United States and one on Johnston Island in the Pacific Ocean. Non-stockpile materiel is defined in the United States as including all other chemical weapon related items, and the U.S. Army has defined five broad categories of chemical warfare materiel as non-stockpile materiel [130]:

- binary chemical weapons
- former production facilities, including government facilities that produced chemical weapons prior to the signing of the CW
- miscellaneous chemical warfare materiel, including unfilled munitions and devices; research, development, testing and evaluation materials; and equipment designed for the use of chemical weapons
- recovered chemical warfare material, including items recovered from range clearing operations, from burial sites and from research testing ranges
- buried chemical warfare materiel that was buried underground from World War I through the late 1950s, as well as dud munitions from range firing operations

In 1993, the U.S. Army carried out a survey of the locations, types, and quantities of non-stockpile chemical materiel. According to this survey, non-stockpile materiel was located at more than 200 known or suspected sites in the United States and U.S. territories, with one or more such sites being at a single location. Insofar as this report is concerned, attention is focused solely on those aspects of the U.S. non-stockpile chemical materiel project concerned with the destruction of materiel containing chemical agents.

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[130] U.S. Army Non-Stockpile Chemical Materiel Project. *Definitions: Stockpile and Non-Stockpile Chemical Materiel.* Available at http://www-pmcd.apgea.army.mil/nscmp/IP/FS/definitions/index.asp.

38. The U.S. Non-Stockpile Chemical Materiel Project is evaluating technologies, systems, and facilities to identify, provide safe storage of, and treat the contents of recovered chemical warfare materiel. Initially, work commenced on three systems [131]:

    - Explosive destruction system (EDS) is a transportable treatment system designed to safely detonate chemical munitions and neutralize associated chemical agents inside a stainless steel chamber. This system is specifically designed to handle World War I and II era munitions, such as the 75-mm, the 4.2-inch, and the 8-inch Livens projectiles, which are unsafe or unsuitable for transport. In late January/early February 2001, the EDS safely destroyed six GB bomblets found during clean-up operations at Rocky Mountain Arsenal (RMA), Colorado. A further four such bomblets found in June 2001 at RMA were safely disposed of in July 2001.
    - Munitions management devices (MMDs) provide the capability to receive, contain, access, monitor, and treat range-recovered or buried chemical warfare materiel such as bombs, artillery projectiles, and vials or bottles of agent of various configurations. Three MMDs were planned. MMD-1 was to be housed on two 15-m tractor trailers, one for processing and one for control, and will treat non-explosively configured chemical warfare materiel. The chemical treatment process is in three stages: first to access the chemical container, second to analyze the chemical, and third to neutralize the chemical using a suitable reagent. In the MMD, the major neutralizing reagents used to react with the chemical agents are aqueous solutions of monoethanolamine (MEA) and/or sodium hydroxide depending on the agent: For mustard and sarin, the reagent is an aqueous solution of MEA, for VX, aqueous MEA and sodium hydroxide, and for phosgene, sodium hydroxide and water. MMD-2 was to be designed to safely treat explosively configured chemical warfare materiel such as 4.2-inch mortars, 5-inch rocket warheads, and 100-lb bombs. In addition, the MMD-2 would have a separate module to allow it to handle bulk items such as ton containers and commercial high-pressure bottles. MMD-2 would be housed on five trailer-mounted units: a munition processing trailer, a bulk item processing trailer, an agent neutralization trailer, a preparation trailer, and a control trailer. MMD-3 was to be designed to treat large bulk containers containing chemical warfare materiel. However, on 7 March 2001, the U.S. Army announced that it had decided to terminate the MMD program owing to the successes of the EDS and RRS systems [132].
    - The rapid response system (RRS) provides the capability to receive, contain, characterize, monitor, and treat (or repackage) chemical agent identification sets (CAIS) recovered at burial sites. Various types of CAIS were produced from 1928 until 1969 containing various types of chemicals and used as a training aid. Sulfur mustard (HD), nitrogen mustard (HN), and lewisite (L) will be decontaminated by hydrolysis using 1,3-dichloro-5,5-dimethylhydantoin (DCDMH) during RRS processing. The reaction is intended to reduce the concentration of agent to less than 50 ppm. The products of reaction with mustard are reported to include chlorinated sulfoxides, sulfones, chlorinated ethanes and butanes, aldehydes, and

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131. U.S. Army Non-Stockpile Chemical Materiel Project. *Technologies, Transportable Treatment Systems, and Facilities.* Available at http://www-pmcd.apgea.army.mil/NSCMP/nscmp_h_dtsf.asp.
132. U.S. Army Press Release. *U.S. Army Terminates Testing of Chemical Weapons Treatment System,* 7 March 2001.

substituted hydantoins [133]. Other former chemical warfare agents now classified as industrial chemicals such as phosgene, cyanogen chloride, chloroacetophenone, Adamsite, chloropicrin, triphosgne, and an ester mixture will be repackaged for disposal by current industrial methods. The prototype system uses two trailers with chemical operations, including repackaging and neutralization taking place within a glove box in the operations trailer. The RRS completed testing at the Deseret Chemical Depot (DCD) of 31 December 2000; during testing the RRS safely neutralized some 381 CAIS and then was used at DCD to destroy further CAIS, resulting in the destruction of 1226 CAIS previously stored at DCD [134].

39. A study [135] was carried out by the NRC in 1999 to review the U.S. Army's proposals to the U.S. Congress on the treatment and disposal of CAIS. The study pointed out that most CAIS contain relatively small quantities of chemical ingredients—typically a few millilitres—and that the risk posed by proper treatment of small quantities of such chemicals is less than the risk posed by the larger quantities of highly hazardous industrial chemicals that are already handled by the chemical industry and the commercial hazardous waste treatment facilities. The NRC study recommended *inter alia* that the U.S. Army should reconsider its interpretation of CAIS as chemical warfare materiel under U.S. laws so that CAIS could be regulated as hazardous waste and that the U.S. Army should, in states with stockpile chemical weapon destruction facilities, engage the community in a discussion of alternatives including the potential use of the stockpile destruction facility for CAIS disposal.

40. The emphasis in the U.S. Army program is very much on transportable systems that will destroy the chemical warfare materiel at the site at which it is found rather than on systems to transport the materiel to a destruction site. Indeed, until recently, U.S. law prohibited the use of the stockpile destruction facilities for any other purpose, including the disposal of non-stockpile chemical warfare materiel even if it was stored at the same location as the stockpile chemical warfare materiel. The U.S. Congress in October 1999 modified the law to remove this prohibition, provided that the State in which the stockpile destruction facility was located permits it. The U.S. Army is now considering the feasibility and cost-effectiveness of using the stockpile destruction facilities to destroy non-stockpile chemical warfare materiel stored at the same location; no consideration is being given to moving non-stockpile chemical warfare materiel between stockpile destruction facilities.

41. Attention is also being given to how to dispose of the reaction products resulting from the neutralization of the agents treated in the mobile systems: MMD and RRS. The term "neutralent" is used in the United States to describe the product from neutralization of the agents in non-stockpile materiel processed in the MMD or RRS. In the MMD, the main neutralizing reagents are aqueous solutions of monoethanolamine (MEA) and/or sodium hydroxide whereas in the RRS the treatment reagent is 1,3-dichloro-5,5-dimethylhydantoin (DCDMH). The agents and the reagents used in both the MMD and the RRS are summarized in Table 10.

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[133] National Research Council, Committee on Review and Evaluation of the Army Non-Stockpile Chemical Materiel Disposal Program. *Disposal of Chemical Agent Identification Sets,* p. 77, National Academy Press, Washington, DC (1999).

[134] U.S. Army Press Release. *Army Mobile Weapons Disposal Terchnology Heads to Huntsville, Alabama,* 30 July 2001.

[135] National Research Council, Committee on Review and Evaluation of the Army Non-Stockpile Chemical Materiel Disposal Program. *Disposal of Chemical Agent Identification Sets,* National Academy Press, Washington, DC (1999).

Table 10 Reagents used in the MMD and RRS to treat chemical agents.

Non-stockpile materiel chemicals	
MMD	**Reagent**
Sulfur mustard (HD)	Monoethanolamine (MEA) and water
Sarin (GB)	Monoethanolamine (MEA) and water
VX	Monoethanolamine (MEA), sodium hydroxide and water
Phosgene	Sodium hydroxide and water
RRS	**Reagent**
CAIS	
Nitrogen mustard (HN-1), sulfur mustard, and lewisite in chloroform solution	1,3-dichloro-5,5-dimethylhydantoin (DCDMH), chloroform, *t*-butyl alcohol and water
Neat sulfur mustard (H/HS/HD)	DCDMH, chloroform, *t*-butyl alcohol and water
Nitrogen mustard and sulfur mustard adsorbed onto charcoal	DCDMH in chloroform
Lewisite (L) adsorbed onto charcoal	DCDMH, chloroform, *t*-butyl alcohol and water

42. Six technologies for neutralent post-treatment have been evaluated by a 7-member independent Technical Evaluation Panel [136]. These technologies were:

    - *Catalytic hydrothermal conversion technology* using high temperature and a metal carbonate catalyst to pyrolyze and gasify organic materials.
    - *Catalytic transfer hydrogenation technology* involving treatment of wastes with a reagent mixture consisting of a heavy hydrocarbon, sodium hydroxide and a proprietary catalyst. At 300 °C, the reagent is said to produce highly reactive atomic hydrogen, which can cleave many carbon–heteroatom bonds.
    - *Gas-phase chemical reduction* in which the materials to be treated are vaporized in a hydrogen and steam environment at 540 °C for 15 min followed by transfer to the chemical reduction reactor at 875 °C in which the agents break down primarily to methane and the heteroatoms form hydrochloric acid, hydrogen fluoride which is then converted to sodium salts in the subsequent scrubber.
    - *MGC PLASMOX process* using a plasma reactor design operated at subatmospheric conditions.
    - *Solvated electron/persulfate oxidation technology* using a 4 % solution of liquid sodium in liquid ammonia.
    - *Supercritical water oxidation* at 250 bar and 550–650 °C.

43. The technology evaluation report recommends that, for near-term application, by 1 January 2003, supercritical water oxidation and gas-phase chemical reduction be tested together with MGC PLASMOX pending confirmation that a plasma system can be approved for use at least at some of the sites in the United States. The report notes that the MGC PLASMOX is the most proven of

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136. US Army Non-Stockpile Chemical Materiel Project. *Technology Evaluation Panel Report: Evaluation of Neutralent Post-Treatment Technologies for the Non-Stockpile Chemical Materiel Program,* 18 September 2000. Available at http://www-pmcd.apgea.army.mil/nscmp/ip/r/tepoct00/index.asp

the three processes for agent destruction, including arsenic-containing lewisite, and has been approved and in operation in Switzerland and Germany for 10 years. The process has, however, yet to be approved for use in the United States.

44. The U.S. non-stockpile chemical warfare materiel is thus following a broadly similar approach to that being followed in Europe, although the U.S. approach is more complex owing to the prohibition on transportation of chemical warfare materiel and the public opposition to the use of the well-proven incineration technology, even though the non-stockpile chemical warfare materiel presents a much smaller risk than does stockpile chemical warfare materiel.

X. TECHNOLOGY COMPARISONS

1. This report has considered a number of technologies, both high-temperature and low-temperature, that have been used for the destruction of chemical weapons and chemical weapon agents. These are summarized in the two following tables. Table 11 provides a comparison of high-temperature technologies, and Table 12 provides a comparison of low-temperature technologies. For each technology, a summary statement is provided in the tables under the following six headings:

   - Process description
   - Scientific principles
   - Technology status
   - Quantity of agent destroyed
   - Safety considerations
   - Environmental impact

   The information presented in the tables shows that the technique that has most widely been used for the destruction of chemical weapons and agents is incineration, with greater than 16 000 tonnes of agent destroyed. Next is neutralization using aqueous sodium hydroxide, calcium hydroxide, or monoethanolamine, with about 4000 tonnes of agent destroyed.

2. Attention in this report has been focused primarily on technologies for the destruction of stockpile chemical weapons—for which the agent filling is known—although consideration has also been given to approaches dealing with old recovered chemical weapons, for which the nature of the filling will frequently be uncertain. Furthermore, it is recognized that as stockpiled chemical weapons have to be destroyed, to comply with the requirements of the Chemical Weapons Convention, by 29 April 2007 with a possible extension until 29 April 2012, this favors the selection of a proven technology such as incineration or neutralization as the time for development and demonstration and proving of other technologies is fast disappearing.

3. In contrast to the situation with stockpiled chemical weapons, old recovered chemical weapons are likely to continue to be found in a number of countries for decades to come and will need to be destroyed safely as they are discovered. The options for the destruction technology to be selected are wider as (1) the numbers of recovered chemical weapons requiring destruction are likely to be significantly less than for the stockpile destruction situation, and (2) there is time for an alternative technology, to incineration or neutralization, to be developed and proven, should that be required under the circumstances prevailing in the country concerned.

4. In all cases, regardless of the technology, the destruction of chemical agent results in three product streams—gas, liquid, and solid. Some technologies may be designed so as to minimize one or more of these product streams, there will always be one or more product streams that will need to be monitored and treated to ensure that whatever is released to the environment is safe. Each of these needs to be monitored and checked to demonstrate that the product stream is safe for release into the environment and meets the appropriate standards to protect public health and the environment.

Table 11 Comparison of high-temperature destruction technologies.

Process	Incineration	Plasma pyrolysis	Molten metal technology	Hydrogenolysis	Destruction of arsenicals
Process description	Incinerator at 1480 °C followed by afterburner at 1090 °C then scrubbing.	Plasma torch at 1000 to 20 000 °C.	Molten metal at 1425 to 1650 °C.	Hydrogen and steam at 850 °C and nominally atmospheric pressure.	Thermal destruction and vitrification using plasma technology.
Scientific principles	Thermal decomposition and subsequent oxidation at high temperatures.	Plasma dissociates agent into molecules, atoms, ions, and electrons. Recombines to form a product gas.	Agent thermally decomposed to simple inorganic molecules. Recombines to form a product gas.	High-temperature reduction to yield methane and inorganic molecules such as HCl.	Plasma dissociates agent into molecules, atoms, ions, and electrons. Gaseous products oxidized at 1200 °C for >2 s.
Technology status	More chemical agent has been destroyed by incineration than by any other technology.	Robust technology in industrial applications. Recently used for agent destruction.	Wide range of commercial wastes evaluated in bench-scale units.	Commercial units in use in Australia and Canada to destroy DDT and PCB, respectively.	Robust technology in industrial applications. Recently used for agent destruction.
Quantity of agent destroyed	>17 000 tons	Arsenicals destroyed in Germany and lewisite destroyed in Switzerland.	HD and VX destroyed in bench-scale tests.	HD destroyed in small bench-scale tests.	Arsenicals destroyed in Germany and lewisite destroyed in Switzerland.
Safety considerations	Monitor to prevent release through stack of agent. Gaseous emissions—products of incomplete combustion, dioxins, heavy metals.	Molten metal discharges, flammable gas storage, agent containment. Gaseous emissions.	Molten metal.	High-temperature hydrogen, agent containment.	Molten slag discharges, agent containment.
Environmental impact	Environmental burden should be nondetectable.	Primarily solid vitrified waste. Potential to have virtually no environmental impact.	Metal, hydrochloric acid, and sulfur for commercial reuse. Ceramic slag to landfill.	Inorganic substances to landfill. Steam boiler discharges through stack.	Primarily solid vitrified waste. Potential to have virtually no environmental impact.

Table 12 Comparison of low-temperature destruction technologies.

Process	Hydrolysis of mustard	Hydrolysis of mustard and nerve agents using aqueous NaOH	Reaction of mustard and nerve agents using amines and other reagents	Electrochemical oxidation	Solvated electron technology
Process description	Hydrolysis with hot water.	Hydrolysis with aqueous sodium hydroxide.	Hydrolysis with monethanolamine followed by bitumenization of reaction products (or incineration).	Ag(II)/Ag(I) electrochemical cell.	Reduction by solution of metallic sodium in anhydrous liquid ammonia.
Scientific principles	Reaction of mustard with water to produce thiodiglycol and hydrochloric acid.	Hydrolysis reaction products dependent on agent and neutralizing reagent concentrations.	Hydrolysis reaction products dependent on agent and neutralizing reagent.	Ag(II) in acidic medium is one of the most powerful oxidizing agents known.	Reduction of mustard to sodium chloride and of GB to sodium fluoride. VX uncertain.
Technology status	Used to detoxify mustard agent.	Extensively used to detoxify mustard and GB agent.	Kuasi mobile system used in Russia to destroy H, GB, GD munitions.	Yet to be operated on a commercial scale.	Yet to be operated on a commercial scale.
Quantity of agent destroyed	>150 kg H	>700 tonnes H >3800 tonnes GB	>300 tonnes H, GB, GD in Kuasi system with incineration of products.	Pilot plant scale (~10 kg quantities) with HD, GB, VX.	0.64 kg HD, 0.59 kg GB, 0.45 kg VX
Safety considerations	Semibatch process with nonflammable low-temperature (90 °C) aqueous streams at atmospheric pressure.	Semibatch process with nonflammable low-temperature (90 °C) aqueous streams at atmospheric pressure.	Batch process with low-temperature (100 °C) aqueous monoethanol-amine/RD-4 streams at atmospheric pressure. Bitumenization at 180–200 °C.	Highly corrosive or reactive materials—aqueous concentrated nitric acid—at 90 °C and atmospheric pressure.	Liquid sodium and liquid ammonia are highly reactive. Sodium persulphate and hydrogen peroxide solutions are reactive oxidizers.

(*continued on next page*)

Table 12 (*Continued*).

Process	Hydrolysis of mustard	Hydrolysis of mustard and nerve agents using aqueous NaOH	Reaction of mustard and nerve agents using amines and other reagents	Electrochemical oxidation	Solvated electron technology
Environmental impact	Test prior to release. Waste salts to landfill. Water recycle or dilute aqueous discharge to treatment plant.	Test prior to release. Waste salts to landfill. Water recycle or dilute aqueous discharge to treatment plant.	Ability of bitumenized blocks to withstand leaching needs to be determined.	Test prior to release. Aqueous waste salts with low silver concentrations.	Effluents not sufficiently characterized.

XI. TECHNOLOGIES AND CONSTRAINTS: MAKING INFORMED DECISIONS

1. The IUPAC Working Party on Evaluation of Chemical Weapon Destruction Technologies has examined and evaluated the technologies for the destruction of chemical weapons that have been demonstrated on 1 kg or more of agent. The Working Party has recognized that all chemical agents are highly toxic chemicals, which were made available for use in chemical weapons programs from ongoing work in chemistry. There is, therefore, a sense in which chemical agents are merely members of a vast array of chemicals of varying toxicity. Consequently, it is logical to consider the destruction of chemical agents as being no different from the consideration of the destruction of other chemicals that can be as highly toxic**. Chemical agents therefore need not be regarded as being a special class of materials whose destruction demands unique precautions—they are merely members of the vast family of chemicals, and their destruction, as that of any chemicals, requires the taking of appropriate precautions to safeguard worker safety, public health, and the environment.**

2. The Chemical Weapons Convention, which entered into force on 29 April 1997, totally prohibits the development, production, transfer, acquisition, stockpiling, retention, and use of chemical weapons. It obliges all States Parties to destroy any stockpiles of chemical weapons within 10 years from the entry into force of the Convention—by 29 April 2007—with the possibility of an extension, should that be necessary, for up to 5 years to 29 April 2012. There is consequently a tight time line under the treaty for the destruction of stockpiled chemical weapons and agents. This requires that destruction facilities be designed, constructed, and brought into operation in a short time frame, while at the same time protecting public health and the environment. This seriously constrains opportunities for significant technology development. These stockpiled weapons and agents are primarily filled with mustard or with nerve agents. Abandoned or old chemical weapons—sometimes referred to as non-stockpile chemical weapons—also have to be destroyed. As such abandoned chemical weapons are often found during building works and excavations or as a result of farming activities, they will continue to be found for decades in countries where chemical weapons have previously been used or held. The quantities found from time to time are likely to be small and variable at widely dispersed locations. Moreover, the nature of the weapon—whether it is a chemical weapon, still contains chemical agents, and what type of chemical agent—is unlikely to be known. In practice, therefore, there are two principal categories of chemical weapons:

   a. stockpiled chemical weapons in known quantities with known fillings and which have to be destroyed by 29 April 2007 with a possible extension to 29 April 2012, and

   b. abandoned chemical weapons in unknown types and quantities at unknown locations that are found from time to time and which have to be destroyed also by 29 April 2007 unless the Executive Council decides to modify the provisions on the time limit.

3. Following the entry into force of the CWC, a total figure has been published by the Organization for the Prohibition of Chemical Weapons (OPCW) for the chemical agents declared and destroyed. The figure as of 30 June 2001 for the total declared is 69 863 agent-tonnes, and the total destroyed is 5734 agent-tonnes. The principal contributors to the global stockpile are the United States and the Russian Federation; the United States has declared its stockpile as comprising some 31 495 agent-tons (short tons) [137] which corresponds to 28 570 agent-tonnes,

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137. U.S. Department of Defense News Release. *U.S. Chemical Weapons Stockpile Information Declassified,* Reference Number No. 024-96, 22 January 1996. Available at http://www.defenselink.mil/news/ Jan1996/b12496_bt024-96.htm

whereas the Russian Federation has declared [138] a stockpile of about 40 000 agent-tonnes. As India and one other country, known from non-OPCW information, to be South Korea, have also declared chemical weapons, the combined stockpiles for these two countries can be deduced as being about 1500 agent-tonnes. As of July 2001, the United States had destroyed using incineration 20 % [139] of its stockpiled chemical weapons—or some 5700 agent-tonnes. In addition to stockpiled chemical weapons, there are also quantities of old and abandoned chemical weapons in several countries around the world—notably in Europe primarily from World War I, in China from World War II as well as in the United States—which also need to be destroyed.

4. The quantity of chemical weapons that have been destroyed during the past 40 years in a number of countries has been in excess of 20 000 tonnes. Most of this, over 16 000 tonnes, has been destroyed by incineration, and 4000 tonnes have been destroyed by neutralization. **More chemical weapons have been destroyed by incineration than by any other technology.**

5. Although incineration is well proven and had been used in the United States at the full-scale destruction facilities at Johnston Atoll and at Tooele Army Depot, Utah to destroy by October 2001 over 6700 tonnes of the U.S. declared stockpile of 28 500 tonnes, and is to be used to destroy over 80 % of the total U.S. stockpile, there has been considerable attention paid particularly in the United States to alternative technologies to incineration for the destruction of stockpiled chemical weapons and agents. The reason for the attention given to alternative technologies has arisen from a number of constraints that are **specific** to the United States. First, the United States found itself in a situation where the U.S. Congress passed a law that prohibited the transportation of chemical weapons from one storage site to another storage site, thus precluding the option of carrying out all destruction at a single or a few destruction facilities. This situation appears illogical when it is recalled that the stockpiles of chemical weapons were created by transporting agent and munitions from manufacturing facilities to the stockpile sites and any deployment of these weapons prior to use would have necessitated transportation of the weapons to the battlefield. Part of the justification for the prohibition of the transportation of the stockpiled chemical weapons arose from the age, and thus the uncertain state, of the chemical weapons (which are all over 30 years old and some are over 55 years old) and the reluctance of individual States to allow transport of these munitions across State boundaries. Second, and most importantly, although the U.S. Army had proposed the construction of similar incineration facilities to those at Johnston Atoll and Tooele at the other seven storage sites in the continental United States, some groups and individuals have claimed that the incineration technology poses risks to the surrounding populations and the environment and that these risks could be reduced, it is claimed, by using alternative technologies. The U.S. Congress has accordingly directed the U.S. Army to examine alternative disposal technologies.

6. The U.S. consideration of alternative technologies for the destruction of stockpiled chemical weapons and agents has been tightly constrained by the available resources and the time prior to the Chemical Weapons Convention deadline for destruction to be completed by 29 April 2007.

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138. Government of the Russian Federation, Resolution No. 510 of 5 July 2001, *On Making Amendments and Additions to the Resolution by the Government of the Russian Federation of March 21, 1996 (No. 305) On Approving the Federal Special Program "Chemical Weapons Stockpiles Destruction in the Russian Federation"*. Available at http:www.armscontrol.org

139. A. Johnson-Winegar. *The U.S. Chemical Demilitarization Program,* Statement before the Senate Armed Services Committee, Sub-Committee on Emerging Threats and Capabilities, United States Senate, 12 July 2001.

The first extensive study of alternative technologies was carried out in 1993 when the National Research Council report [140] concluded that "*There are many possible destruction processes.*" The report went on to point out that "*new components would likely require 5 to 12 years for research and demonstration.*" A further National Research Council report [141] a year later recommended that the disposal program "*should continue on schedule with implementation of the baseline [incineration] system, unless and until alternatives are developed and proven to offer safer, less costly, and more rapidly implementable technologies.*" In respect of alternatives, the same report "*determined that four neutralization based systems offer the most promise for agent destruction*" and recommended that "*neutralization followed by transport should be examined, as an alternative at the Aberdeen and Newport sites*" as these sites only have ton containers of agent and have no filled chemical munitions. The design and construction of neutralization facilities to destroy the bulk agent at the Aberdeen and Newport sites is now underway, with destruction planned to commence in 2004–2005.

7. Insofar as the remaining five storage sites in the continental United States that all contain assembled chemical weapons as well as, in most cases, one-ton containers, incineration continues to be the planned approach for disposal. However, in late 1996, the U.S. Congress stopped any work on construction of incineration facilities at two sites (Lexington, Kentucky and Pueblo, Colorado) until the U.S. Department of Defense had completed an assessment of the chemical demilitarization program for destruction of assembled chemical munitions and of the alternative demilitarization technologies and processes (other than incineration) which could be used for the destruction of chemical agents. It was also specified that not less than two alternative technologies should be identified and demonstrated. This Assembled Chemical Weapons Assessment (ACWA) program led to the identification of seven "technology packages", which were reviewed and evaluated by the National Research Council [142]. The National Research Council report made a general finding that "*The chemistries of all four of the primary technologies, (hydrolysis, SILVER II, plasma arc and SET) as proposed, can decompose the chemical agents with destruction efficiencies of 99.9999 per cent. However, each technology package raises other technical issues which must be resolved. One of the crucial issues is the identity and disposition of by-products.*" Another general finding was that "*An extraordinary commitment of resources will be necessary to complete the destruction of the assembled chemical weapons stockpile in time to meet the current deadline using any of the ACWA technology packages. This would demand a concerted national effort. It is unlikely that any of the technology packages could meet this deadline.*" In July 1998, the Department of Defense selected three technologies, two relying on hydrolysis as the primary treatment process and the third on plasma arc technology, for demonstration. A further National

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140. National Research Council, Committee on Alternative Chemical Demilitarization Technologies. *Alternative Technologies for the Destruction of Chemical Agents and Munitions,* National Academy Press (1993).
141. National Research Council, Committee on Review and Evaluation of the Army Chemical Stockpile Disposal Program. *Recommendations for the Disposal of Chemical Agents and Munitions,* National Academy Press (1994).
142. National Research Council, Committee on Review and Evaluation of Alternative Technologies for Demilitarization of Assembled Chemical Weapons. *Review and Evaluation of Alternative Technologies for Demilitarization of Assembled Chemical Weapons,* National Academy Press, Washington, DC (1999).

Research Council report [143] examined the results of demonstration tests carried out on these three technologies. A general finding was that "*The committee reiterates that none of the unit operations has been integrated into a complete system. The lack of integration remains a major concern as a significant obstacle to full-scale implementation.*"

8. Currently, incineration facilities are under construction at Anniston, Alabama; Pine Bluff, Arkansas; and Umatilla, Oregon. These facilities are similar to the facility currently in operation at Tooele, Utah, with the main difference being the addition of a carbon filter on the pollution abatement system. The technology decision for Pueblo, Colorado is scheduled to be made in September 2001. Four technological approaches are being considered for use at Pueblo: baseline incineration (as at Anniston, Pine Bluff, and Umatilla); modified baseline incineration (with energetics removal and off-site disposal, freezing of mustard rounds, and processing of the mustard rounds in a single furnace); and two ACWA-developed technologies: hydrolysis/biotreatment and hydrolysis/supercritical water oxidation. The situation in respect of the U.S. stockpiled chemical munitions is summarized in Table 13.

Table 13 Schedule for destruction of U.S. stockpiled chemical munitions (as of October 2001)[a].

Site	Agent short tons	% U.S. stockpile	Stockpile nature	Technology	Full-scale destruction
Aberdeen	1625 tons	5.2 %	HD containers	Neutralization	2005–2006
Anniston	2254 tons	7.2 %	HD, HT, GB, VX munitions HD containers	Incineration	2002–
Blue Grass	523 tons	1.7 %	H, GB, VX munitions	On hold	
Johnston Atoll	2030 tons	6.4 %	HD, GB, VX munitions and containers	Incineration	1989–2000 **Completed**
Newport	1269 tons	4.0 %	VX containers	Neutralization	2004
Pine Bluff	3850 tons	12.2 %	HD, HT containers GB, VX munitions	Incineration	2003–
Pueblo	2611 tons	8.3 %	HD, HT munitions	**On hold**[b]	
Tooele	13 616 tons	43.2 %	HD, L, GA, GB, VX containers H, HD, HT, GB, VX munitions	Incineration	1996– **39.4 % destroyed**
Umatilla	3717 tons	11.8 %	HD containers GB, VX munitions	Incineration	2002
Total	**31 495 agent-tons**	**100 %**			**23.5 % destroyed**
Total	28 572 agent-tonnes	100 %			23.5 % destroyed

[a] This is based on stockpile information available at http://www.defenselink.mil/news/Jan1996 /b012496_bt024-96.html and information on destruction schedules at individual storage sites available at http://www-pmcd.apgea.army.mil/

[b] Technology decision expected in late 2001.

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143. National Research Council, Committee on Review and Evaluation of Alternative Technologies for Demilitarization of Assembled Chemical Weapons. *Review and Evaluation of Alternative Technologies for Demilitarization of Assembled Chemical Weapons A Supplemental Review,* National Academy Press, Washington, DC (2000).

It is evident that over 23.5 % of the U.S. stockpile has already been destroyed. **Overall, 80.8 % is to be destroyed by incineration, 9 % is planned to be destroyed by neutralization, and 10 % is currently on hold.**

9. This Working Party is acutely aware that much of the information presented in this report is based on U.S. experience. However, this is hardly surprising as the United States had along with the Russian Federation by far the largest stockpiles of chemical weapons and agents anywhere in the world. The United States has made much progress in destroying its stockpile of chemical weapons and agents and has also done more work than any other country to examine alternative technologies for the destruction of chemical weapons and agents. This report therefore draws heavily on the U.S. experience. However, the **national decisions** to be taken by countries faced with the destruction of chemical weapons and agents **need to be made in the light of the particular national conditions and standards**—and thus may well result in a decision to use different approaches from those adopted by the United States. National decisions in other countries will need to consider the size and nature of their stockpiled chemical weapons in determining both where and how to destroy them in accordance with the requirements of and the deadline established in the Chemical Weapons Convention. **The aim of this report is to provide information to enable countries to make informed decisions that are appropriate for that country**.

GLOSSARY OF ACRONYMS

AC	hydrogen cyanide (a blood agent)
ACAMS	automated continuous air monitoring system
ACW	abandoned chemical weapons
ACWA	assembled chemical weapons assessment
Ag	silver
AltTech	NRC Panel on Review and Evaluation of Alternative Chemical Disposal Technologies
AOP	advanced oxidation process
BATNEEC	best available techniques not entailing excessive costs
BBC	α-bromobenzylcyanide; 1-bromo-1-tolunitrile; also known as CA
BPEO	best practical environmental option
CA	1-bromo-1-tolunitrile; α-bromobenzylcyanide; also known as BBC
CAIS	chemical agent identification sets
CAMDS	Chemical Agent Munitions Disposal System at the Tooele Army Depot, Utah, USA
CEP	catalytic extraction processing, a molten metal process
CG	phosgene (a choking gas)
CK	cyanogen chloride (a choking gas)
CN	1-chloroacetophenone (a tear gas agent)
CO	carbon monoxide
CO_2	carbon dioxide
CW	chemical weapon
CWC	Chemical Weapons Convention
DA	diphenylchloroarsine (Clark I) (an irritating and vomiting agent)
DAP	Destruction Advisory Panel established by UNSCOM
DAAMS	depot area air monitoring system
DC	diphenylcyanoarsine (Clark II) (an irritating and vomiting agent)
DCD	Deseret Chemical Depot, USA
DCMDH	1,3-dichloro-5,5-dimethylhydantoin
DDT	dichloro diphenyl trichloroethane
DERA	Defence Evaluation and Research Agency, UK
DFS	deactivation furnace
DM	Adamsite (a tear gas agent)
DNT	dinitrotoluene
DRE	destruction removal efficiency
DRES	Defence Research Establishment Suffield, Canada
EMPA	ethyl methyl-phosphonic acid
EOD	explosive ordnance disposal
EPA	U.S. Environmental Protection Agency
GA	tabun (a nerve agent)
GAC	granular activated charcoal
GB	sarin (a nerve agent)
GD	soman (a nerve agent)
H	mustard (a blister agent)
HCl	hydrogen chloride
HD	distilled mustard (a blister agent)
HE	high explosive
HEPA	high-efficiency particulate air
HN	nitrogen mustard

HN-1	bis(2-chloroethyl)ethylamine, a nitrogen mustard
HN-2	bis(2-chloroethyl)methylamine, a nitrogen mustard
HN-3	bis(2-chloroethyl)amine, a nitrogen mustard
H_2O	water
H_2S	hydrogen sulfide
HT	a low freezing-point blister agent, also known as Runcold, produced by reacting thiodiglycol and hydrogen chloride so as to yield a product containing about 60 % mustard and 40 % bis-(2-chloroethylthioethyl) ether
I	incineration
ISO	International Standards Organization
ITEQ	international toxic equivalency
IUPAC	International Union of Pure and Applied Chemistry
JACADS	Johnston Atoll Chemical Agent Disposal System
JI	Johnston Island
L	lewisite (a blister agent)
LIC	liquid incinerator
MACT	maximum achievable control technology
MEA	monoethanolamine
MECC	mobile explosion containment chamber
MILVANS	standard transportation vans
MMD	munitions management device
MPA	methyl phosphonic acid
MPF	metal parts furnace
N	neutralization
NAA	neutron activation analysis
NO	nitric oxide
NaOH	sodium hydroxide (caustic soda)
NBC	nuclear biological chemical
NRC	National Research Council of the U.S. National Academy of Sciences
OCW	old chemical weapons
OPCW	Organization for the Prohibition of Chemical Weapons
OSHA	Occupational Safety and Health Act, a U.S. law passed in 1970
OVT	operational verification test
PACOM	U.S. Pacific Command
PAR	projectile agent removal system
PCB	polychlorinated biphenyl
pH	hydrogen ion concentration
PICs	products of incomplete combustion
ppb	parts per billion
PS	chloropicrin (a tear gas)
PWC	plasma waste converter
RCRA	Resource Conservation and Recovery Act
RMA	Rocky Mountain Arsenal, USA
RRS	rapid response system
SBR	sequencing batch reactor
SCWO	supercritical water oxidation
SET	solvated electron technology
S/S	stabilization and solidification
TNT	trinitrotoluene
TOCDF	Tooele Chemical Agent Disposal Facility at Tooele Army Depot, Utah, USA

TSCA	Toxic Substances Control Act
TSDF	treatment, storage, or disposal facility
UK	United Kingdom
UNSCOM	United Nations Special Commission on Iraq
UNSCR	United Nations Security Council Resolution
U.S.	United States
USA	United States of America
USARPAC	U.S. Army Pacific
UV	ultraviolet
VOCs	volatile organic compounds
VR	a nerve agent, Russian VX, *O*-isobutyl *S*-[2-diethyamino ethyl] methyl phosphonothiolate
VX	a nerve agent, *O*-ethyl *S*-2-diisopropylaminoethyl methyl phosphonothiolate
WWI	World War I
WWII	World War II