
**Preliminary Screening of Alternative Technologies
to Incineration for Treatment of Chemical-Agent-
Contaminated Soil, Rocky Mountain Arsenal**

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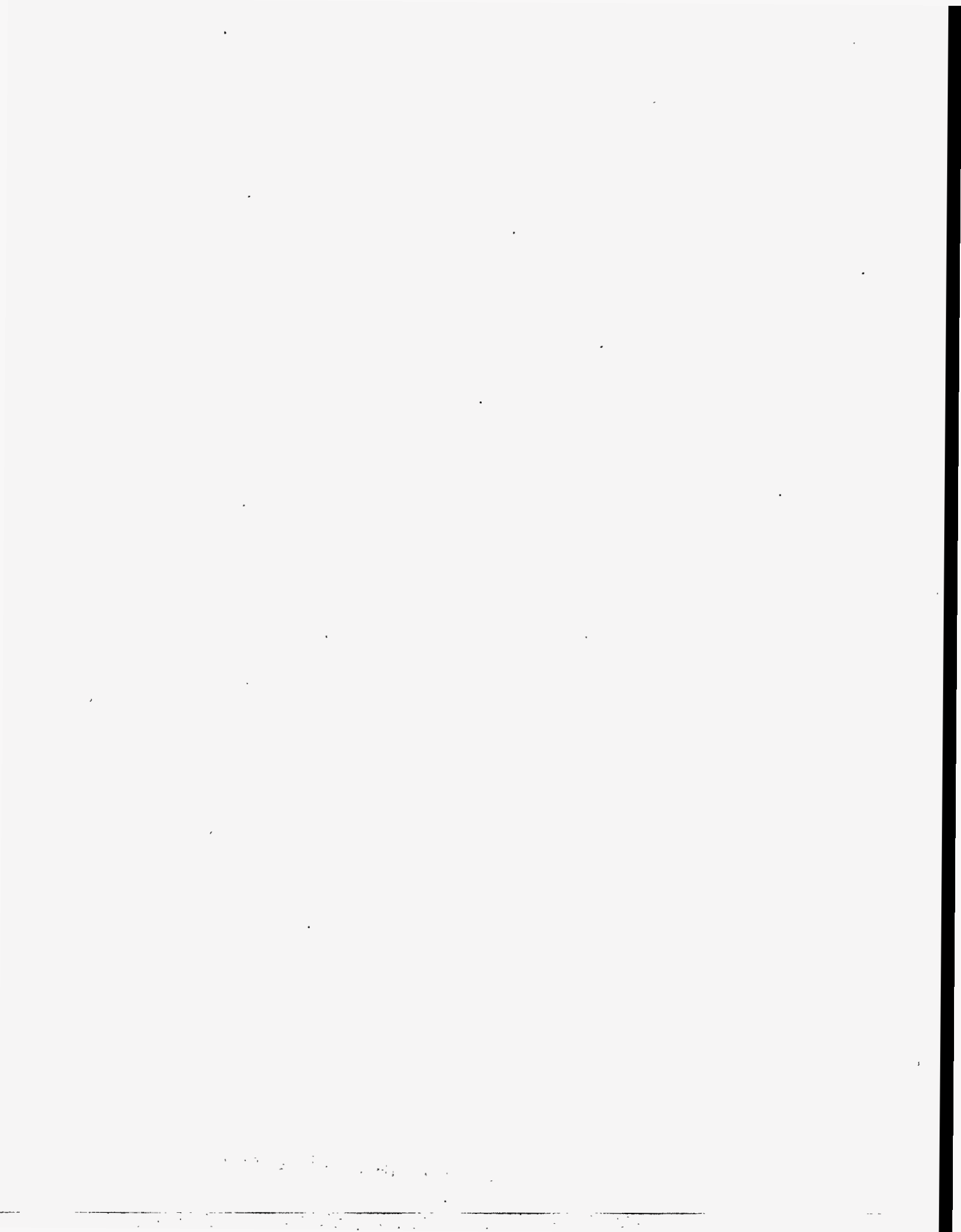
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Initialisms and Abbreviations

ANL	Argonne National Laboratory
APEG	alkaline polyethylene glycol
APCD	air pollution control devices
BCF	bioconcentration factor
CRDEC	Chemical Research, Development, and Engineering Center
CERCLA	Comprehensive Environmental Response, Compensation, and Liability Act
CST	critical solution temperature
C	concentration \times time
CO ₂	carbon dioxide
CVAA	2-chlorovinylarsonous acid
CVAOA	2-chlorovinylarsonic acid
CVAO	2-chlorovinylarsine oxide (see also LO)
DAM	Decontaminating Agent, Multipurpose
DIMP	diisopropylmethylphosphonate
DMMP	dimethylmethylphosphonate
DoD	U.S. Department of Defense
EMPA	ethylmethylphosphonic acid
EPA	U.S. Environmental Protection Agency
ERDEC	U.S. Army Edgewood Research, Development, and Engineering Center
FFA	Federal Facilities Agreement
GB	sarin
H	mustard
h	hours
ICt ₅₀	median incapacitating product of vapor concentration \times time
IMPA	isopropylmethylphosphonic acid
IRA	Interim Response Action
ISV	in situ vitrification
KPEG	potassium polyethylene glycolate
L	lewisite
LCt ₅₀	concentration \times time that is lethal to 50% of a population
LD ₅₀	dose lethal to 50% of the population
LO	2-chlorovinylarsine oxide (see also CVAO); LO is also lewisite oxide

Initialisms and Abbreviations (Cont.)

MPA	methylphosphonic acid
NPL	National Priorities List
O&M	operation and maintenance
PAH	polyaromatic hydrocarbon
PCB	polychlorinated biphenyl
PMRMA	Program Manager, Rocky Mountain Arsenal
PPLV	Preliminary Pollutant Limit Values
RI/FS	Remedial Investigation/Feasibility Study
RMA	Rocky Mountain Arsenal
SFE	supercritical fluid extraction
S/S	solidification/stabilization
SVE	soil vapor extraction
TCE	trichloroethylene
VX	o-ethyl s-(2-(diisopropylamino)ethyl)methyl-phosphonothioate

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Abstract

In support of the U.S. Army's efforts to determine the best technologies for remediation of soils, water, and structures contaminated with pesticides and chemical agents, Argonne National Laboratory has reviewed technologies for treating soils contaminated with mustard, lewisite, sarin, o-ethyl s-(2-(diisopropylamino)ethyl)methyl-phosphonothioate (VX), and their breakdown products. This report focuses on assessing alternatives to incineration for dealing with these contaminants. For each technology, a brief description is provided, its suitability and constraints on its use are identified, and its overall applicability for treating the agents of concern is summarized. Technologies that merit further investigation are identified.

Summary

The U.S. Army, through the Program Manager, Rocky Mountain Arsenal (PMRMA), is conducting an installation restoration program at the Rocky Mountain Arsenal (RMA) that includes the remediation of structures, water, and soils contaminated with pesticides, chemical agents, or toxic degradation products. Two blister agents, mustard (H) and lewisite (L), and a nerve agent, sarin (GB), were produced at RMA beginning in the early 1940s. Another nerve agent, o-ethyl s-(2-(diisopropylamino)ethyl)methyl-phosphonothioate (VX), was shipped to the site for use in munitions assembly. Production of pesticides by private industry also took place on the RMA premises. Using accepted disposal methods of the time, the occupants of the site released chemical agents, pesticides, solvents, and heavy metals to the environment — contaminating structures, surface and groundwater, and soil.

Today the Army is completing a number of activities to remediate contaminated areas under the provisions set forth by both the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) and a Federal Facilities Agreement (FFA) between state, federal, and private organizations. One of these activities is to review remediation technologies for soils contaminated with the chemical agents mustard, lewisite, sarin, and VX and their breakdown products. Because of the highly unstable nature of lewisite in the presence of moisture, it is more

likely that the hydrolysis product, lewisite oxide (LO), rather than lewisite, is present in the soil. For this reason, LO is the one breakdown product that is specifically discussed in this document.

In situ technologies, including soil vapor extraction, soil flushing, solidification/stabilization, and vitrification, may be undesirable for remediation of the agent-contaminated soil because of the difficulty in determining whether remediation goals have been met. Because of the nature of in situ technologies, it cannot be proven that all of the agent would be treated or mobilized. In general, in situ technologies could be applied for treatment or removal of sarin with predictable success. However, treatment or removal of mustard, lewisite, LO, and VX would be less successful — the persistence of mustard in the environment and its insolubility in water, the arsenic content in lewisite and LO, and the toxic breakdown products of VX make treatment of these agents by in situ technologies difficult.

The use of ex situ biotreatment technologies for agent-contaminated soils is a new and innovative field. The biodegradation of agents has only been researched in terms of stockpiled agent; virtually nothing is known about the behavior of naturally occurring microorganisms in agent-contaminated soil. Predictions from stockpiled-agent research suggest that sarin and VX have the potential to be directly affected by microorganisms. Mustard has proven to be too toxic to organisms, and the arsenic-containing lewisite or LO may also be too toxic, although they have not been specifically tested.

Ex situ physical pretreatment of the soil will hydrolyze and, possibly, volatilize sarin. Hydrolysis of the other agents would also occur to some extent. Ex situ solidification/stabilization could immobilize the contaminants in the soil, but the possibility of future agent release would have to be addressed.

The use of solvents, such as supercritical fluids (e.g., carbon dioxide) and critical solution temperature solvents (e.g., triethylamine), to treat agent-contaminated soils is promising but untested. Solvent washing technology should be useful for soils contaminated with mustard, sarin, and VX. Little is known about the behavior of LO with solvents; if removal of LO were successful using solvent washing technologies, further treatment would be needed to detoxify the extract and isolate the arsenic in a form suitable for disposal. Additional treatment would also be required for VX extract. In general, optimal treatment conditions would be required for critical/supercritical fluid extraction to successfully remove agents from the soil, because the effectiveness of this technology is highly dependent on pressure, temperature, and the presence of co-solvents. Any solvent washing process may be cost prohibitive unless the solvent can be easily isolated for reuse.

Soil-washing technologies, including alcoholysis or cleavage with a strong basic solution, dehalogenation with alkaline polyethylene glycol, and chemical oxidation, have potential for removing or treating agent-contaminated soil. Because of mustard's low solubility in water, hydrolysis and oxidation by dissolved oxidants would require the use of nonaqueous or mixed aqueous/nonaqueous solvents. The basic solutions used for alcoholysis/cleavage or dehalogenation with alkaline polyethylene glycol or any of the oxidizing solutions listed in Section

6.7 should be effective. Soil washing with a strongly alkaline aqueous solution, at 50°C or higher, should be adequate to cleave LO to inorganic arsenic (arsenite) and acetylene plus some vinyl chloride. Soil washing with an alkaline solution will also hydrolyze sarin and VX. In general, alcoholysis, dehalogenation, and chemical oxidation would be effective in treating small volumes of agent-contaminated soil; these processes may be cost prohibitive for larger volumes because of the cost of the additive or the processing necessary to treat the waste solution.

Thermal technologies have proven effective in the removal or treatment of organics and some metals. Costs for several thermal technologies are high, ranging from \$300 to \$2,700 for treatment of one ton of soil. These high costs are partly attributable to intensive energy requirements and the required air pollution control devices. Low- and high-temperature thermal desorption technologies do not require the extreme temperatures and high energy inputs that are needed for incineration, pyrolysis, vitrification, and plasma-torch treatment, but are still effective in removing solid contaminants. Low- or high-temperature desorption and pyrolysis should remove mustard, sarin, and VX from soil. Adding sodium bicarbonate would probably decompose the mustard and, through carbon dioxide generation, help carry the vapor-state products to the secondary combustion chamber. However, sodium bicarbonate would likely decompose the VX to other, still somewhat toxic, compounds. Thorough mixing of solid bleach, such as chlorinated lime or supertropical bleach, into the soil, followed by moderate heating (approximately 120°C), should be effective in oxidizing VX residuals to less-toxic derivatives. The effect of low- or high-temperature desorption or pyrolysis on LO-contaminated soil cannot be predicted reliably. Adding sodium bicarbonate to soil would probably cause cleavage of the LO to inorganic arsenic and acetylene plus some vinyl chloride. Because the volatility of the various arsenic species that might be involved is uncertain, the concentrations of arsenic in each effluent stream or residue should be investigated further.

1 Introduction

Rocky Mountain Arsenal (RMA) was established in 1942 by the Department of the Army (Army) to manufacture, store, load, test, and demilitarize toxic chemical surety materials (chemical agents) and munitions as part of the World War II efforts. Two blister agents, mustard (H) and lewisite (L), and a nerve agent, sarin (GB), were manufactured at the arsenal. Another nerve agent, o-ethyl s-(2-(diisopropylamino)ethyl)methyl-phosphonothioate (VX), was shipped to RMA for use in the assembly of munitions. Following the war, some of the property and buildings on RMA were leased to private industry for commercial production of pesticides. As a result of chemical production, and following accepted disposal methods of the time, chemical agents, pesticide-production-related organic compounds, solvents, and heavy metals were released to the environment, contaminating structures, sewer lines, water (both surface and groundwater), and soil.

Today portions of RMA are on the U.S. Environmental Protection Agency's (EPA's) National Priorities List (NPL) of contaminated sites and the Army must follow regulatory actions set forth in the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) for cleaning the site. The Army has initiated a number of remediation activities under the provisions set forth by the Federal Facilities Agreement (FFA) between the Army, Shell Oil Company, the U.S. Department of the Interior, the State of Colorado, EPA, and the Agency for Toxic Substances and Disease Registry. Thirteen Interim Response Actions (IRAs) identified in the FFA address issues such as fugitive dust control, asbestos removal, groundwater intercept and treatment systems, closure of abandoned wells, and sewer remediation. Since 1984, the Army, through the Program Manager, Rocky Mountain Arsenal (PMRMA), has also conducted various Remedial Investigation/Feasibility Study (RI/FS) tasks in compliance with CERCLA and the National Contingency Plan and has prepared numerous draft reports describing site conditions and contamination levels.

Currently, the Army is funding studies to determine the best technologies to remediate soils, water, and structures contaminated with pesticides and chemical agents. In support of the Army's search for appropriate remediation technologies, Argonne National Laboratory (ANL) has prepared this document to review technologies for treating soils contaminated with mustard, lewisite, sarin, and VX and their breakdown products. As directed by the Army, this report focuses on assessing alternatives to incineration but also includes information on incineration for comparative purposes. The objectives of ANL's work are to (1) provide a brief description of each technology, its general cost, its current status, and residuals (if any) that will require further handling or treatment; (2) identify the suitability and/or constraints of each technology in terms of soil type, agents of concern, and other soil contaminants; (3) present a summary discussion of the overall applicability of each technology in treating the agents of concern; and (4) identify technologies that merit further investigation. The study should not be considered an exhaustive review of all possible technologies or a complete evaluation of the technologies described. The technologies reviewed were included either because they represent a wide variety of state-of-the-art remediation techniques or because they are innovative technologies that may hold some promise for remediation of agent-contaminated soils.

2 Physicochemical Profiles of the Contaminants

2.1 Methods for Estimating Physicochemical Properties

Physicochemical properties for the chemical agents (mustard, lewisite, sarin, and VX) described in this report were obtained from reference sources, if available. Not all of the properties relevant to environmental behavior have been experimentally determined or reliably estimated for the contaminants of concern. For this reason, relevant properties that were not available in the literature were estimated, if appropriate. Details of how the estimates were derived are presented in Appendix A.

Physicochemical properties for the breakdown products of the agents are not provided here because of the number of potential breakdown products and their chemical obscurity. Table 1 lists the more prominent degradation products known for the four chemical agents of concern. Degradation products are more likely to be found than the agents themselves after 30 or more years of weathering; thiodiglycol, dithiane, and isopropyl methylphosphonic acid have been detected at RMA in the past (Environmental Science and Engineering, Inc., and Harding Lawson Associates 1988; Environmental Science and Engineering, Inc., et al. 1988) and other degradation products may be present. Additional information on degradation products and the environmental fate of the agents can be found in Appendix B.

2.2 Physicochemical Properties of the Individual Compounds

Tables 2 through 6 list properties of the individual potential contaminants of concern. Although not a surety material, LO is listed separately because it is the product to which lewisite would invariably be converted, even after very brief residence in soil.

For some physicochemical properties, most of the information necessary for inclusion in this report was available in generally reliable secondary sources. For others, data were sparse, and values for some contaminants (for example, heats of fusion) could neither be found nor estimated. The secondary sources did not always provide references to the primary sources. Occasionally the sources contradicted one another; in such cases, inquiries were made at the U.S. Army Edgewood Research, Development, and Engineering Center (ERDEC) to determine which data were more correct. The relative quality of the physicochemical data or estimates is indicated in Tables 2 through 6.

Information on the chemical reactivities of the contaminants, including detoxification reactions, is presented in Appendix C.

TABLE 1 Degradation Products of Chemical Agents Associated with RMA

Agent	Degradation Product	Agent	Degradation Product
Mustard	Thiodiglycol ^a	Sarin	Isopropyl methylphosphonic acid (IMPA) ^a
	1,4-dithiane ^a		Hydrogen fluoride
	1,4-thioxane		Isopropyl alcohol
	Chloroacetic acid ^a		Sodium isopropyl methylphosphonate
	2-chloroethyl hydroxyethyl sulfide		Sodium fluoride
	2-chloroethyl hydroxyethyl sulfone		1,3-diisopropylurea
	2-chloroethyl hydroxyethyl sulfoxide		Dimethyl methylphosphonate (DMMP) ^{a,b}
	bis(2-hydroxyethyl) sulfonone		Diisopropyl methylphosphonate (DIMP) ^{a,b}
	bis(2-hydroxyethyl) sulfoxide		Methylphosphonic acid (MPA) ^a
	2,2'-dichloroethyl disulfide		VX
	2-chloroethyl vinyl disulfide	O-ethyl methylphosphonic acid (EMPA)	
	2-chloroethyl vinyl sulfone	2-(diisopropylamino)ethanethiol	
	2-chloroethyl vinyl sulfoxide	bis-(2-diisopropylaminoethyl) disulfide	
	Divinyl sulfide	S-(2-diisopropylaminoethyl)methylphosphonothioate	
	Divinyl sulfone	O-ethylmethylphosphonothioate	
	Divinyl sulfoxide	bis-2-(diisopropylaminoethyl)sulfide	
	Hydrogen sulfide	bis(O-ethyl methylphosphonic) anhydride	
Vinyl chloride	2-diisopropylaminoethanol		
Lewisite	2-chlorovinylarsine oxide (LO or CVAO)	2-diisopropylaminoethanethiol salt of O-ethyl methylphosphonic acid	
	2-chlorovinylarsonic acid (CVAOA)	1,3-diisopropylurea	
	2-chlorovinylarsonous acid (CVAA)	Diisopropylamine	
	Arsenic acid	Dicyclohexylurea	
	Arsenic salts	Didyclohexylcarbodiimide	
	Arsenic ^a		

^a These products have been detected in soil samples collected from RMA as part of the Remedial Investigation (Environmental Science and Engineering, Inc., and Harding Lawson Associates 1988; Environmental Science and Engineering, Inc., et al. 1988).

^b DIMP is a by-product formed during the manufacture of sarin. DMMP may be a production by-product or a degradation product of sarin.

TABLE 2 Environmentally Relevant Properties of Mustard

Property	Data	Data Quality	Reference
Empirical Formula	C ₄ H ₈ Cl ₂ S	N/A	N/A
Molecular Weight (MW), g/mol	159.08	N/A	N/A
Density (at 25°C), g/mL	1.2685	Good	a
Melting Point, °C	-14.445	Good	b
Boiling Point, °C	217.5	Good	a
Heat of Fusion, cal/g	26.4	Good	a
Heat of Vaporization, cal/g	94.3	Good	a
Vapor Pressure (at 22°C), torr ^c	0.082 ^c	Good	a
Vapor Pressure (at 25°C), torr ^c	0.1059 ^c	Good	a
Volatility, mg/m ³	910		d
Log K _{ow}	1.37	Good	e
	2.026	Fair	f
Aqueous Solubility, g/L	0.92/22°C	Fair	g
K _H , atm•m ³ /mol	1.87 x 10 ⁻⁵	Fair	h
	2.57 x 10 ⁻⁵	Fair	f
Diffusion Coefficient (air) (at 25°C), cm ² /s	0.060	Fair	a
Diffusion Coefficient (H ₂ O) (at 25°C), cm ² /s	7.5 x 10 ⁻⁶	Fair	i
Log K _{oc}	2.0-2.1	Poor	f
Bioconcentration factor (BCF) (fish)	6.5, 20.4	Poor	f

N/A - not applicable.

^a Samuel et al. 1983.

^b Penski 1992.

^c Derived from Antoine Equation.

^d Refer to Section 2.2.

^e Authors' estimate from fragment constants (see App. A, Sec. A.1) in agreement with Small 1984 and EPA 1986.

^f Sage and Howard 1989.

^g Edgewood Arsenal 1974.

^h Authors' estimate (see App. A, Sec. A.2).

ⁱ Authors' estimate (see App. A, Sec. A.4).

TABLE 3 Environmentally Relevant Properties of Lewisite

Property	Data	Data Quality	Reference
Empirical Formula	C ₂ H ₂ AsCl ₃	N/A	N/A
Molecular Weight (MW), g/mol	207.35	N/A	N/A
Density (at 25°C), g/mL	1.8793	Good	a
Melting Point, °C	-18 ± 0.1	Good	b
Boiling Point, °C	195.9	Good	a
Heat of Fusion, cal/g	Unavailable		
Heat of Vaporization, cal/g	74.8	Good	a
Vapor Pressure (at 25°C), torr	0.35	Good	a
Volatility, mg/m ³	3,900		c
Log K _{ow}	Unavailable		
Aqueous Solubility, g/L	0.5	Poor	d,e
K _H , atm•m ³ /mol			e
Diffusion Coefficient (air), cm ² /s			
	0.064/25°C	Fair	a
Diffusion Coefficient (H ₂ O), cm ² /s			e
Log K _{oc}			e
BCF (fish)			e

N/A - not applicable.

^a Samuel et al. 1983.

^b Edgewood Arsenal 1974.

^c Refer to Section 2.2.

^d *Beilsteins Handbuch* 1942.

^e Lewisite is so rapidly hydrolyzed on contact with water that this water-related constant would have no meaning.

TABLE 4 Environmentally Relevant Properties of Lewisite Oxide

Property	Data	Data Quality	Reference
Empirical Formula	C ₂ H ₄ AsClO ₂ (gem-diol)	N/A	N/A
	C ₂ H ₂ AsClO (arsenoxide)	N/A	N/A
Molecular Weight (MW), g/mol	170.45 (gem-diol)	N/A	N/A
	152.45 (arsenoxide)	N/A	N/A
Density, g/mL	Unavailable		
Melting Point, °C	131 (<i>cis</i>) ^a	Good	b
	143 (<i>trans</i>) ^a	Good	b
	140 (<i>trans</i> polymer)	Fair	c
Boiling Point, °C	Unavailable		
Heat of Fusion, cal/g	Unavailable		
Heat of Vaporization, cal/g	Unavailable		
Vapor Pressure, torr	Unavailable		
Volatility, mg/m ³	0-100 (estimated)		d
Log K _{ow}	-0.07	Fair	e
Aqueous Solubility, g/L	~10	Poor	c
K _H , atm•m ³ /mol	Unavailable		
Diffusion Coefficient (air), cm ² /s	Unavailable		
Diffusion Coefficient (H ₂ O), cm ² /s	Unavailable		
Log K _{oc}	0.27	Poor	f
BCF (fish)	0.27	Poor	g

N/A - not applicable.

^a Arsenoxide form.

^b Hewett 1948.

^c Rosenblatt et al. 1975.

^d ERDEC 1994.

^e Major 1989.

^f Authors' estimate (see App. A, Sec. A.5).

^g Authors' estimate (see App. A, Sec. A.6). Neglects chemical binding.

TABLE 5 Environmentally Relevant Properties of Sarin

Property	Data	Data Quality	Reference
Empirical Formula	C ₄ H ₁₀ FO ₂ P	N/A	N/A
Molecular Weight (MW), g/mol	140.1	N/A	N/A
Density (at 25°C), g/mL	1.0887	Good	a
Melting Point, °C	-56.9	Fair	a
Boiling Point, °C	157.8	Good	a
Heat of Fusion, cal/g	15.0 (estimated)	Fair	b
Heat of Vaporization, cal/g	80.66	Good	a
Vapor Pressure at 25°C, torr	2.94	Good	a
Volatility, mg/m ³	22,000		c
Log K _{ow}	0.15 ^k	Poor	d
	0.54	Good	e
Aqueous Solubility, g/L	Infinitely miscible		f
K _H (at 25°C), atm•m ³ /mol	4.0 x 10 ⁻⁷	Poor	g
Diffusion Coefficient (air) (at 25°C), cm ² /s	0.061	Fair	a
Diffusion Coefficient (H ₂ O) (at 25°C), cm ² /s	8.0 x 10 ⁻⁶	Fair	h
Log K _{oc}	0.45	Poor	i
BCF (fish)	0.40	Poor	j

N/A - not applicable.

^a Samuel et al. 1983.

^b Penski and Domalski 1987.

^c Refer to Section 2.2.

^d Britton and Grant 1988.

^e King and Brown 1993.

^f Headquarters, Department of the Army et al. 1990.

^g Based on estimated vapor pressure of 0.136 kPa for 0.1 mole fraction (circa 3.34 M) of sarin in water, K_H = 0.00134 atm/(3,340 mol/m³) from Figure 2 of Preston and Starrock (1983).

^h Authors' estimate (see App. A, Sec. A.4).

ⁱ Authors' estimate (see App. A, Sec. A.5). Small (1984) estimated 1.8.

^j Authors' estimate (see App. A, Sec. A.6).

^k The authors of this report estimated log K_{ow} by regression equations (see App. A, Sec. A.1) involving distribution coefficients for four solvents (Rosenthal et al. 1956), with log K_{ow} values ranging from 0.12 to 1.30 and a mean of 0.74.

TABLE 6 Environmentally Relevant Properties of VX

Property	Data	Data Quality	Reference
Empirical Formula	C ₁₁ H ₂₆ NO ₂ PS	N/A	N/A
Molecular Weight (MW), g/mol	267.38	N/A	N/a
Density (at 25°C), g/mL	1.0083	Good	a
Melting Point, °C	-50	Fair	a
Boiling Point, °C	298.4	Good	a
Heat of Fusion, cal/g	23.9 (estimated)	Fair	b
Heat of Vaporization, cal/g	80.8	Good	a
Vapor Pressure, torr	6.2 x 10 ⁻⁴ /25°C	Good	a
Volatility, mg/m ³	8.9		c
Log K _{ow}	2.36 (estimate)	Poor	d
	2.09 (estimate)	Poor	e
	1.992 (estimate)	Poor	f
	1.57, 1.80 (estimates)	Fair	g
Aqueous Solubility (at 25°C), g/L	30	Fair	h
K _H (at 25°C), atm•m ³ /mol	7.2 x 10 ⁻⁹	Poor	i
Diffusion Coefficient (air) (at 25°C), cm ² /s	0.034	Fair	a
Diffusion Coefficient (H ₂ O) (at 25°C), cm ² /s	4.9 x 10 ⁻⁶	Fair	j
Log K _{oc}	1.18 ^k	Poor	f
BCF (fish)	19	Poor	f

N/A - not applicable.

^a Samuel et al. 1983.

^b Penski and Domalski 1987.

^c Refer to Section 2.2.

^d Britton and Grant 1988.

^e Small 1984.

^f Sage and Howard 1989.

^g King 1993.

^h Edgewood Arsenal 1974.

ⁱ Authors' estimate (see App. A, Sec. A.2).

^j Authors' estimate (see App. A., Sec. A.4).

^k Small (1984) estimated a value of 2.5.

Volatility values (C) included in Tables 2 through 6 are saturation concentrations calculated (from vapor pressures [P] in torr and molecular weight [MW] taken from Tables 2 through 6) by the equation

$$C \text{ (mg/m}^3\text{)} = P \times MW \times 10^6 / [R \times T \text{ (K)} \times 760] \quad (1)$$

where the gas constant (R) is

$$R = 0.08205 \frac{\text{L atm}}{\text{mol K}}$$

L = liters

atm = atmosphere

mol = moles

K = degrees Kelvin

For 25°C (298.16 K), this becomes

$$C \text{ (mg/m}^3\text{)} = P \times MW \times 53.785 \quad (2)$$

In addition to the environmentally relevant data in Tables 2 through 6, the following temperature relationships were reported (Samuel et al. 1983) for :

Mustard $\log P \text{ (torr)} = 7.4749753 - \frac{1,940.711}{204.6712 + T \text{ [}^\circ\text{C]}}$

for density, $d = 1.2954 - [0.00107 T(^\circ\text{C})]$

Lewisite $\log P \text{ (torr)} = 6.40361 - 1,237.03/[155.2 + T(^\circ\text{C})]$

for density, $d = 1.9210 - [0.00167 T(^\circ\text{C})]$

sarin $\log P \text{ (torr)} = 7.48160 - 1,773.82/[227.9 + T(^\circ\text{C})]$

for density, $d = 1.1182 - [0.00118 T(^\circ\text{C})]$

$$\text{VX} \quad \log P \text{ (torr)} = 7.28100 - 2,072.10/[172.5 + T(^{\circ}\text{C})]$$

$$\text{for density, } d = 1.0290 - [0.00083 T(^{\circ}\text{C})]$$

3 Toxicological Profiles and Preliminary Pollutant Limit Values

3.1 Toxicological Profiles

Toxicological studies of blister and nerve agents have focused primarily on the effects of exposure to neat agent in the solid, liquid, or vapor phase. The Army has developed drinking water standards for most of the agents of concern (Watson et al. 1992), but levels of agents in soils have not been addressed. A review of the toxicology literature is provided in Appendix D. The following is a brief discussion of toxic exposure levels for each of the agents of concern.

Mustard

The human respiratory LC₅₀ (concentration × time that is lethal to 50% of a population) for mustard is 1,500 mg•min/m³ (Headquarters, Department of the Army et al. 1990; Safety Office, U.S. Army Chemical Research, Development, and Engineering Center [CRDEC] various dates¹). The percutaneous LC₅₀ for masked personnel is estimated at 10,000 mg•min/m³ (Witten 1969). According to CRDEC records, the estimated human oral LD₅₀ (dose lethal to 50% of the population) for mustard is 0.7 mg/kg; this estimate seems low in view of the intragastric LD₅₀ of 17 mg/kg for rats reported by Edgewood Arsenal (1974). The information obtained from CRDEC indicated a human percutaneous LD₅₀ of 100 mg/kg. A percutaneous air Ct (concentration × time) for masked personnel of as little as 1,000 mg•min/m³ can be incapacitating (Edgewood Arsenal 1974; Headquarters, Department of the Army et al. 1990).

Eye injury from mustard (Edgewood Arsenal 1974) occurs at an air Ct of about 100 mg•min/m³. Effects of mustard are not immediately manifest; the latent period for appearance of ocular symptoms is 4 to 12 h after mild exposure, 3 to 6 h after moderate exposure, and 1 to 3 h after severe exposure (Edgewood Arsenal 1974).

Lewisite

Unlike most other toxic chemical agents, the blister agent (vesicant) lewisite retains much of its toxicity following hydrolysis (to LO) at physiological pH, although with some noticeable differences in the effects. The human LC₅₀ for lewisite via inhalation has been estimated at 1,200 to 1,500 mg•min/m³ (CRDEC various dates), which, for a breathing rate of 0.015 m³/min, would amount to an LD₅₀ of 0.26 to 0.32 mg/kg for this route. The human LC₅₀ for exposure to lewisite vapor via the skin only is estimated at a much higher level, 100,000 mg•min/m³ (CRDEC various dates). The intraocular IC₅₀ (median incapacitating product of vapor concentration × time)

¹ CRDEC sources are Material Safety Data Sheets. Each "safety sheet" is actually a packet of sheets, generally consisting of ten sections. An individual information packet has been prepared for each chemical of interest to CRDEC; the packets are updated at regular intervals.

is less than $300 \text{ mg}\cdot\text{min}/\text{m}^3$ (CRDEC various dates). In animals, the LD_{50} of lewisite (presumably as a liquid) via the dermal route is invariably higher than via the subcutaneous route; for example, in the rat, the values are $24 \text{ mg}/\text{kg}$ and $1 \text{ mg}/\text{kg}$, respectively (Goldman and Dacre 1989). Curiously, the rat oral LD_{50} is reported as $50 \text{ mg}/\text{kg}$ (Goldman and Dacre 1989); this value is even higher than the skin LD_{50} (Goldman and Dacre 1989). Another rat oral LD_{50} of $5 \text{ mg}/\text{kg}$ has been reported (Lewis 1992).

Direct comparisons can be made between the toxicities of lewisite and LO in two cases: (1) intravenous LD_{50} (dose lethal to 50% of the animals) — rabbit, $0.5 \text{ mg}/\text{kg}$ (lewisite) vs. $1 \text{ mg}/\text{kg}$ (LO); and (2) subcutaneous LD_{50} — guinea pig, $1 \text{ mg}/\text{kg}$ (lewisite) vs. $0.2 \text{ mg}/\text{kg}$ (LO) (Lewis 1992). These demonstrate opposite relationships, but the values are on the same order of magnitude.

Sarin

Respiratory exposure usually results in onset of symptoms in two to five minutes; lethal doses kill in less than 15 minutes. The LCt_{50} value for sarin, estimated for humans breathing at the rate of $15 \text{ L}/\text{min}$, was $70 \text{ mg}\cdot\text{min}/\text{m}^3$ (Edgewood Arsenal 1974). Assuming that the compound is completely absorbed and acts systemically, the corresponding LD_{50} value would be $0.015 \text{ mg}/\text{kg}$.

VX

Respiratory exposure usually results in onset of symptoms in two to five minutes; lethal doses kill in less than 15 minutes. The LCt_{50} value for VX, estimated for humans breathing at the rate of $15 \text{ L}/\text{min}$, was $30 \text{ mg}\cdot\text{min}/\text{m}^3$ (Edgewood Arsenal 1974). Assuming that the compound is completely absorbed and acts systemically, the corresponding LD_{50} value would be $0.0064 \text{ mg}/\text{kg}$. The LD_{50} calculated for a man exposed to liquid VX on the volar forearm (i.e., the palm side) is $0.26 \text{ mg}/\text{kg}$, which is considerably higher than the foregoing values. A median dose of $0.057 \text{ mg}/\text{kg}$ would cause only mild signs of intoxication (Edgewood Arsenal 1974).

3.2 Preliminary Pollutant Limit Values

No minimum acceptable values have been set for chemical agents present in soil. The Army has established regulations for the decontamination of agents with respect to handling of neat agent and contaminated materials related to the manufacture of agents (such as manufacturing, laboratory, or field equipment, and buildings). These regulations (U.S. Department of the Army 1986), define two levels of decontamination. The first (3X) is based on determining vapor concentrations following surface decontamination and containment of the material (using approved procedures). Material that is "3Xed" is not to leave Army possession; on-site disposal and

continued Army possession of the land are required. The other level (5X) calls for total destruction of the agent by incineration, although vapor concentrations equivalent to 5X destruction have been established in DA Pamphlet 385-61 (Headquarters, Department of the Army 1992) for sarin, soman (GD — another nerve agent similar to sarin), and VX. No vapor concentration equivalent has been set for mustard, although development of such an equivalent is possible.

Neither of these levels (3X or 5X) is practical for remediation of large quantities of soil. The 5X requirement (incineration) renders any alternative method unnecessary and is very costly. Decontamination of the soil using the Army's current approved procedures would also be costly, especially for large quantities of soil, and failure to detect agent vapors above the soil does not necessarily indicate that the soil is free of agents and does not reveal the level of agent that may be present in the soil. Also, totally destroying the agent by incinerating the soil or ensuring that the contaminated soil remains in Army possession may not be necessary from a health and safety standpoint. Risk assessment and toxicity data are needed to determine safe levels. The U.S. Army Environmental Center is currently working with Oak Ridge National Laboratory to develop toxicity levels and risk assessment procedures to determine safe levels of various agents in the environment (Opresko et al. 1994). The Non-Stockpile Program administered by the Army Chemical Material Destruction Agency is also tasked with determining acceptable threshold levels of agents in various environmental media. This second program has not yet resulted in a report.

Because of the urgent need to establish clean-up levels for the agents in soil, PMRMA conducted its own study. Preliminary Pollutant Limit Values (PPLVs) were identified for the chemical agents of concern (Table 7) in *Exposure Assessment for Rocky Mountain Arsenal, Vol. IV, Preliminary Pollutant Limit Value (PPLV) Methodology, Version 2.1, July, 1989*, but they were removed in subsequent assessment reports (Ebasco Services, Inc. 1993). Appendix E provides information on how the PPLVs were developed.

TABLE 7 Preliminary Pollutant Limit Values for Chemical Agents and Degradation Products of Concern

Contaminant	PPLV (mg/kg) ^a			
	Nature Preserve	Recreational	Commercial	Industrial
Sulfur mustard	21	3.8	20	1.6
Dithiane	688,000	123,400	658,400	52,330
Thiodiglycol	>10 ⁶ ^b	>10 ⁶	>10 ⁶	103,600
Lewisite	688	123	658	52
LO	688	123	658	52
Sarin	30	5.3	28	2.3
Diisopropylmethyl phosphonate	>10 ⁶	493,700	>10 ⁶	209,300
Isoprophylmethyl phosphonate	>10 ⁶	>10 ⁶	>10 ⁶	784,900

^a Source: Ebasco Services, Inc., et al. 1989.

^b The permissible soil concentrations calculated using the PPLV method exceed 1×10^6 mg/kg. This indicates that, for these contaminants, the allowable soil concentrations are equivalent to exposure to pure compound over all direct soil-contact pathways (at the media intake rates assumed in the analysis).

4 Criteria for Preliminary Screening of Technologies

4.1 Criteria

Six criteria were used to screen each technology presented in Sections 5 through 8 for its effectiveness in treating soils contaminated with mustard, lewisite, sarin, VX, and their breakdown products, and for comparing the cost of treatment, waste streams generated, and ability to treat other soil contaminants. The criteria are:

- Applicability to general soil characteristics,
- Applicability to the four toxic agents of concern,
- Usefulness for treating other soil contaminants,
- Cost of the treatment (where it can be estimated),
- Current status of the technology, and
- Residuals or waste streams.

Each of these six criteria is discussed briefly below.

Applicability to General Soil Characteristics

Soil composition and texture may influence the rate of action of some of the treatment technologies or make them inapplicable. This criterion discusses typical soil textures for which the technology is best suited and considers limitations on the basis of such soil characteristics.

Applicability to the Four Toxic Agents of Concern

This criterion considers whether the technology is capable of either mobilizing, treating, or reducing the volume of each of the contaminants of concern.

Usefulness for Treating Other Soil Contaminants

This criterion addresses whether the considered technology can be used to mobilize, treat, or reduce the volume of other contaminants in the same soil. This question is not answered for

individual contaminants but for categories of contaminants, such as organics, inorganics, volatiles, semivolatiles, and heavy metals.

Cost of the Treatment

This criterion is broken down into four categories: low, medium, high, and inadequate information. These are defined in EPA's document, *Remediation Technologies Screening Matrix and Reference Guide* (EPA 1993), as follows:

- Low — less than \$100/ton,
- Medium — \$100 to \$300/ton, or
- High — more than \$300/ton.

Note that costs in this report reflect estimated costs for treating soils contaminated with non-agent-related compounds. For application to agents, all costs will increase due to the extra safety precautions necessary when handling agent-contaminated materials. Also, costs reflect the capital and operational costs of the particular process being reviewed. Costs associated with excavation of soil, pretreatment handling, and air pollution abatement systems are not included.

Current Status of the Technology

This criterion evaluates whether the technology is commercially available and at what level: bench scale, pilot scale, or full scale.

Residuals or Waste Streams

For this screening criterion, each waste stream that results from the treatment technology is identified. The streams in which the contaminants or breakdown products may be located are also identified. If further treatment of these waste streams is needed, possible suggestions for treatment are made.

4.2 Approach to Discussion

In Sections 5 through 8, an introductory subsection, entitled "Nature of the Process," begins the discussion for each technology, and a subsection entitled "Comments" ends the

discussion. The introductory portion explains the technology and its application, focusing on how the technology addresses contamination — by treatment, mobility, or volume reduction. The body of each discussion revolves around the six criteria listed above. The "Comments" subsection may include additional information about the technology, especially advantages and disadvantages of its application. This portion also presents reasons why the technology should or should not be considered further for treatment of agent-contaminated soil.

The technologies discussed in Sections 5 through 8 are listed in Table 8. The EPA's *Remediation Technologies Screening Matrix and Reference Guide* (1993) was used as a baseline reference to develop the initial list of technologies. Much of the basic information on each technology was taken from that document. Additional technologies not listed in the EPA document were also considered. Where applicable, other sources are referenced.

TABLE 8 Soil Treatment Technologies to be Screened^a

Section 5	In Situ Technologies
5.1	Biostimulation
5.2	Bioventing
5.3	Soil Vapor Extraction without Thermal Enhancement
5.4	Soil Vapor Extraction with Thermal Enhancement
5.5	Soil Flushing
5.6	Solidification/Stabilization
5.7	Vitrification
5.8	Natural Attenuation
Section 6	Ex Situ Physicochemical Technologies
6.1	Physical Pretreatment ^b
6.2	Solidification/Stabilization
6.3	Solvent Extraction ^b
6.4	Soil Washing — General
6.5	Alcoholysis or Cleavage with a Strong Basic Solution ^b
6.6	Dehalogenation with Alkaline Polyethylene Glycol
6.7	Chemical Oxidation
Section 7	Ex Situ Biological Technologies
7.1	Slurry-Phase Biological Treatment
7.2	Land Farming
7.3	Controlled Solid-Phase Biological Treatment
Section 8	Ex Situ Thermal Technologies
8.1	Low-Temperature Thermal Desorption
8.2	High-Temperature Thermal Desorption
8.3	Dehalogenation with Heated Sodium Bicarbonate
8.4	Incineration
8.5	Pyrolysis
8.6	Vitrification
8.7	Plasma-Torch Treatment

^a Except as noted, these technologies are essentially as listed in EPA 1993.

^b These technologies were added to the basic list provided in EPA 1993.

5 In Situ Technologies

In situ technologies treat soil without removing it from the site. The following in situ technologies are discussed in this section:

- Biostimulation,
- Bioventing,
- Soil vapor extraction without thermal enhancement,
- Soil vapor extraction with thermal enhancement,
- Soil flushing,
- Solidification/stabilization, and
- Vitrification.

Several of these technologies can be adapted for ex situ use, but only in situ applications are discussed in this section.

5.1 Biostimulation

Nature of the Process. Typically used for groundwater treatment, biodegradation or biostimulation is also used to treat contaminated soil in place. Microorganisms naturally present in the contaminated area are stimulated by circulating aqueous solutions of oxygen and nutrients through the soil. Water is fortified with oxygen and nutrients, circulated into the ground, and recaptured. This technology provides treatment for some contaminants and mobilization for others. For contaminants that are mobilized, aboveground treatment may be necessary before the water is recharged to the ground. In situ biostimulation should be used only where the groundwater is near the surface and is already contaminated, because this technology is likely to spread the contaminant to the groundwater. Careful containment and control of the water charged to the ground may be necessary to limit the spread of contaminants.

Applicability to General Soil Characteristics. The flow of injected solutions is influenced by preferential flow paths. Therefore, the process is most effective where homogeneous soils are present. In non-homogeneous or fractured soils, the solutions will be distributed unevenly through the soil, leading to a decrease in contaminant/solution contact and, potentially, to contamination of previously unaffected areas. Other contaminants in the soil, such

as heavy metals and highly chlorinated organic compounds or inorganic salts, may be toxic to the organisms and may inhibit growth, especially at high concentrations.

Applicability to Agents of Concern. Few data on the biodegradation of agents in soil by naturally occurring microbes are available. However, data on biodegradation of mustard, sarin, VX, and their breakdown products for application to neat agent stockpile destruction are more readily available (National Research Council 1993). Sarin and VX can be detoxified by numerous enzyme-based systems and have the potential to be treated in dilute form by cellular-based systems. In the soil environment, however, sarin and VX most likely would volatilize or hydrolyze before they would biodegrade. Neat mustard is toxic to most microorganisms, and direct biotransformation of mustard using cellular- or enzyme-based systems has not been demonstrated (Harvey and DeFrank 1993). This technology has been shown to be more successful for thiodiglycol and other mustard products following hydrolysis or chemical oxidation. However, these mustard breakdown products are already nontoxic. Biodegradation of lewisite and LO is uncertain. Research is needed to better understand the biodegradation of these agents in soil.

Usefulness for Treating Other Soil Contaminants. Compounds that have been treated by biostimulation in the past include nonhalogenated volatile and semivolatile organics and fuel-related hydrocarbons. Some halogenated volatiles and semivolatiles and pesticides could also be treated (with less efficiency) by biostimulation. Volatiles tend to mobilize before treatment can occur. Heavy metals and some highly chlorinated compounds may actually inhibit microbial activity.

Relative Cost of the Treatment. Costs are low to medium. Operation and maintenance (O&M) are intensive.

Current Status. This technology has been widely used at full scale, where applicable.

Residuals. Saline water, containing refractory water-soluble contaminants and degradation products, may remain in the soil or be transported to the groundwater. The relative concentrations of these contaminants and products determine whether pretreatment of the water is necessary before discharge to the aquifer. Repeated recirculation would be limited by the salinity of post-treatment water.

Biodegradation products that would be left in the residual water are hard to predict, because many of these contaminants have not yet been tested in the laboratory. Degradation products currently present at RMA may result from natural biodegradation that may be occurring at the site. The intermediate biodegradation products that could be formed from these agents are probably similar to the oxidation products discussed in Appendix C. Microbial oxygenates would most

likely result in similar products, but the desirable products would be carbon dioxide and mineral acids.

Comments. Because the biodegradation potential of agents, especially in soils, is not well known, a great deal of research is needed to evaluate the effectiveness of this technology. In addition, because of the potential for the spread of contamination, the geography of the area, and the inhibitory effects of heavy metals, a thorough understanding of the site conditions would be required before applying this technology.

5.2 Bioventing

Nature of the Process. Like biostimulation, bioventing stimulates the activity of naturally occurring microorganisms capable of biodegrading the soil contaminants. But instead of injecting a water-based solution into the soil, air is forced into the soil through either injection or extraction. Low air-flow rates are used to provide enough oxygen to stimulate microbial action and to minimize volatilizing and mobilizing the contaminants. Air is usually humidified before injection into the ground to assure necessary moisture for microbial activity.

Applicability to General Soil Characteristics. This process is most applicable to soils with a moderate moisture content. Bioventing may also be applied in areas with a high water table by employing a drawdown process, although that may be an expensive alternative. The process would be less effective for soils with low moisture content, because drying of the soil may be a problem. Off-gases may need to be monitored at the soil surface.

Applicability to Agents of Concern. Few data on biodegradation of agents by naturally occurring microbes are available. However, data on biodegradation of mustard, sarin, VX, and their breakdown products for application to neat agent stockpile destruction are more readily available (National Research Council 1993). Sarin and VX can be detoxified by numerous enzyme-based systems and have the potential to be treated in dilute form by cellular-based systems. In the soil environment, however, sarin and VX most likely would volatilize or hydrolyze before they would biodegrade. Neat mustard is toxic to most microorganisms, and direct biodegradation of mustard using cellular-based or enzyme-based systems has not been demonstrated (Harvey and DeFrank 1993). This technology has been shown to be more successful for thiodiglycol and other mustard products following hydrolysis or chemical oxidation. However, these mustard breakdown products are already nontoxic. Biodegradation of lewisite and LO is uncertain. Research is needed to better understand the biodegradation of these agents in soil.

Usefulness for Treating Other Soil Contaminants. Many organic contaminants have the potential to be biodegradable. An important issue for bioventing is treatment time — can

enough oxygen be delivered to degrade contaminants in a reasonable time? Bioventing must keep air movement to a minimum to prevent stripping. Bioventing uses air movement that will flush between one and two pore volumes a day. High concentrations of heavy metals and highly chlorinated compounds might inhibit microbial activity.

Relative Cost of the Treatment. The process is neither capital- nor O&M-intensive. The treatment cost is low, typically \$15 per cubic yard.

Current Status. This technology is being used increasingly at full scale, where appropriate.

Residuals. There are no residuals.

Comments. Because the biodegradation potential of agents, especially in soils, is not well known, a great deal of research is needed to evaluate the effectiveness of this technology. Preferential flow paths would limit the effectiveness of injected gas in contaminated regions. The geography of the area would make it difficult to predict the movement of the injected air, limiting contaminant/air contact and potentially spreading volatile contaminants. Monitoring of off-gases at the soil surface would be required. When soil is low in moisture, bioventing tends to dry out the soil, thereby limiting biodegradation.

5.3 Soil Vapor Extraction without Thermal Enhancement

Nature of the Process. In soil vapor extraction (SVE), a vacuum is applied through extraction wells advanced into the vadose zone, creating a pressure gradient that induces volatiles to mobilize and diffuse through the soil to the wells. Once extracted from the ground, the vapors can be treated by processes such as granular activated carbon, catalytic oxidation, internal-combustion engines, or incineration.

Applicability to General Soil Characteristics. SVE is most effectively used to treat highly permeable homogeneous soils. Soils with high humic content tend to bind the volatile organic contaminants, making mobilization difficult. Inconsistent removal rates can result from SVE treatment of highly heterogeneous soils.

Applicability to Agents of Concern. The vapor pressure of sarin is high enough to permit the use of SVE, but the volatility of the three other soil contaminants is too low for this method to be successful.

Usefulness for Treating Other Soil Contaminants. SVE is applicable for mobilizing volatiles and some semivolatiles. SVE is a favored technology for removing trichloroethylene (TCE) from soil.

Relative Cost of the Treatment. Cost is low, but the method is O&M-intensive. The typical cost is under \$50 per ton, excluding treatment of off-gases.

Current Status. This technology is commercially available at full scale.

Residuals. Residuals include vapors or their condensate.

Comments. Preferential flow paths could result in uneven removal rates. Monitoring for toxic off-gases at the soil surface would be required. Because of the nonvolatile nature of lewisite, mustard, and VX, SVE without thermal treatment would not be effective for these contaminants.

5.4 Soil Vapor Extraction with Thermal Enhancement

Nature of the Process. In soil vapor extraction with thermal enhancement, a vacuum is applied through extraction wells in a vadose zone, creating a pressure gradient that induces volatiles to diffuse through the soil to the wells. At the same time, steam/hot-air injection or electric/radio-frequency heating is used to increase the mobility of volatiles and some semivolatiles and to facilitate extraction.

Applicability to General Soil Characteristics. SVE is most effectively used to treat highly permeable homogeneous soils. Soils with high humic content tend to bind the volatile organic contaminants, making mobilization difficult. Treatment of highly heterogeneous soils using SVE may result in inconsistent removal rates.

Applicability to Agents of Concern. The vapor pressure of sarin makes this agent a potential candidate for thermally enhanced SVE treatment. Mustard, lewisite, VX, and perhaps LO would potentially be mobilized at elevated temperatures.

Usefulness for Treating Other Soil Contaminants. This technology is applicable to volatile organics and some semivolatile organics. Use of SVE with thermal enhancement may mobilize organic contaminants in the soil. Some thermally enhanced SVE methods may effectively treat certain pesticides (Sresty et al. 1992). This technology does not address heavy metal contamination.

Relative Cost of the Treatment. This treatment is both capital- and O&M-intensive, but has a low overall cost. The typical cost is \$50 to \$75 per ton, excluding treatment of off-gases.

Current Status. This technology is commercially available.

Residuals. Residuals include vapors and condensate.

Comments. Monitoring and treatment of toxic off-gases at the soil surface would be required. Site soil structure might be modified by some variants of the process. This technology may not reach all of the contaminated soil, because of the preferential flow paths of the injected air.

5.5 Soil Flushing

Nature of the Process. Water (or water-based solutions containing surfactants, biodegradable surfactants, or other additives to enhance contaminant solubility) is applied to or injected into the soil or groundwater to saturate the contaminated area and mobilize contaminants into the groundwater. The groundwater is then extracted. The extracted water containing the mobilized contaminants is subjected to aboveground treatment before being recharged back into the ground.

Applicability to General Soil Characteristics. Soil porosity must be sufficient to allow saturation of the contaminated areas. The injected water must also be contained to prevent contamination of clean areas.

Applicability to Agents of Concern. In the time taken for the process to be completed, any sarin in the soil would be hydrolyzed. With water alone or with a surfactant, mustard would not be solubilized; VX might be carried along through the cycle or redistributed through the soil. The properties of LO are not known well enough for any prediction to be made. Note that the hydrolysis products of the slowly hydrolyzed VX are themselves toxic.

Usefulness for Treating Other Soil Contaminants. Contaminants typically targeted for soil flushing are halogenated and nonhalogenated volatile organics and inorganics. This technology may also be applied (with limited efficiency) to some semivolatile organics, fuels, and pesticides. With additives, some metals and other compounds may also be mobilized by flushing. However, using additives may introduce new toxics into the environment and may not be acceptable for in situ treatment.

Relative Cost of the Treatment. Available cost information is inadequate. The process is O&M-intensive.

Current Status. The technology is being tested at the pilot-scale level.

Residuals. The extracted liquid would contain both contaminants and additives. The contaminants would need to be separated and treated or disposed, and the additives would need to be recovered for reuse.

Comments. Adherence of surfactants or other additives to soil reduces effective soil porosity. Preferential flow paths limit the effectiveness of injected aqueous solutions in contaminated regions and may cause the spread of contaminants. Soil flushing can be applied only to sites where the soil-flushing fluids and contaminants can be contained.

5.6 Solidification/Stabilization

Nature of the Process. Solidification/stabilization (S/S) immobilizes the contaminants by physically binding or enclosing them in a solid mass (solidification) or producing a chemical reaction between the stabilizing agent and contaminant (stabilization). Stabilization is not always accompanied by solidification. Solidifying agents are applied with mixing paddles and augers that

blend the soil with a stabilizing agent fed through the center of each tool's shaft (Holden et al. 1989). If contamination is within the first few feet of the soil surface, conventional earth-moving equipment, such as a backhoe, can be used (Conner 1990).

Most S/S technologies use inorganic binders with cementitious or pozzolanic activity, such as portland cement, fly ash, lime, kiln dust, clays, or blast furnace slag. Organic binders are sometimes used, but are more expensive. A variety of reagents can be added to improve physical properties or chemical binding. These include silicates, silica, sulfides, phosphates, and proprietary additions. S/S treatment is most successful when used to chemically bind inorganic contaminants. In situ oxidation of arsenite to arsenate, followed by in situ treatment with ferric sulfate, stabilizes arsenic as insoluble ferric arsenate (Dragun 1988). The mobility of contaminated soil is typically reduced by greater than 95%. Mobility of organics can be reduced by addition of such sorbents as activated carbon, modified clays, and other organic sorbents. The alkaline environment present in most treated materials can promote hydrolysis of some organic compounds (Harris 1990).

Applicability to General Soil Characteristics. High levels of soil organic matter may inhibit some S/S processes (Hessling et al. 1993). The amount and types of binder/reagents used may need to be adjusted for different soil conditions; for instance, when variable soil types and moisture levels are present at the site.

Applicability to Agents of Concern. Solidification could reduce the mobility of the four military-related agents. Furthermore, the high pH conditions in the treated material would promote hydrolysis of residual agents. Under the high pH conditions expected in S/S-treated materials, the half-lives of the agents would range from a few seconds for sarin (Clark 1989) to several hours for VX (Epstein et al. 1974). However, hydrolysis of the parent compound does not necessarily mean reduction of toxicity, particularly in the case of VX (Yang et al. 1992). Oxidants that reduce toxicity, such as those used in decontaminants, might be effective as S/S reagents.

S/S might be an effective method for containing and destroying agents in soils. However, no data have been developed to document the effectiveness of specific S/S technologies applied to these types of compounds. Inorganic arsenic formed during suitable pretreatment of lewisite or LO could be further treated by S/S.

Usefulness for Treating Other Soil Contaminants. This process is potentially applicable to other contaminants, particularly heavy metals and low levels of organics. Stabilization of wastes containing both organics and inorganics has typically been difficult. The organics tend to diminish the effectiveness of the stabilization process. Historically, the practice is to treat organics first and then stabilize inorganics to immobilize them.

Relative Cost of the Treatment. The cost ranges from low to medium; the typical cost is between \$50 and \$250 per ton (EPA 1990). Much of the cost depends on the type and amount of binder/reagents required and the depth of contamination.

Current Status. This technology is commercially available and widely used for treatment of toxic inorganics and low concentrations of organics.

Residuals. Residuals are solid. The solidified material would be essentially infertile.

Comments. The effectiveness and cost of treatment depend on the depth of contamination. Also, certain wastes are incompatible with this process, and some S/S processes may result in a significant increase in the volume of waste products. Difficulty is often encountered in mixing consistent amounts of binder/reagent with the soil. This problem intensifies when there are high levels of variability in soil type and moisture level at the site, which can lead to variability in the amounts of binder/reagent that should be added. Treatability studies would be required to determine the suitability of the technology to specific soils and contaminants. Potentially, this technology is suitable for soils containing the agents of concern. However, if the agents are not made less toxic in the process, this technology may not be favorable.

5.7 Vitrification

Nature of the Process. The in situ vitrification (ISV) process converts contaminated soil and other substrates into a stable glass and crystalline product. An electrode-feed system inserts a square array of four graphite electrodes into the contaminated site. This mechanism allows the electrodes to sink to increasingly greater depths as the molten glass increases in volume. Processing continues until the desired treatment level is reached, or until a processing depth is reached.

Because soil is not electrically conductive when moisture has been driven off, a conductive mixture of flaked graphite and glass frit is placed between the pairs of electrodes as a starter path. The resultant power heats the starter path and surrounding soil to around 2,000°C, well above initial soil-melting temperatures of 1,100°C to 1,400°C (typical operating temperatures are 1,600°C to 2,000°C). As the molten or vitrified zone grows, it incorporates the contaminants into the melt and pyrolyzes organic compounds. The pyrolyzed by-products migrate to the surface of the vitrified zone, where they combust in the presence of oxygen. A hood placed over the vitrified area directs the gaseous effluents to an off-gas treatment system.

The normal processing rate for the large-scale system is three to five tons per hour. The maximum depth demonstrated thus far has been 17 to 19 ft. The average processing operation lasts about 150 to 200 hours, depending upon the depth and electrode spacing.

Applicability to General Soil Characteristics. Vitrification can be applied to most soils. The treated waste may vitrify nonuniformly if the treated soil is not homogeneous.

Applicability to Agents of Concern. The agents of concern would either pyrolyze or be collected in a concentrated form for other treatment.

Usefulness for Treating Other Soil Contaminants. The process has potential for treating other contaminants. Organics tend to be pyrolyzed, and nonvolatile inorganics tend to be encapsulated in the vitrified material.

Relative Cost of the Treatment. The process is both capital- and O&M-intensive. Estimated cost ranges from \$600 to \$900 per ton. The cost for operations alone is in the range of \$350 to \$500 per ton.

Current Status. The technology has been licensed to one vendor. ISV is the preferred remedy or an alternative remedy at eight private, Superfund, and U.S. Department of Defense (DoD) sites (Hansen 1993).

Residuals. Residuals are liquids (condensate) and the solid vitrified mass.

Comments. The process is limited to depths of approximately 20 feet and is very energy-intensive. After treatment, the resulting land is relatively inert. High treatment costs and the resulting "inert" state of the site make this technology an undesirable choice.

5.8 Natural Attenuation

Nature of the Process. Natural attenuation is the process by which contaminants are allowed to naturally degrade (through volatilization, biodegradation, and adsorption) and/or chemically react with the soil and other subsurface materials, without enhancements. It is different

from a "no action" alternative in that frequent monitoring of the site is required to make sure the process is meeting clean-up objectives.

EPA can approve special circumstances in which natural attenuation may be applied. Such cases may arise when the removal or treatment of the contamination is technically impracticable, when the contaminants are inaccessible and not migrating, or when treatment technologies would not speed up the remediation. To obtain the proper approval in such cases, remediators must monitor and model the attenuation and movement of contamination. The site may have to be fenced or otherwise secured until contaminant levels are sufficiently reduced. Natural attenuation should be used only where no impacts on potential receptors exist.

Applicability to General Soil Characteristics. Natural attenuation is allowed only under special circumstances that must be decided case by case, regardless of the type of soil.

Applicability to Agents of Concern. Sarin easily hydrolyzes to relatively nontoxic materials. Lewisite hydrolyzes to LO, which is similarly toxic. Ultimately, the arsenic in the lewisite will remain. The hydrolysis products of VX are also toxic. Mustard, once dissolved in water, hydrolyzes quickly. However, the solubility of mustard in water is very low. The surface of a mustard clump or globule will polymerize and form a protective film on the outside of the globule, leaving the inner mustard unreacted. This unreacted mustard could potentially remain in the soil for an undetermined amount of time; it is known to have been present in soil for decades (Sage and Howard 1989).

Usefulness for Treating Other Soil Contaminants. Natural attenuation can be applied to a variety of contaminants (e.g., organics that can be degraded by natural organisms and heavy metals that are relatively nonmobile and are shown to be stable at the site of concern).

Relative Cost of the Treatment. Cost is low. There may be modest costs for sampling, analysis, modeling, and (if required) long-term monitoring.

Current Status. This alternative is not well-accepted by regulators and therefore has not been widely used.

Residuals. There are no residuals.

Comments. Persistent mustard globules and toxic degradation products of VX and lewisite may persist for a long period and therefore make this alternative undesirable.

6 Ex Situ Physicochemical Technologies

The ex situ remedial technologies and processes described in Sections 6, 7, and 8 fall into three categories: Ex Situ Physicochemical Processes (Section 6), Ex Situ Biological Processes (Section 7), and Ex Situ Thermal Technologies (Section 8).

The first process described in this section, physical pretreatment, is not a remedial technology per se, but rather a soil handling process that is necessary before all ex situ processes. However, in the pretreatment of soil, some contaminants that are easily oxidized or volatilized may be treated or removed as a consequence of handling. For the sake of discussing how each of the ex situ technologies will affect the contaminants of concern, it will be presumed that these contaminants may be present in the soil after pretreatment.

Ex situ physicochemical processes use chemicals to bind, stabilize, remove, or degrade contaminants in the soil. Technologies discussed in this section include the following:

- Physical pretreatment,
- Solidification/stabilization,
- Solvent extraction using critical/supercritical fluids, and
- Soil washing.

Soil washing is treated in four parts, as follows:

- General,
- Alcoholysis or cleavage with a strong basic solution,
- Dehalogenation with alkaline polyethylene glycol, and
- Chemical oxidation.

Note that solidification/stabilization can be used in situ or ex situ. Only ex situ applications are discussed in this section.

6.1 Physical Pretreatment

Nature of the Process. The preparation needed for the various ex situ processes may vary. However, physical pretreatment should precede all other processes, and one pretreatment

facility may be used to prepare for several later operations. Pretreatment may consist of excavating, drying, reducing the size, removing scrap metal and structural debris, and blending solids. Typically, large objects (greater than 1.5 to 2.0 in.) are screened from the feedstock and rejected as oversized; however, for some later processes, particles may have to be as small as 0.125 in. in diameter. The feed material is either stored for later use or delivered to the treatment operation.

The feed pretreatment area will require a fully enclosed building with storage capacity for three to five days worth of feed material, segregated by point of origin or type of contaminant. The building will enclose the contaminated soil handling, sizing, and mixing equipment, as well as the feed hoppers. Other equipment may include a magnetic separator, primary shredder, disk classifier, and final shredder to reduce the largest clay soil lumps to a diameter of 1.4 in. or less.

Applicability to General Soil Characteristics. Physical soil pretreatment is not limited by soil type.

Applicability to Agents of Concern. Sarin would hydrolyze and some of it might volatilize but would react with moisture in the air. Depending on the moisture content of the soil, hydrolysis of the other agents may occur to some degree.

Usefulness for Treating Other Soil Contaminants. The applicability of this process does not depend highly on the contaminant type. Pretreatment of soils is a typical and often necessary preparatory step for most ex situ technologies. The degree of pretreatment depends on the treatment technology and remediation goals.

Relative Cost of the Treatment. Cost data are highly variable and dependent on the treatment train. In reviewing the various ex situ treatment technologies, pretreatment costs are not included in treatment costs quoted.

Current Status. Physical pretreatment is available.

Residuals. Residuals are solids that will need further treatment.

Comments. Pretreatment, or handling of the soil before ex situ treatment, is necessary in almost all cases. With regard to handling and pretreatment of agent-contaminated soil, extra attention must be given to worker safety to guard against exposure to agents or their vapors.

6.2 Solidification/Stabilization

Nature of the Process. S/S immobilizes the contaminants by physically binding or enclosing them in a solid mass (solidification) and producing a chemical reaction between the stabilizing agent and contaminant (stabilization). Stabilization is not always accompanied by solidification. Most S/S technologies use inorganic binders with cementitious or pozzolanic activity, such as portland cement, fly ash, lime, kiln dust, clays, or blast furnace slag. Organic binders are sometimes used, but are more expensive. A variety of reagents, such as silicates and phosphates, can be added to improve physical properties or chemical binding. S/S treatment is most successful when used to chemically bind inorganic contaminants. Oxidation of arsenite to arsenate, followed by treatment with ferric sulfate, stabilizes the arsenic as the insoluble ferric arsenate (Dragun 1988). The mobility of contaminated waste is typically reduced by greater than 95%.

The mobility of organics can be reduced by adding such sorbents as activated carbon, modified clays, and other organic sorbents. The alkaline environment present in most treated materials can promote hydrolysis of some organic compounds (Harris 1990). Degradation reactions are not typically considered in S/S.

Coarse screening may be required before the soil is mixed with binder/reagents in a pug mill, and this oversized material may be a sidestream requiring disposal. The treated material may be replaced in its original location or placed in a secure landfill. The treated material occupies a larger volume than untreated material, because of the added binder/reagents.

Laboratory-scale testing is typically required to determine requirements for binder/reagents at a specific site.

Applicability to General Soil Characteristics. High levels of soil organic matter may inhibit some processes (Hessling et al. 1993). The amount and types of binder/reagents used may need to be adjusted for different soil conditions.

Applicability to Agents of Concern. Solidification could considerably reduce the mobility of the four military-related agents. Furthermore, the high pH conditions in the treated material would promote hydrolysis of residual amounts of the agents. Under the high pH conditions expected in S/S-treated materials, agent half-lives range from a few seconds for sarin (Clark 1989) to several hours for VX (Epstein 1974). Data indicate that these agents should be substantially eliminated over the period of years during which the agents would be contained within the treated soil (Zamejc 1985). However, hydrolysis of the parent compound does not necessarily mean reduction of toxicity, particularly in the case of VX (Yang et al. 1992). To more effectively reduce toxicity, oxidants such as those used in decontaminants might be effective as S/S reagents that promote oxidative destruction.

Inorganic arsenic formed in a suitable pretreatment of lewisite or LO could be further treated by S/S. Pretreatment should always be employed if agent concentrations are high.

Usefulness for Treating Other Soil Contaminants. Ex situ S/S is potentially applicable to other contaminants, particularly heavy metals and low levels of organics. Stabilization of wastes containing both organics and inorganics has typically been difficult. The organics tend to diminish the effectiveness of the stabilization process. Historically, the practice is to treat organics first and then stabilize inorganics to immobilize them.

Relative Cost of the Treatment. The cost ranges from low to medium, with typical costs ranging from \$50 to \$250 per ton (EPA 1990; EPA 1993). Much of the cost depends on the type and amount of binder/reagents required and the cost of disposing the treated material.

Current Status. This technology is commercially available and widely used at full scale for treatment of toxic inorganics and low concentrations of organics.

Residuals. The residual is solid. The stabilized mass would have to be disposed as hazardous waste.

Comments. Certain contaminants are incompatible with the S/S process, and some processes may result in a significant increase in the volume of waste products. If oxidants could be successfully used as an additive in the process, to decontaminate the agents in the soil as solidification takes place, this process could be effective for the soils of concern. Extensive treatability studies would be required to determine the suitability of the technology to agent-contaminated soils. The residual solid may require disposal in a hazardous waste landfill.

6.3 Solvent Extraction

Nature of the Process. The process of solvent extraction relies on the unique nature of specific solvents to extract contaminants from soil particles. Solvent extraction is a separation technique that relies on the contaminant's higher affinity for the solvent than for the contaminated matrix. There are three different types of solvent extraction: standard solvents, critical fluids/liquefied gases, and critical solution temperature (CST) solvents (EPA 1992). The standard solvent process uses organic solvent, usually at ambient temperatures. The critical fluids/liquefied gases method, known as supercritical fluid extraction (SFE), employs supercritical temperatures and pressures to obtain high solubility with organic contaminants. When the temperatures and

pressures from the solution are lowered below the supercritical point, organic contaminants are released from solution and are amenable to extraction. The CST solvents method uses unique solubility properties of certain solvents that allow for the solvent and contaminant to be soluble at one temperature and insoluble at another, making extraction from soil and separation of solvent/contaminant possible.

Standard solvents used in solvent extraction include alkanes, alcohols, or similar liquid solvents (EPA 1992). Critical fluids/liquefied gases include butane, isobutane, propane, carbon dioxide (CO₂) or similar gases, liquefied under pressure at room temperature. The pressure range for supercritical CO₂ is usually 70 to 100 atm (1,000 to 1,500 psi); the standard range for propane is 15 to 30 atm (200 to 450 psi) (Shallis 1994). A CST solvent, triethylamine, has the unique property of being soluble in water below 40°C, but insoluble in water at higher temperatures (EPA 1991). The ability of the near-critical fluids/liquefied gases and CST solvents to be soluble with the contaminants at one temperature or pressure and insoluble at another allows for ease in separation of the solvent and contaminant and the ability to recycle the solvent used in these processes.

Applicability to General Soil Characteristics. The main disadvantage of the various types of solvent extraction processes in regard to soil types is the inability to remove contaminants from fine particles. Supercritical fluids have been shown to extract from most types of soils (Bruno and Ely 1991). Problems have been encountered in desolving contaminants from fine particles by using CST solvents. Methods to solve this problem are presently being studied (Wilde 1993). Other difficulties encountered with CTS solvents include separating fines from the wastewater and high humic content inhibiting desorption.

Applicability to Agents of Concern. The solubility of the agents of concern in most solvents used in this process is uncertain. Research conducted by Greist et al. (1992) concluded that a temperature and pressure above 60°C and 300 atm, with CO₂ containing 5% methanol is necessary to efficiently extract simulants of sarin, mustard, and VX. Triethylamine, because of its alkalinity, would behave as more than a solvent; to a degree, it may react chemically with the agents, reducing and altering toxicity but not always eliminating the agent. The kinetics of such reactions are beyond present knowledge. Other solvents used in solvent extraction may be applicable to LO if it behaves like an arsenical compound.

Usefulness for Treating Other Soil Contaminants. Solvent extraction is generally applicable to organic compounds. Its use with inorganics is limited; it may have some application for organometals. Heavy metal chelates are soluble in critical/supercritical fluids, but simple salts or oxides are not (Shallis 1994). Pesticide contaminants, particularly dieldrin, aldrin, and chlordane, could potentially be treated by this method. CST solvents like triethylamine have been used to treat pesticides, herbicides, polychlorinated biphenyls (PCBs), and polyaromatic hydrocarbons (PAHs) (Wiemer et al. 1992).

Relative Cost of the Treatment. The general cost for solvent extraction processes is in the high range (greater than \$300/ton) due to high capital and O&M costs. For the CF System supercritical fluid process, the vendor estimates a cost of \$150 to \$400 per ton (Erikson 1993). A process using the CST solvent triethylamine could range between \$94 and \$507 per ton depending on the feed rates of the soil (EPA 1992 and Jones et al. 1991). Costs for solvent extraction processes are also dependent on feed-soil moisture.

Current Status. Solvent extraction processes are used at full scale on a very limited basis.

Residuals. There are three product streams from solvent extraction processes: treated soils, concentrated contaminants, and separated water. Inorganic contaminants such as metals will most likely remain in the soil, requiring further treatment. The solvent should be recycled to make the process economical. Some solvent extraction systems may require emissions scrubbing to prevent harmful releases (EPA 1994).

Comments. The wide variety of solvents used in the three types of solvent extraction processes can provide different results. The solvents vary in their ability to sorb to fine particles in the soil, their ability to treat a wide range of contaminants, the ease in separating the solvent and contaminant after extraction, and in their energy requirements (EPA 1992). A problem occurs in selecting a particular solvent that would be compatible with all the contaminants. For the supercritical process, the pressure-temperature-solubility relationships of the solvent would have to be determined in order to precisely control process conditions. Some of the solvents used in the solvent extraction process, such as triethylamine, are flammable, toxic, or both (EPA 1994). Therefore care must be taken in using these solvents. Some products, such as arsenic and other toxic products, may require treatment, solidification, and/or disposal in a hazardous waste landfill. Research would be necessary to determine the solubilities of the agents in the solvents prior to testing.

6.4 Soil Washing — General

The next group of technologies (6.5-6.7) comprises several versions of soil washing. This section describes soil washing in general; the following sections describe the applicability of three variations on soil washing.

Nature of the Process. Soil washing involves the mixing or agitation of excavated, contaminated soil with an aqueous solution to separate coarse and fine soil particles and promote the desorption of contaminants from the soil particles. Agitative energies must be high enough to promote the collision of soil particles, to aid in soil particle and soil/contaminant separation.

Additives to the solution, including basic leaching agents, surfactants, pH adjusters, and chelating agents, may aid in mobilizing the contaminant from the soil particles. Often the water and additives are recovered for reuse (Wilde 1993). There is some controversy regarding whether this technology can actually mobilize or solubilize the sorbed contaminants from the soil particles in the short residence times used, or whether the technology simply separates by particle size. In the latter case, this technique is considered to be a volume-reduction technique, in which the contaminated soil particles are separated out. Soils may need to be washed three or more times to reach remediation goals. Soils with multiple contaminants (i.e., heavy metals and organics) make formulating an appropriate soil washing solution difficult.

Applicability to General Soil Characteristics. This process is most effective on coarse-grain soil. Desorbing contaminants from fine particles is difficult, but the problem is being studied (Wilde 1993). Size distribution of the soil should be well known before soil washing is considered.

Applicability to Agents of Concern. In the time taken for the process to be completed, any sarin or lewisite in the soil would be hydrolyzed. Mustard would not be solubilized, although droplets might be mobilized, carried as an emulsion, and even (to some extent) hydrolyzed. If the solution were sufficiently basic, VX would be converted to other toxic products. Depending on the alkalinity of the solution and the temperature, some or all of the LO could be converted to inorganic arsenite.

Usefulness for Treating Other Soil Contaminants. This technology has been successfully used to treat soils contaminated with heavy metals. Organics are more difficult to separate from the soils. The technology depends largely on the particle size and humic content of the soil.

Relative Cost of the Treatment. The relative cost is medium. EPA estimates a cost range between \$120 and \$200 per ton, including excavation. The process is O&M- and capital-intensive.

Current Status. This technology is commercially available at full scale.

Residuals. Residuals include liquid and solid fines that might require further treatment or disposal. Other solid waste streams may need to be landfilled or further treated if the contaminant concentrations are not reduced to levels that permit the waste to be placed back at the site. Solution additives may need to be recovered for reuse to make the process economical.

Comments. This technology may be useful in treating sarin and VX, simply for its hydrolyzing effect. However, careful consideration must be given to choosing solution additives when numerous contaminants are found in the soils. Separating fines from wastewater is difficult and expensive. High humic content may inhibit desorption. This technology should be investigated further to find additives that would be effective and reusable for agent-contaminated soils.

6.5 Alcoholysis or Cleavage with a Strong Basic Solution

Nature of the Process. This process represents an extension of the soil washing process into a highly alkaline range. Contaminants sorbed on soil particles are slurried in a batch reactor with a solvent mixture such as DS2 solution (a very alkaline solution of 2% sodium hydroxide in 28% 2-methoxyethanol/70% diethylenetriamine) or the solution of a strong base (alkoxide) in the biodegradable solvent n-ethyl-2-pyrrolidinone. The soil is then washed with water, which is combined with used solvent mixture, reconcentrated, filtered, and recycled. Such treatment has not been employed with soils, but has been used successfully by the Army to decontaminate solid surfaces of chemical agents (specifically, mustard, sarin, and VX).

Applicability to General Soil Characteristics. As with general soil washing, the process is most effective on coarse-grain soil. Successful chemical treatment of contaminants strongly bonded to soil fines or humic matter may be difficult (Wilde 1993).

Applicability to Agents of Concern. Any sarin, mustard, or VX present would be degraded. The LO would most likely be converted to inorganic arsenite, along with acetylene and vinyl chloride. Application of heat (90°C) would enable the use of 5% aqueous sodium hydroxide to detoxify sarin and mustard and to mineralize LO (Yang et al. 1992). The treatment would completely hydrolyze VX while leaving a residue of toxic product (Small 1983; Sage and Howard 1989).

Usefulness for Treating Other Soil Contaminants. This treatment could be used to remove heavy metals and possibly some organics.

Relative Cost of the Treatment. The cost is potentially high, because of the cost of additives. The process is O&M-intensive.

Current Status. This technology is not commercially available and has been used by the Army only to demilitarize solid surfaces of chemical agents.

Residuals. A large volume of spent solutions, as well as some solids, would require treatment or disposal.

Comments. Not all of the chemistry for this process is known. Some of the products might have to be disposed in a hazardous waste landfill. Separating fines from the wastewaters is difficult and expensive. Before this technology is considered, the particle-size distribution of the soil should be well known. This methodology would be worth pursuing for relatively small amounts of soil containing mustard or LO. In the case of LO, the arsenite product would have to be isolated for disposal. For large volumes of soil, the potentially high cost and environmental risk of handling the spent solution would make this technology an unattractive alternative.

6.6 Dehalogenation with Alkaline Polyethylene Glycol

Nature of the Process. This process is similar to the one described in Section 6.5, but an alkaline polyethylene glycol (APEG) reagent is used together with a slight increase in temperature to enhance the chemical reaction; potassium polyethylene glycolate (KPEG) is the most common APEG. Contaminated soils are mixed with the reagent in a batch reactor and heated.

Applicability to General Soil Characteristics. As with general soil washing, this method is most effective on coarse-grain soil. Desorbing contaminants from fine particles is difficult, but the problem is being studied (Wilde 1993).

Applicability to Agents of Concern. Any sarin, mustard, or VX present should be broken down in the presence of an alkaline solution such as APEG (Yang et al. 1992; Small 1984). However, some of the products of VX might still be toxic. LO would most likely be converted to inorganic arsenite, acetylene, and a little vinyl chloride.

Usefulness for Treating Other Soil Contaminants. Other organic contaminants, particularly dieldrin, aldrin, and chlordane, could be treatable by this method.

Relative Cost of the Treatment. Presumably, the cost is high because of the cost of the reagent. The process is capital- and O&M-intensive.

Current Status. This technology is commercially available and has been used at full scale to detoxify PCBs through removal of chlorine atoms.

Residuals. Residuals include a large volume of spent solutions, as well as some solids, which would require treatment before disposal.

Comments. Not all of the chemistry involved in this process is known. If the water content of the soil exceeds 20%, an excessive amount of reagent will be required (EPA 1993). Some of the products might have to be disposed in a hazardous waste landfill. Separating fines from the wastewater is difficult and expensive. Before this technology is considered, the particle-size distribution of the soil should be well known. This methodology, perhaps without heat, might be worth pursuing for relatively small amounts of soil containing mustard and LO. In the case of LO, the arsenite product would have to be isolated and disposed safely. This technology would not be economical for large quantities of soil unless a method could be developed to recover the solvent for reuse.

6.7 Chemical Oxidation

Nature of the Process. Chemical oxidation technology, as discussed here, represents another extension of soil washing. The chemistry of solid calcium hypochlorite and organochlorinating agents with military-relevant compounds is discussed in Appendix B. Oxidizing solutions or liquid decontaminants may be applied, as in conventional soil washing. After treatment, the soil is washed with water combined with used solvent mixture. Both solvent and water may be treated and recycled. Such decontaminants have not been employed with soils, but have been used successfully by the Army to decontaminate surfaces that contain chemical agents (specifically, mustard, sarin, and VX). Some decontaminants that have been used are strong aqueous hypochlorite solutions; Decontaminating Agent, Multipurpose (DAM); peroxyorganic acid solutions; and oxone, a commercial mixture of the peroxy compound KHSO_5 with KHSO_4 and K_2SO_4 in 2:1:1 proportions (Yang et al. 1992).

Applicability to General Soil Characteristics. Desorbing contaminants from fine particles is difficult. However, chemical oxidation of a clay soil contaminated with TCE has been shown to be successful (Gates and Siegrist 1993). High humic content might make the contaminants inaccessible to the oxidants or may consume the oxidants.

Applicability to Agents of Concern. Mustard and VX potentially would be oxidized. Sarin would hydrolyze with the aqueous decontaminant treatments (due to catalysis) and with solid bleaches. LO, if not completely mineralized, potentially would be converted to the less toxic pentavalent arsenic compound.

Usefulness for Treating Other Soil Contaminants. The application of chemical oxidation to soils is most typically applied to inorganic contamination. However, nonhalogenated volatiles and semivolatiles, fuel hydrocarbons, and some pesticides may also be treated by oxidation. Chemical oxidation is known to be used for organic contaminants in Hazardous waste treatment.

Relative Cost of the Treatment. Cost is medium to high on a per-ton basis, but inexpensive if the scale of use is limited. Soils with high contaminant concentrations might be costly to treat because of the large amounts of oxidizing agents required.

Current Status. The general technology of oxidation is commercially available and has been applied at full scale.

Residuals. A large volume of spent solutions will require disposal. Depending on the additives required for treatment, the treated soil may require disposal in a sanitary landfill if the chlorinated organics form between humic soil constituents and the chlorinating agents.

Comments. Treatment with active chlorine bleaches may create undesirable organochlorine products. For LO, the arsenic-containing product will require isolation and treatment or disposal. Separating fines from the wastewaters is difficult and expensive. Before this technology is considered, the particle-size distribution of the soil should be well known. This methodology would be worth pursuing for soils containing relatively small amounts of mustard, LO, VX, and sarin. Otherwise, the high cost and the environmental risk caused by the large amount of decontaminating solution that is required would make this process undesirable.

7 Ex Situ Biological Technologies

The ex situ biological processes discussed in this section are as follows:

- Slurry-phase biological treatment,
- Land farming, and
- Controlled solid-phase biological treatment.

7.1 Slurry-Phase Biological Treatment

Nature of the Process. Contaminated soil is mixed with an aqueous solution enriched with nutrients and oxygen to promote microbial activity. Seed microorganisms may be added, although microorganisms already present in the soil may be adequate (Holden et al. 1989). The resulting slurry is continually agitated or mixed to promote bioavailability and ultimate biodegradation of the contaminants. When the slurry has reached a predetermined contaminant-reduction goal or has been mixed for a predetermined time, it is dewatered. Resulting soil and water may need further treatment before disposal or reintroduction to the environment. Pre- and post-treatment handling of the soil, excavation, sizing, determining contaminant loading rates, and dewatering can prove to be extensive and expensive.

Applicability to General Soil Characteristics. This technology is designed to remediate biodegradable contaminants in soil fines. Coarse material is usually separated out of the process before treatment.

Applicability to Agents of Concern. Data on the biodegradation of warfare agents in soil are not available. However, the biodegradation of mustard, sarin, and VX and their breakdown products has been studied for application to stockpile destruction (National Research Council 1993). Sarin and VX can be detoxified by numerous enzyme-based systems and have the potential to be treated in dilute form by cellular-based systems. Neat mustard is toxic to most microorganisms, and direct biotransformation of mustard using cellular-based or enzyme-based systems has not been demonstrated (Harvey and DeFrank 1993). Biodegradation has been shown to be more successful for thiodiglycol and other mustard products, following hydrolysis or chemical oxidation. However, these breakdown products are already nontoxic. Biodegradation of lewisite and LO is uncertain. Research is needed to better understand the biodegradation of these agents in soil.

Usefulness for Treating Other Soil Contaminants. Slurry-phase biotreatment is most effective in treating nonhalogenated volatile organics and fuel hydrocarbons. Some halogenated volatiles and semivolatiles, and some nonhalogenated semivolatiles and pesticides, have been treated using this technology. Most organics including many chlorinated organics and pesticides, however, tend to inhibit microbial growth, especially at high concentrations. High concentrations of heavy metals will also inhibit microbial growth and, by their elemental nature, are not biodegradable.

Relative Cost of the Treatment. Costs are rated as medium by EPA (1993) but can be high, depending on the intensity of pre- and post-treatment required. Unlike other technologies, this technology tends to have unit costs that increase as the volume increases, depending on the volume range. The process is both capital- and O&M-intensive.

Current Status. Slurry-phase biotreatment is available at the commercial level for full-scale implementation.

Residuals. Both waste soils and aqueous solutions may need further treatment. Replacement or disposal of the soil would be required.

Comments. Sizing of materials can be difficult and expensive. An acceptable method for disposing of wastewaters is required. Extensive research would be necessary before this technology is employable to treat agent-contaminated soils. Most likely, the agents would have to be hydrolyzed before biotreatment; hydrolysis products for some of the agents are not very toxic and may not need further treatment.

7.2 Land Farming

Nature of the Process. This technique involves the turning or tilling of contaminated soils to enhance the aeration necessary for biodegradation to take place. Contaminated soils are either excavated, placed on another site and tilled into the underlying soil (ex situ), or tilled in place (in situ). (Only ex situ applications are discussed here.) Such additives as nutrients, organic matter, and moisture may be applied to encourage microbial activity. Liners can be used for better control of the leachates. If contaminants are water-soluble, liners may be necessary. Volatile organic concentrations in the soil often decrease through volatilization during soil handling, rather than by biodegradation.

Applicability to General Soil Characteristics. This technology can be applied to most soils. This process is most effective on fertile, vegetated soil where microbial activity is abundant; it is not effective on very sandy or very clayey soils.

Applicability to Agents of Concern. This technology utilizes microbial species indigenous to the soil to act upon the contaminants. In general, sarin and VX can be detoxified by numerous enzyme-based systems and have the potential to be treated in dilute form by cellular-based systems (National Research Council 1993). Mustard is toxic to most microorganisms, and direct biodegradation using cellular-based or enzyme-based systems has not been demonstrated (Harvey and DeFrank 1993). Following hydrolysis or chemical oxidation, biodegradation has been shown to be more successful with thiodiglycol and other mustard products. However, these products of H already are not toxic. Biodegradation of lewisite and LO is uncertain. Research is needed regarding the biodegradation of these agents in soil. When the soil is tilled in the presence of moisture, sarin, lewisite, and VX should hydrolyze. Mustard might hydrolyze to some degree. Tilling activities would also promote the evaporation of sarin.

Usefulness for Treating Other Soil Contaminants. Land farming is most effective in treating or volatilizing nonhalogenated volatile organics and fuel hydrocarbons. Some halogenated volatiles and semivolatiles, and some nonhalogenated semivolatiles and pesticides, have been treated using this technology. Many chlorinated organics and pesticides, however, tend to inhibit microbial growth, especially at high concentrations. High concentrations of heavy metals also inhibit microbial growth and, by their elemental nature, are not biodegradable. If concentrations of inhibitory contaminants are lowered by adding soil and/or organic matter, their inhibiting effect may be reduced or eliminated.

Relative Cost of the Treatment. Cost is relatively low. The process is neither capital- nor O&M-intensive.

Current Status. This technology has been used frequently to treat petroleum-contaminated soils at full scale.

Residuals. Replacement or disposal of the soil would be required. Arsenic or other metals would remain and would need to be removed or stabilized.

Comments. Land farming requires a great deal of space allocated for an extended period of time. Extensive research is needed to determine the biodegradability of the agents. Research is also needed to determine the metabolites for degradation of these contaminants and what their toxicity may be. The buildup of toxic metabolites might limit the process. Other contaminants in

the soil might inhibit microbial activity, although amendments to the soil could decrease or eliminate this problem. This technology would not be a good choice for sarin because of its volatility, nor for lewisite or LO because of their arsenic content.

7.3 Controlled Solid-Phase Biological Treatment

Nature of the Process. This technology takes excavated soil land farming one step further by extensively controlling the environment where the biotreatment is taking place. The excavated soil is placed in prepared treatment beds, biotreatment cells, or compost piles where leachates can be collected and aeration or turning of the soil can be performed. Moisture, temperature, oxygen levels, and pH are usually monitored and controlled. Often the soil is amended with straw or other coarse organic material to increase pore space and aid in the movement of air and moisture within the pile.

Applicability to General Soil Characteristics. This technology can be applied to most soils. This process is most effective on fertile, vegetated soil where microbial activity is abundant; it is not effective on very sandy or very clayey soils.

Applicability to Agents of Concern. This technology utilizes microbial species indigenous to the soil to act upon the contaminant. Among neat agents, sarin and VX can be detoxified by numerous enzyme-based systems and have the potential to be treated in dilute form by cellular-based systems (National Research Center 1993). Mustard is toxic to most microorganisms, and direct biodegradation using cellular-based or enzyme-based systems has not been demonstrated (Harvey and DeFrank 1993). However, following hydrolysis or chemical oxidation, this treatment has been more successful on thiodiglycol and other mustard products. These breakdown products are already nontoxic, however, and would not require further treatment. Biodegradation of lewisite and LO is uncertain; research is needed to evaluate the biodegradation of these agents in soil. When the soil is tilled or moisture is added, sarin, VX, and lewisite should hydrolyze. Mustard might hydrolyze to some degree. Tilling activities would also promote the evaporation of sarin.

Usefulness for Treating Other Soil Contaminants. Controlled solid-phase biotreatment is most effective in treating nonhalogenated volatile organics and fuel hydrocarbons. Some halogenated volatiles and semivolatiles, and some nonhalogenated semivolatiles and pesticides, have been treated using this technology. Many chlorinated organics and pesticides, however, tend to inhibit microbial growth, especially at high concentrations. High concentrations of heavy metals will also inhibit microbial growth and are, by their elemental nature, not biodegradable.

Relative Cost of the Treatment. Cost is relatively low. The process is neither capital- nor O&M-intensive.

Current Status. This technology is available at full scale.

Residuals. Replacement or disposal of the soil would be required. Arsenic or other metals would remain and would need to be removed or stabilized.

Comments. Large amounts of space and time are required to complete this process. Because little is known about the biodegradability of agents and their products, extensive treatability studies would be required and therefore, possible implementation would be in the future. This technology would not necessarily be applicable for sarin remediation because sarin would theoretically be lost to the air or hydrolyze before biodegradation could take place. If lewisite could be degraded, the arsenic would have to be removed or stabilized before replacement of the soil.

8 Ex Situ Thermal Technologies

The remaining seven technologies, all categorized as thermal treatment, vary in temperature range and application. These seven technologies are as follows:

- Low-temperature thermal desorption,
- High-temperature thermal desorption,
- Dehalogenation with heated sodium bicarbonate,
- Incineration,
- Pyrolysis,
- Vitrification, and
- Plasma-torch treatment.

Note that vitrification can be used both in situ and ex situ. Only ex situ applications are discussed in this section.

8.1 Low-Temperature Thermal Desorption

Nature of the Process. Low-temperature thermal desorption physically separates organic contaminants from soil particles by heating the soil to between 93°C and 315°C and volatilizing the organics, essentially mobilizing the contaminants from the soil. A carrier gas or vacuum system transports volatilized water and organics to the gas-treatment system, where the intact, but still toxic, contaminants may be treated.

Applicability to General Soil Characteristics. Thermal treatment of soils is not dependent on soil texture. However, soil moisture, particulates in the emissions, and their relation to soil texture are concerns to be addressed when engineering the process.

Applicability to Agents of Concern. At the higher range of temperatures, the agents will start to decompose. To what extent the arsenic species in the lewisite and LO will volatilize is not known.

Usefulness for Treating Other Soil Contaminants. The process is primarily applicable for halogenated and nonhalogenated volatile organic compounds and fuels. Halogenated and nonhalogenated semivolatile organic compounds and pesticides may be less effectively treated by this technology. The technology is not applicable to most metals, although some metals may partially volatilize. In the case where the metals volatilized, the gas stream would have to be treated before being emitted to the atmosphere.

Relative Cost of the Treatment. Cost is less than \$100 per ton, excluding soil pretreatment and treatment of volatilized contaminants. The cost will depend on the type of thermal desorption used. The technology is both capital- and O&M-intensive.

Current Status. This technology is commercially available at full scale.

Residuals. Residuals include vapors and liquids (condensates). Residual soil may contain additional contaminants that require further treatment. Arsenic from lewisite and LO may remain in the soil residue or volatilize, in which case it would need to be captured by using APCDs.

Comments. Pretreatment of the soil may require moisture adjustment by drying the soil or mixing in dryer soil. Mobilized contaminants will also require treatment, usually in an afterburner. Low-temperature thermal desorption has potential for the treatment of the chemical agents of concern.

8.2 High-Temperature Thermal Desorption

Nature of the Process. Like low-temperature thermal desorption, high-temperature thermal desorption physically separates organic contaminants from soil particles; however, it uses a temperature range of 315°C to 538°C to volatilize the organics and some metals. A carrier gas or vacuum system transports volatilized water and organics to the gas treatment system, where the intact, but still toxic, contaminants may be treated.

Applicability to General Soil Characteristics. Thermal treatment of soils is not dependent on soil texture. However, soil moisture, particulates in the emissions, and their relation to soil texture are concerns to be addressed when engineering the process.

Applicability to Agents of Concern. The technology will volatilize all of the agents of concern; all might also be expected to decompose to some degree. To what extent the arsenic species in the lewisite and LO will volatilize is not known.

Usefulness for Treating Other Soil Contaminants. The process is primarily applicable to halogenated and nonhalogenated semivolatile organic compounds and pesticides. Most organic contaminants and some heavy metal salts or oxides are treatable by this method.

Relative Cost of the Treatment. Cost range is \$100 to \$300 per ton (medium), excluding soil pretreatment and treatment of volatilized contaminants. The cost would depend on the type of thermal desorption used. The technology is both capital- and O&M-intensive.

Current Status. This technology is commercially available at full scale.

Residuals. Residuals include vapors and liquids (condensates). Residual soil may contain additional contaminants that need further treatment.

Comments. The high temperatures used in this process could volatilize certain metals, such as mercury and arsenic, so a properly designed APCD will be required to capture the metals. Pretreatment of the soil may involve moisture adjustment by drying the soil or mixing in dryer soil. Mobilized contaminants will require treatment, usually in an afterburner. This technology appears to be an efficient way to mobilize agents from the soil. Degradation of the agents may occur at operating temperatures; treatability studies are needed to determine the required temperatures.

8.3 Dehalogenation with Heated Sodium Bicarbonate

Nature of the Process. Dehalogenation is an ex situ remedial technology that was developed in a joint venture between the Navy and EPA as an inexpensive method to treat soils contaminated with chlorinated organic compounds. The process targets halogenated semivolatile organic compounds and pesticides and, less effectively, halogenated volatile organic compounds. Soil is screened, crushed, mixed with sodium bicarbonate, and heated to 333°C in a rotary reactor to decompose or volatilize the organic compounds. The bicarbonate loses carbon dioxide at temperatures above 270°C, potentially providing carbonate ion, a stronger base, or the still more basic hydroxide ion.

Applicability to General Soil Characteristics. This process can be applied to most types of soils. Soils with high moisture and clay content will increase treatment costs.

Applicability to Agents of Concern. Sarin, mustard, or VX will likely volatilize or react with a basic species generated from sodium bicarbonate. Degradation products of VX may be toxic. LO should convert to inorganic arsenite, acetylene, and a small amount of vinyl chloride.

Usefulness for Treating Other Soil Contaminants. Organic soil contaminants, such as dieldrin, aldrin, and chlordane, are potentially treatable by this method. The process is not effective in treating heavy metals. Certain nonhalogenated volatiles would be treated in the process by thermal desorption.

Relative Cost of the Treatment. The cost is unknown, but probably in the medium range. The process is anticipated to be capital- and O&M-intensive. Soils with high moisture and clay content increase treatment costs.

Current Status. This technology is not commercially available. It has been employed at full scale, but on a very limited basis.

Residuals. Emissions scrubbing of vapor emitted from the process may be required before release.

Comments. Not all of the chemistry involved in the process is known. If the water content of the soil is excessive, treatment costs will increase. Some of the products may require further treatment, such as solidification and/or disposal in a hazardous waste landfill, because of the arsenic-containing LO residue. This methodology is attractive for treating relatively small amounts of soil, but would require considerable research to establish its effectiveness in removing the four chemicals of concern. This technology may be a viable alternative in that, when soils are suspected to contain the agents, sodium bicarbonate could be added and the soil could be treated in the same thermal desorption unit as non-agent-contaminated soils.

8.4 Incineration

Although this document presents a screening of technologies other than incineration, which is a proven technology for agent destruction, incineration is included to allow comparison and provide a complete evaluation.

Nature of the Process. Incineration uses thermal decomposition by means of oxidation to convert a waste to a less bulky, toxic, or noxious material. Three types of incineration technologies are currently in use: rotary kiln, fluidized bed, and multiple hearth. Depending on the type of incinerator used, the soil is heated to a temperature of 1,600°C to 1,800°C in the combustion zone of the incinerator in the presence of a gas stream containing oxygen (to volatilize water and some heavy metals and to combust the organics). A secondary combustion chamber (afterburner) operating at about 1,200°C, followed by a gas scrubber, is used to ensure destruction of all toxic organics.

Applicability to General Soil Characteristics. The rotary kiln offers a high degree of flexibility for soils, sludges, and solids, because the residence time can be varied over a wide range of values.

Applicability to Agents of Concern. The technology should work well for sarin, mustard, and VX. Lewisite and LO are expected to decompose at these high temperatures also, but the resulting arsenic species will have to be isolated and safely disposed. Any system dealing with arsenic emissions would be designed for capture and treatment of such vapors.

Usefulness for Treating Other Soil Contaminants. Incineration is used to treat halogenated and nonhalogenated, semivolatile and volatile organic compounds, pesticides, and fuels. Most organic contaminants and some heavy metal salts or oxides are also treatable by this method.

Relative Cost of the Treatment. Costs depend on the type of incinerator technology used and the volume of soil to be treated. For treatment of 20,000 tons of material, the average cost would be \$300 per ton, excluding afterburner and scrubber costs. Costs could be as high as \$800 per ton; the cost per ton generally decreases with increased volume. The technology is both capital- and O&M-intensive.

Current Status. This technology is commercially available. All three incineration technologies (rotary kiln, fluidized bed, and multiple hearth) have been employed at full scale.

Residuals. Residuals include liquids and solids. Arsenic will be present in the vapors and possibly in the solid residue in some form. Other metals may be present in solids and would need to be treated or disposed.

Comments. The high temperatures used in this process will volatilize certain metals, such as mercury and arsenic, so a properly designed APCD will be required to capture the metals. Post-treatment, such as an afterburner and scrubber, would be needed to destroy toxic by-products (acid gases, chlorinated dibenzodioxins, etc.) and/or remnants of the parent contaminants. This technology is applicable to chemical agents, as demonstrated by its proven efficacy with neat agent (National Research Council 1993), and to soil remediation (Ebasco Services, Inc. 1987). A small incinerator might be used to treat low-volume toxic residues from other processes, such as SFE.

8.5 Pyrolysis

Nature of the Process. Soil is heated at 425°C to 760°C in the absence of oxygen to volatilize water and some heavy metals and to either volatilize or decompose the organic compounds. In a second step, the volatiles that were driven off initially are incinerated, to ensure destruction of all hazardous components. A secondary combustion chamber (afterburner) operating at about 1,200°C and a gas scrubber are used to ensure destruction of all remaining toxic organics.

Applicability to General Soil Characteristics. Thermal treatment of soils is not dependent on soil texture. However, soil moisture, particulates in the emissions, and their relation to soil texture are concerns to be addressed when engineering the process.

Applicability to Agents of Concern. This technology is expected to decompose sarin, mustard, and VX (to some degree). Lewisite and LO are also expected to decompose at these high temperatures, but the resulting arsenic species would have to be isolated and safely disposed.

Usefulness for Treating Other Soil Contaminants. Organic contaminants and some heavy metal salts or oxides are treatable by this method.

Relative Cost of the Treatment. Costs are similar to those for incineration. For 20,000 tons of material, costs will average \$300 per ton, excluding afterburner and scrubber costs. The technology is both capital- and O&M-intensive.

Current Status. This technology is commercially available at the full scale.

Residuals. Residuals include solids and liquids. Arsenic would be present in the vapors and possibly in the solid residue in some form. Other metals that may be present in solids would need to be treated or disposed.

Comments. The temperatures used in this process will volatilize certain metals, such as mercury and arsenic, so a properly designed APCD would be required to capture the metals. Post-treatment equipment, such as an afterburner and scrubber, would be required to break down any toxic by-products (acid gases, chlorinated dibenzodioxins, etc.) or remnants of the parent contaminants. The technology requires the soil feed to have low moisture levels; pretreatment to adjust soil moisture may be required.

8.6 Vitrification

Nature of the Process. A glassy crystalline structure is created by melting contaminated soils to 1,650°C in Joule process heating furnaces. The heat is sufficient to volatilize or pyrolyze organic and some inorganic compounds. Most metals would be encapsulated in the crystalline structure, thereby immobilizing them. Typically, the off-gas and particulates are drawn off and treated through a cyclone separator, a baghouse, and an acid-gas scrubber. The vitrified mass will resist leaching for geologic time periods.

Applicability to General Soil Characteristics. Vitrification is not dependent on soil texture and can be applied to most soils.

Applicability to Agents of Concern. The agents will most likely pyrolyze during the process. Arsenic from the lewisite and LO, if volatilized, could be collected in a concentrated form for further treatment.

Usefulness for Treating Other Soil Contaminants. The process has potential applicability in treating other contaminants. Organics tend to be pyrolyzed, and nonvolatile inorganics encapsulated in the vitrified material.

Relative Cost of the Treatment. The cost is high, approximately \$700 per ton. The process is both capital- and O&M-intensive.

Current Status. This technology is available in various proprietary forms at full scale.

Residuals. Residuals include liquids and solids.

Comments. The high temperatures used in this process will volatilize certain metals, such as mercury and arsenic, thereby requiring a properly designed APCD to capture the metals. The vitrified soil must be disposed.

8.7 Plasma-Torch Treatment

Nature of the Process. Contaminated soils are heated to between 1400°C and 2000°C, depending on the application, to produce a vitreous glassy slag with very low leaching characteristics (Staley 1992). The plasma torch heats by means of an ionized stream of gas, which is a conductor of electrical current. The conducting stream of superheated ionized gas is referred to as a plasma arc. Plasma gases can be mixtures of various gases; gas selection is governed by the waste stream to be treated. Plasma-torch treatment systems generate less waste gas than conventional systems based on fossil-fuel heating and can be completely contained and designed to operate below atmospheric pressure.

Applicability to General Soil Characteristics. Plasma-torch treatment is not highly dependent on soil texture and can be applied to most soils.

Applicability to Agents of Concern. The chemical agents sarin, mustard, and VX would most likely be broken down by this technology. The arsenic species derived from LO will potentially be trapped in the vitreous glassy slag or captured by the off-gas scrubbing system.

Usefulness for Treating Other Soil Contaminants. The plasma torch will break down organic contaminants. Heavy metals will either be captured in the vitreous glassy slag or captured by the off-gas scrubbing.

Relative Cost of the Treatment. The cost is high. Treatment costs can vary widely, depending on the size of the plasma torch treatment unit employed; costs range from \$700 to \$2,500 per ton.

Current Status. This technology is commercially available.

Residuals. Residuals include vitreous glassy slag, scrubbing effluent, and particulate matter (fly ash).

Comments. The closed-system, subatmospheric-pressure capability is a positive feature of the technology. Material feed systems must be designed to be versatile, rugged, continuous, and reliable. The high temperatures used in this process will volatilize certain metals, such as mercury and arsenic, so a properly designed APCD will be required to capture the metals. The high cost of this technology may inhibit wide application, but the process may be useful for some very limited areas (e.g., mixed organic/inorganic contamination).

9 Summaries

9.1 Summary Matrix of Technologies

Table 9 shows a matrix summarizing the technologies screened in Sections 5 through 8. The matrix emphasizes the applicability of each technology in treating, mobilizing, or reducing the volume of the agent-contaminated soil, the applicability in treating other contaminants, relative cost, current status, and residuals. Other information specific to the technology is also summarized.

9.2 Summary Discussion of Technologies by Type

In Sections 5 through 8, we reviewed 25 technologies to evaluate their applicability in treating or removing the four agents of concern from soil, their applicability in treating other types of contaminants that may be present in the soil, their general costs, residuals expected, and additional pertinent information. Using the information outlined in Sections 5 through 8, this section discusses and compares the technologies in terms of implementability, cost, and effectiveness in treating or removing the contaminants of concern. Where appropriate, technologies are discussed by type — in situ and ex situ, biological, physicochemical, and thermal. Not all types are discussed in terms of each of these three criteria.

In Situ Technologies. The first category of remediation technologies discussed is in situ technologies (Section 5). These technologies may be undesirable for treatment of agent-contaminated soil, because of the difficulty in determining whether remediation goals have been met. Because of the nature of in situ technologies, it cannot be proven that all of the agent will be treated or mobilized. The possibility of spreading the contamination, especially with the injection of liquid or air into the soil (as in biostimulation, bioventing, soil flushing, or soil venting), also makes these technologies less likely to be applied to treat chemical agents in soil.

In general, in situ technologies could be applied for treatment or removal of sarin with predictable success. The rapid reaction of sarin with water would render the compound nontoxic. However, the treatment or removal of mustard, lewisite, LO, and VX would be less successful. The ability of mustard to persist in the environment and its insolubility in water, the arsenic content in lewisite and LO, and the toxic breakdown products of VX (see Appendix B) suggest that in situ technologies would not be effective for treatment of these agents. If an in situ S/S process could be developed to detoxify the agents, this technology could potentially be applied.

TABLE 9 Summary Matrix for Technologies

Section No.	Technologies ^a	Remediation Effect	Applicable to Agent ^b	Potentially Applicable to Agent	Applicability Unknown for Agent	Applicability to Other Soil Contaminants	Relative Cost	Current Status	Residuals
5	In Situ Technologies								
5.1	Biosimulation	Mobilize, Treat	None	GB, VX	L	Organics	Low to Medium	Full	Liquids
5.2	Bioventing	Treat, Mobilize	None	GB, VX	L	Organics	Low	Full	None
5.3	Soil Vapor Extraction without Thermal Enhancement	Mobilize	GB	None	None	Volatiles	Low	Full	Vapors
5.4	Soil Vapor Extraction with Thermal Enhancement	Mobilize	GB	H, L, VX	None	Volatiles	Low	Full	Vapors
5.5	Soil Flushing	Mobilize	GB	VX	L	Volatiles, Metals	Unavailable	Pilot	Liquids
5.6	Solidification/Stabilization	Mobilize	None	H, L, VX, GB	None	Metals, Organics	Low to Medium	Full	Solids
5.7	Vitrification	Mobilize, Treat	None	H, L, VX, GB	None	Volatiles, Metals, Organics	High	Limited	Liquids, Solids
5.8	Natural Attenuation	Treat	GB	None	None	Metals, Organics	Low	Limited	None
6	Ex Situ Physicochemical Technologies								
6.1	Physical Pretreatment	Treat, Mobilize	GB	None	None	Volatiles	Unavailable	Full	Solids
6.2	Solidification/Stabilization	Mobilize	None	H, L, VX, GB	None	Metals, Organics	Low to Medium	Full	Solids
6.3	Solvent Extraction	Mobilize	None	H, L, VX, GB	None	Organics	Low to High	Pilot, Full, Limited	Liquids, Solids

TABLE 9 (Cont.)

Section No.	Technologies ^a	Remediation Effect	Applicable to Agent ^b	Potentially Applicable to Agent	Applicability Unknown for Agent	Applicability to Other Soil Contaminants	Relative Cost	Current Status	Residuals
6.4	Soil Washing — General	Reduce Volume, Mobilize	GB, VX	None	H, L	Metals, Organics	Medium	Full	Liquids, Solids
6.5	Alcoholysis or Cleavage with a Strong Basic Solution	Treat	H, L, VX, GB	None	None	Metals, Organics	High	Limited	Liquids, Solids
6.6	Dehalogenation with Alkaline Polyethylene Glycol	Treat	H, L, VX, GB	None	None	Organics	High	Full	Liquids, Solids
6.7	Chemical Oxidation	Treat, Mobilize	GB	H, VX	None	Inorganics, Organics	High	Full	Liquids, Solids
7	Ex Situ Biological Technologies								
7.1	Slurry-Phase Biological Treatment	Treat	GB, VX	H	L	Volatiles, Organics	Medium	Full	Liquids, Solids
7.2	Land Farming	Treat	GB, VX	H	L	Volatiles, Organics	Low	Full	None
7.3	Controlled Solid-Phase Biological Treatment	Treat	GB, VX	H	L	Volatiles, Organics	Low	Full	None
8	Ex Situ Thermal Technologies								
8.1	Low-Temperature Thermal Desorption	Mobilize	None	H, L, VX, GB	None	Volatiles, Semivolatiles	Low	Full	Liquids, Vapors, Solids
8.2	High-Temperature Thermal Desorption	Mobilize, Treat	None	H, VX, GB	L	Volatiles, Metals, Semivolatiles	Medium	Full	Liquids, Vapors, Solids
8.3	Dehalogenation with Heated Sodium Bicarbonate	Treat	None	H, L, VX, GB	None	Organics	Unavailable	Full, Limited	Vapors
8.4	Incineration	Treat	H, L, VX, GB	None	None	ALL	High	Full	Liquids, Solids

TABLE 9 (Cont.)

Section No.	Technologies ^a	Remediation Effect	Applicable to Agent ^b	Potentially Applicable to Agent	Applicability Unknown for Agent	Applicability to Other Soil Contaminants	Relative Cost	Current Status	Residuals
8.5	Pyrolysis	Treat	H, L, VX, GB	None	None	ALL	High	Full	Liquids, Solids
8.6	Vitrification	Mobilize, Treat	H, L, VX, GB	None	None	ALL	High	Full	Liquids, Solids
8.7	Plasma-Torch Treatment	Mobilize, Treat	None	H, L, VX, GB	None	ALL	High	Full	Liquids, Solids

^a More information on the application of these technologies is found in Chapters 5 through 8.

^b Applicability may be influenced by soil type. For instance, some technologies may not be applicable for clay soils.

Ex Situ Physicochemical Technologies. Physical pretreatment of the soil was discussed with ex situ technologies because even though, technically, it is not a remediation technology but a support process, it does address the toxicity of the soil. Pretreatment of the soil could be considered for the removal and treatment of sarin. If any sarin were present in the soil, it would hydrolyze; some may volatilize quickly, hydrolyzing in the air. Therefore, when plans are made to prepare the soils for ex situ treatment, the potential transformation of sarin can be taken into account. Hydrolysis of the other agents would also occur to some extent. When handling soils contaminated with agents, appropriate safety and environmental controls must be employed.

Ex situ S/S is a physicochemical treatment process in a category of its own. This technology could immobilize the contaminants in the soil, but the possibility of future agent release would have to be addressed. Additives, such as oxidants, could transform the agents to a nontoxic state before solidification. However, except in the case of lewisite and LO, for which the concern about arsenic would still be present, once the agent is rendered nontoxic, further treatment (in the form of solidification) would not necessarily be needed. If this technology was being considered for other contaminants where the soil also contained agent, it could be coupled with a pretreatment of oxidation or hydrolysis before solidification. However, the combination of additives to bring about the desired reactions would have to be researched extensively. Residuals of ex situ S/S must also be considered; the process increases the volume of the material and renders it sterile for plant life.

Solvent extraction technologies also have potential for removing or treating soils contaminated by agents. The SFE process is a low-to-medium-cost technology that has been used successfully in treating soils contaminated with organics, specifically semivolatiles. CST solvents, such as triethylamine, have also shown success in treating pesticide- and other organic-contaminated soils. The potential in treating agent-contaminated soil is promising but unknown at this time, and extensive treatability studies to determine temperatures and pressures, in the case of SFE, and proper co-solvents for both SFE and CST would be necessary before the cost effectiveness, implementability, and effectiveness of this technology could be known. For this type of technology to be cost effective, it may be necessary to use a solvent that is easily recyclable.

Soil-washing technologies are also potentially effective in removing or treating agent-contaminated soil. The four soil-washing technologies reviewed in this report are: general, alcoholysis or cleavage with a strong basic solution, dehalogenation with APEG, and chemical oxidation. In general, the soil-washing technologies have the following drawbacks: (1) it is difficult to find a solution to address the various contaminants, (2) fine particles are difficult to remove from the waste stream, and (3) the additive must be recyclable for the process to be economical for large-scale cleanup. If the added components are used up in the reaction or otherwise unrecoverable for reuse in the system, the cost of continually introducing fresh additives may become prohibitive, depending on the additive to be used. Large quantities of waste solutions containing the contaminants may need additional treatment or disposal. For small volumes of agent-contaminated soil, alcoholysis, dehalogenation, and chemical oxidation would be effective and manageable to implement. Soil washing showed potential to be in the low-to-medium cost range, especially if the additive could be recycled. Research on physicochemical treatment has so

far focused on decontamination of neat agent in small quantities where cost and waste residuals were not issues. A soil washing solution that is practical for treating large quantities of agent-contaminated soil has not been identified.

Ex Situ Biological Technologies. The use of biotreatment technologies to remediate chemical agents is a new and innovative field. The biodegradation of agents has only been researched in terms of neat agent. Virtually nothing is known about the behavior of naturally occurring microorganisms in agent-contaminated soil. Predictions from neat-agent research suggest that sarin and VX may potentially be directly affected by microorganisms. Mustard would be toxic to organisms; this may also be true of the arsenic-containing lewisite or LO. Biotreatment technologies are in the preliminary research stages of development, and more time and effort are required before they can be implemented.

Ex Situ Thermal Technologies. Thermal technologies are the most consistently applicable methods for treating chemical agents. The seven thermal technologies discussed in this report are: low-temperature thermal desorption, high-temperature thermal desorption, dehalogenation with heated sodium bicarbonate, incineration, pyrolysis, vitrification, and plasma-torch treatment. The thermal technologies have proven effective in removal or treatment of other soil contaminants, such as volatiles, semivolatiles, organics, and some metals. Most of the thermal technologies have been used for full-scale treatment of contaminants and would require minimal research and development to implement. Of the seven thermal technologies, the four that are effective in treating all agents of concern have overall costs in the very high category, ranging from \$300 to \$2,700 per ton. These high costs are partly attributed to the intensive energy requirements and necessary APCD. Low- and high-temperature thermal-desorption technologies do not require the extreme temperatures and high energy inputs that are required for the other thermal processes reviewed in this report. As a result, these processes are more economical but are still effective in removing soil contaminants. Low- and high-temperature thermal desorption, by definition, mobilize the contaminant from the soil; the off-gases are usually treated by an afterburner, which would require an APCD. Dehalogenation with heated sodium bicarbonate is essentially a thermal desorption process, with sodium bicarbonate being added to the soil during pretreatment to assist in neutralization of the agents. With the addition of the bicarbonate, costs would increase slightly, but the assurance of treating the agents would increase as well.

9.3 Summary Discussion of Technologies by Agent of Concern

Of the 25 technologies reviewed in Sections 5 through 8, seven (not including pretreatment) merit further consideration for the treatment of soil contaminated with mustard, lewisite, sarin, and VX. One of these, ex situ solidification/stabilization, would not be directly applicable to the military-related contaminants but might be used for soils containing toxic transformation products from LO and (in some cases) VX. Preferred technologies to treat the four agents are discussed below.

Mustard. Because of mustard's low solubility in water, hydrolysis and oxidation by dissolved oxidants require the use of nonaqueous or mixed aqueous/nonaqueous solvents. The basic solutions used for alcoholysis/cleavage or dehalogenation with APEG, as well as any of the oxidizing solutions listed, should be effective. The oxidizing solution of 0.1 M aqueous oxone with 15 vol % N-methyl-2-pyrrolidinone has the advantage of not forming organochlorine compounds through reaction with natural soil organic matter; the co-solvent is biodegradable. Mixing the soil with a 5% aqueous sodium hydroxide solution and heating moderately (90°C) would be effective in detoxifying sarin and mustard and mineralizing LO. Research on solvent washing is needed to determine an effective solvent or additive for mustard that would be recyclable and cost-effective on a large scale. All the systems discussed above should be applicable with soil-washing equipment.

Solvent extraction systems (i.e., CST and SFE) should be useful for treating mustard. The first of these might interact chemically with mustard. If SFE were to be used for removal of mustard from the soil, optimal conditions would have to be established; the effectiveness of this technology is highly dependent on pressure, temperature, and the presence of co-solvents. Following removal of mustard from the soil, further treatment would be needed to detoxify the extract.

Either low-temperature desorption, high-temperature desorption, or pyrolysis, all of which might be tested in the same equipment, should remove mustard from soil. Addition of sodium bicarbonate would probably decompose the mustard and, through carbon dioxide generation, help carry the vapor-state products to secondary treatment.

Thorough mixing of solid bleach, such as chlorinated lime or supertropical bleach, with soil, with moderate heating (approximately 120°C), should be quite effective in detoxifying any mustard residuals in soil. Such oxidizers have been used to decontaminate mustard from solid surfaces, but have not been used as a soil treatment technology.

Lewisite Oxide. As discussed earlier, any lewisite that might have been in the soil would rapidly have been converted to LO. All chemical changes used to detoxify LO would only convert it to other, still toxic but perhaps less toxic, arsenic species. Soil containing such species could be treated to solidify it before disposal.

Simple soil washing with a strongly alkaline aqueous solution, at 50°C or higher, should suffice to cleave LO to inorganic arsenic (arsenite) and acetylene plus some vinyl chloride; this would be the least expensive, yet perfectly effective, treatment. The equipment used for soil washing could be employed very effectively (but at higher cost and with more adverse environmental impacts) with the more basic solutions used for alcoholysis/cleavage or dehalogenation with APEG. Also, in such equipment, oxidizing solutions would probably convert the compound to the (theoretically) less-toxic pentavalent organoarsenic compound. These treatments might leave arsenic in the soil or extract it. In the latter case, the low-volume residue

could be converted, in one or two steps, to arsenate and precipitated as the insoluble ferric arsenate for disposal as a hazardous waste.

The use of solvent-extraction systems would have to be tested on LO, because so little is known about its behavior. If SFE were to be used to remove LO from the soil, optimal conditions would have to be established; the effectiveness of this technology is highly dependent on pressure, temperature, and the presence of co-solvents. Following LO removal from the soil, further treatment would be needed to detoxify the extract and isolate the arsenic in a form suitable for disposal.

The effect on LO-contaminated soil cannot be predicted reliably for low- or high-temperature desorption or pyrolysis, all of which might be tested in the same equipment. Addition of sodium bicarbonate to soil subsequently treated by these processes would probably cause cleavage of the LO to inorganic arsenic and acetylene plus some vinyl chloride; carbon dioxide generated in the process would help to carry the vapor-state products to the secondary combustion chamber. Because the volatility of the various arsenic species that might be involved is uncertain, the concentrations of arsenic in each effluent stream or residue should be investigated further.

Thorough mixing of solid bleach, such as chlorinated lime or supertropical bleach, with soil, with moderate heating (approximately 120°C), should be quite effective in oxidizing LO residuals to less-toxic derivatives.

Sarin. Simple soil washing, perhaps with an alkaline additive in the water, will hydrolyze sarin; this would be the least expensive, yet perfectly effective, treatment. The equipment used for soil washing could be employed very effectively (but at higher cost and with more adverse environmental impacts) with the more basic solutions used for alcoholysis/cleavage or dehalogenation with APEG. Also, in such equipment, oxidizing solutions would probably accelerate hydrolysis of sarin.

The triethylamine solvent extraction system would contain enough water at high pH to hydrolyze sarin. If SFE were to be used for removal of sarin from the soil, optimal conditions would have to be established; the effectiveness of this technology is highly dependent on pressure, temperature, and the presence of co-solvents. Following such sarin removal from the soil, further treatment would be needed to detoxify the extract.

Either low-temperature desorption, high-temperature desorption, or pyrolysis, all of which might be tested in the same equipment, should remove sarin from soil. The addition of sodium bicarbonate could only serve to enhance the decomposition and, through carbon dioxide generation, help to carry the vapor-state products to the secondary combustion chamber.

VX. Soil washing with sufficiently alkaline water should hydrolyze VX; for example, at pH 12, the half-life would be 2.5 hours. The half-life could be considerably reduced by elevating the temperature. If the soil-alkaline water mixture were held 24 hours, the VX concentration would be diminished by more than a hundred-fold (taking into account some protective effects of soil adsorption). This might be the least expensive, yet still effective, treatment, but it would require a large holding and stirring capacity for the soil-alkaline water mixture. The equipment used for soil washing could be used very effectively (with a much faster throughput time but at a higher cost and with greater adverse environmental impacts) with the more basic solutions used for alcoholysis/cleavage or dehalogenation with APEG. Following treatment, the soil would have to be washed free of decontaminating solution. The decontaminating solution, and possibly also the soil, might require further treatment to destroy the toxic by-products of decontamination.

The oxidizing solutions (decontaminants) listed in Section 6.7 are all expected to be effective in treating VX. The oxidizing solution of 0.1 aqueous oxone with 15 vol % N-methyl-2-pyrrolidinone has the advantage of not forming organochlorine compounds through reaction with natural soil organic matter; the co-solvent is biodegradable. These treatments could be conducted in soil-washing equipment.

Solvent extraction systems (i.e., CST and SFE) should be useful for VX. If SFE were to be used for removal of VX from the soil, optimal conditions would have to be established; the effectiveness of this technology is highly dependent on pressure, temperature, and the presence of co-solvents. Following VX removal from the soil, further treatment would be needed to detoxify the extract.

Either low-temperature desorption, high-temperature desorption, or pyrolysis, all of which might be tested in the same equipment, should remove VX from soil. The addition of sodium bicarbonate would probably decompose the VX to other, still somewhat-toxic compounds. Carbon dioxide, generated from the sodium bicarbonate, might help carry the vapor-state products to the secondary combustion chamber.

Thorough mixing of solid bleach, such as chlorinated lime or supertropical bleach, with soil, with moderate heating (approximately 120°C), should be quite effective in oxidizing VX residuals to less toxic derivatives.

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Appendix A:
Methods for Estimating
Physicochemical Properties

Appendix A:

Methods for Estimating Physicochemical Properties

For all of the listed substances, there are environmentally relevant physicochemical properties that have apparently never been measured but can be estimated by methods available in the literature. Such methods are described in this appendix. In some cases, estimates had already been made in cited reports, while in other instances (identified as such), the estimates were made by the present authors.

A.1 Octanol/Water Partition Coefficient

The octanol/water partition coefficient, K_{ow} , is the ratio between the concentration of the compound of interest in the octanol phase and its concentration in the aqueous phase when the two phases are in equilibrium. This parameter is commonly expressed as its logarithm, $\log K_{ow}$. Though K_{ow} is an indicator of relative lipophilicity, it is primarily used as a starting point to estimate such properties as bioconcentration factors, aqueous solubilities, and coefficients of adsorption to soil and sediment. Numerous experimental values have been reported for $\log K_{ow}$, and these were used if they were available and reliable. Otherwise, values were calculated from fragment constants and structural factors, or from other solvent-water partition coefficients, through linear regression equations (Lyman et al. 1990).

A.2 Henry's Law Constant

The Henry's Law constant, K_H , applied here to the aqueous solutions in contact with air, is a measure of the ratio of the concentration of a compound in the gaseous state to its concentration (as a nonionic species) in solution (Lyman et al. 1990). K_H is commonly estimated as a ratio of vapor pressure at a particular temperature to saturation solubility at the same temperature. For most of the data tables, the following equation was used to calculate K_H from the vapor pressure P (torr or mm of mercury), molecular weight (MW), and solubility S (mg/L):

$$K_H (\text{atm}\cdot\text{m}^3/\text{mol}) = (P \times \text{MW}) / (S \times 760)$$

Because environmental concerns are usually with exposures to low concentrations of potentially toxic materials, namely with the Henry's Law constant at infinite dilution, this kind of estimation is most valid for compounds of low solubility. It could not be used for the infinitely miscible GB, in which case the ratio of a measured pair of concentration values at equilibrium was used for the calculation.

If K_H is expressed in torr M^{-1} , it may be converted to $\text{atm}\cdot\text{m}^3/\text{mol}$ through division by 760,000; also, if K_H is expressed in the latter units, multiplication by the constant 40.88 $\text{mol}/(\text{m}^3\cdot\text{atm})$ converts it to the dimensionless form for 25°C.

A.3 Air Diffusion Constants

Air diffusion constant values were estimated, as required, by the Fuller-Schettler-Gittings method (Lyman et al. 1990). The reference, which provides certain input properties of air and the necessary atomic and structural diffusion volume increments for H, C, O, N, Cl, S, and aromatic or heterocyclic rings, indicates that one may use slightly corrected LeBas molar volume increments (see Section A.4 below) for other elements. The only other inputs were molecular weights and structures.

A.4 Water Diffusion Constants

Water diffusion constants could not be found for any of the contaminants; consequently, they were estimated by the method of Hayduk and Laudie (Lyman et al. 1990). For this method, required inputs were water viscosity and LeBas additive volume increments from the referenced chapter, plus the molecular structure. The reference did not list a volume increment for phosphorus, but a volume increment of 27.0 cm^3/mol for this element was found in another source (Coulson and Richardson 1990).

A.5 Soil Organic Carbon/Water Partition Coefficient, K_{oc}

The soil organic carbon/water partition coefficient, K_{oc} , is defined as (μg adsorbed chemical per g organic carbon)/(μg chemical per mL of solution). Estimation of the actual partition coefficient, K_d , of a chemical between soil and water from this value is based on the assumption that the soil's organic content is the only determinant of the sorption of a compound from water to soil. Thus, $K_d = f_{oc} \times K_{oc}$, where f_{oc} is the fraction of organic carbon in the soil. The organic *matter* content may be converted to f_{oc} by multiplying it by 0.58. Log K_{oc} was calculated from log K_{ow} by the following equation (Lyman and Loreti 1987):

$$\log K_{oc} = 0.824 \log K_{ow} + 0.328$$

A.6 Bioconcentration Factor (Fish)

BCF (fish), the water-to-aquatic organism (or simply "fish") bioconcentration factor, is defined as a concentration ratio determined at equilibrium by analyzing fish (whole, wet weight) and the aqueous media with which they have been in contact. For the present list of compounds,

there were few literature values for BCF. Indeed, some of the compounds may be too reactive with water or with cellular material to permit the necessary equilibration between the water and the organism. In the absence of literature values, despite some doubts, the log BCF was estimated by the following equation (Isnard and Lambert 1988):

$$\log \text{BCF} = 0.80 \log K_{ow} - 0.52$$

A.7 References

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Appendix B:

**Environmental Fate and Degradation Products
of Agents in Water and Soil**

Appendix B:

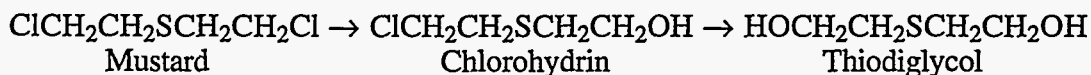
Environmental Fate and Degradation Products of Agents in Water and Soil

B.1 Mustard

In some instances, mustard (H) can be a very persistent agent in the environment. A mass of mustard buried some distance beneath the surface of the soil, or mustard in a leaky UXO or other protective container, could survive intact for many years. It is not known exactly what specific environmental conditions must be present for mustard to persist. At the opposite extreme, small droplets or films of mustard, especially near the surface, would long ago have evaporated or undergone hydrolysis.

Because it is very insoluble in water and has a slow rate of solution, mustard is very persistent in the environment. People have been burned by mustard residuals 50 years after their production (Sage and Howard 1989). A study at Edgewood Arsenal concluded that when mustard contamination of the soil is deep and not allowed to vaporize or be removed by weathering, there is potential for long-term persistence of the contaminant. Mustard residuals were found in trace amounts in the O Field at Edgewood Arsenal 30 years after the mustard was deposited in the soil (Epstein et al. 1973).

Despite its insolubility, once dissolved in water, mustard has a very high first-order rate constant for hydrolysis. Many degradation products form as the result of a complex hydrolysis pattern, which is affected by a variety of initial and ambient conditions. Simplistically, the hydrolysis of mustard may be considered to involve replacement of first one and then the other chlorine with hydroxyl, the second step being relatively rapid, so that there is no buildup of the intermediate monochloro compound. The dihydroxy compound, thiodiglycol, which is itself nontoxic, is usually the major end product under optimal hydrolytic decontamination conditions:



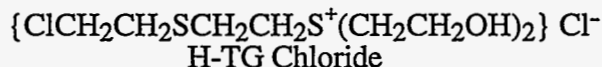
D'Agostino and Provost (1985) demonstrated, however, that decontaminating mustard by aqueous hydrolysis (to thiodiglycol) produced many products, some nearly as toxic as mustard. The process included large-scale hydrolysis in the presence of lime to neutralize the hydrochloric acid in the mustard. Up to 25 non-ionic compounds were found in the liquid and sludge. The main product was thiodiglycol, yet the hydrolysate contained significant amounts of 1,4-thioxane, 1,4-dithiane, 2-vinylthioethanol, and in some cases half-hydrolyzed mustard. The sludge formed in the process contained a number of organic compounds, including bis(2-chlorethyl) trisulfide,

which may have mustard-like toxic properties. Dithiane and thioxane have frequently been reported in groundwater in the vicinity of suspected mustard burial sites. The presence of thiodiglycol, dithiane, or oxathiane (compounds that are not themselves exceedingly toxic) in groundwater is strong presumptive evidence for the presence of a nearby mustard burial site; these compounds are stable and mobile and would tend to be carried to the aquifer by recharge rainwater.

A study conducted at Aberdeen Proving Ground tested the properties of mustard in water. The test consisted of allowing a two-phase mixture of equal volumes of mustard and water to stand for two months. The main organic constituent of the aqueous phase was the ionic product $S(CH_2CH_2S^+[CH_2CH_2OH]_2)_2$ (known as H-2GT). Ions of this type retain much of the toxicity and vesicancy of mustard (Yang et al. 1987). Therefore, a reaction of mustard with limited volumes of water can result in the loss of mustard without corresponding losses in toxicity.

A review by Dacre and Burrows (1988) indicated that a pool of mustard at the bottom of a water body, relatively undisturbed by currents, would diminish in depth by 1 cm every 100 days at 20°C. This suggests that bulk mustard would be able to persist deep in soil or as an oily layer under relatively quiescent water for years.

In the absence of sufficient water in the immediate vicinity, several sulfonium salt oligomers have been shown to form, such as that from mustard and thiodiglycol (Yang et al. 1987):



Such water-soluble sulfonium salts are quite vesicant, although their physical properties differ substantially from those of mustard. The persistence of deeply buried masses of mustard can be attributed to the formation of oligomeric degradation products of limited hydrolysis that coat the surface of the mustard mass. Samples of soil and/or groundwater with this coating around the mustard mass might show no trace of the active mustard agent (Small 1984).

Testing has shown that mustard is relatively nonpersistent when contamination is on the surface of the soil. The influence of natural environmental conditions, including hydrolysis and volatilization, causes the decomposition of the mustard in two to three weeks (Epstein et al. 1973; Small 1984). Medium-depth soils have been found to remain vesicant for at least three years after contamination, while mustard in containers has been known to remain stable for longer periods of time (Epstein et al. 1973). As mentioned above, mustard has been known to persist in the environment for decades.

Temperature variations have been found to affect the persistence of mustard in soil. A study was conducted on heavily loaded soil, under calm dry conditions, with an initial contamination level of 50,000 mg/m² at a temperature of 0°C. The contamination level was predicted to decay to 33 mg/m² after two months. When the temperature was changed to 25°C, the

predicted decay time under the same conditions was 41.5 h (Small 1984). At low concentrations, pH does not have an effect on mustard degradation.

B.2 Lewisite and Lewisite Oxide

Munitions have never been loaded with lewisite (L) at RMA; therefore, lewisite would not have entered the environment by this means or be present in UXOs. RMA soil is probably free of lewisite but may contain lewisite oxide (LO), derived from lewisite that may have been released into the environment during its manufacture. The detection of lewisite and LO in soil has been found to be difficult because of the unstable nature of lewisite and its ability to readily hydrolyze in soil to LO. The current analytical methods for detecting lewisite in soil are incapable of distinguishing lewisite from LO, so positive detection cannot be a confirmation of lewisite as opposed to LO. Until recently, the identification of arsenic in the soil may have been taken as evidence of the presence of lewisite or LO.

Lewisite can take either the *cis*- or *trans*- forms, or it can be a *cis-trans*- mixture (Whiting 1948). Table 4 in Section 2 of this report lists relevant properties for production-grade *cis-trans*-mixtures. Some properties have been determined for the *cis*- and *trans*- forms. Recently, a geminal isomer of lewisite (1-chlorovinyl dichloroarsine) has been reported (Smith et al. 1993). Information is not presently available on the breakdown and/or properties of this geminal isomer.

Lewisite hydrolyzes to "lewisite oxide" in a very rapid reaction in three forms (Rosenblatt et al. 1975). In the first stage, the lewisite is converted to the *cis-trans* gem-diol mixture, 2-chlorovinylarsonous acid, Cl-CH=CH-As(OH)_2 . The next stage is a conversion to the *cis*- and *trans*- arsenoxide form 2-chlorovinylarsenoxide, Cl-CH=CH-As=O as the first form loses water. The *trans*- form is then slowly polymerized to $(\text{Cl-CH=CHAsO})_x$. These products are collectively referred to as "lewisite oxide" or "LO." Because the ratio of these forms is not fixed, but varies with time and conditions, the properties given for LO in Table 5 in Section 2 of the report apply only approximately to LO, which may be present as a residue from long-past chemical operations. These property values correlate closely with the unpolymerized *cis*- and *trans*- arsenoxide forms.

The usual form (diol, arsenoxide, or polymer), mobility, and soil chemistry of LO in soil are not known. It is conceivable that soil alkalinity would suffice to slowly convert LO, in particular the *trans*- isomers of the diol and arsenoxide forms, to inorganic arsenite. Another possibility is that either LO or inorganic arsenite in aerated soil would be gradually oxidized to the +5 valence state. Once LO is oxidized, decreasing the toxicity of the compound, the analytical methods for LO might be inapplicable (especially the ethanedithiol method) (Fowler et al. 1991).

Tests on pH and temperature of soil contaminated with LO have shown the effects of these properties on LO breakdown products. At high pH levels, the *trans*-lewisite oxide is cleaved by a hydroxyl ion to form the products acetylene and inorganic arsenite. These degradation products are produced even in cold weather. At a temperature of 40°C, the *cis*-compound will react with the sodium hydroxide solution, giving vinyl chloride (with possibly some acetylene) and inorganic arsenite (Rosenblatt et al. 1975).

B.3 Sarin

Sarin (GB) hydrolyzes rapidly and should not be present in RMA soil unless there has been recent leakage from a container, such as a UXO. The products of sarin are hydrofluoric and isopropyl methylphosphonic acids (HF and IMPA). Complete reaction takes a few weeks at most. These products are far less toxic than sarin itself. Like sarin, they are both water-soluble and leachable and would be more likely than sarin to be present in soil contaminated by sarin or by waste products from its manufacture. In fact, IMPA has been detected in the soil during preliminary investigations (Environmental Science and Engineering, Inc., and Harding Lawson Associates 1988; Environmental Science and Engineering, Inc., et al. 1988; Ebasco Services, Inc., and Program Manager, Rocky Mountain Arsenal 1989). RMA groundwater is (or used to be) contaminated by diisopropyl methylphosphonate from sarin manufacturing wastes, plus IMPA and perhaps traces of methylphosphonic acid (Environmental Science Engineering, Inc., et al. 1988). These compounds are relatively low in toxicity and are unlikely to undergo further rapid chemical or biological change in the environment.

Sarin has been found in tests to be relatively nonpersistent in soil. Testing conducted on a loamy soil from Fort McClellan, Alabama, resulted in high contamination-reduction rates. The testing consisted of determining the percent sarin remaining in the soil for two different sample moisture conditions, one collected 24 hours after rainfall and the other collected three days after the rainfall. The bottles were stoppered and stored at room temperature until analysis times for sarin content. The following are the results of the two tests:

Soil Moisture (%)	Sarin Remaining at Indicated Time in Hours (%)				
	12	24	48	72	168
12.8	40	N.D. ^a	—	—	—
1.4	59	27	14	12	5

^a N.D. = no detection.

The results show that the sarin had relatively high loss rates, with the higher rate occurring in the wet soil (Small 1983). Additional tests have shown that sarin has an evaporation rate similar to that of water (Headquarters, Department of the Army et al. 1990).

The persistence of sarin in soil was tested at Aberdeen Proving Ground by using sarin and dry Saudi Arabian sand to record the loss of sarin from the sand by volatility. Gravimetric

measurements were taken with 300-500 mg of sand and 9 mg of sarin under a 0.63-cm/s flow of dry nitrogen. For a typical sample, approximately 90% of the initial 9 mg of sarin was lost in an hour at 23.5°C. After that, the loss in weight appeared to be very slow, possibly due to hydrolysis, despite the soil's dry condition (Penski et al. 1992). The hydrolysis products of sarin are known to have a far lower volatility than sarin itself.

Although sarin has been found to be nonpersistent in a soils medium, the same cannot be concluded for other media. Tests by Black et al. (1993) reported that traces of sarin had recently been found in paint fragments of bombs dropped in the Kurdish sector of Iraq some four years previously.

The pH level of the soil has been found to be a factor in the hydrolytic half-life of sarin. The hydrolytic half-life of sarin is slowest in the pH range of 4-6, with a half-life of about 160 hours at pH 5 and 25°C. The half-life is shorter outside the 4-6 pH range, in either more alkaline or more acidic solutions (Clark 1989). The second-order rate constant for hydroxyl ion-catalyzed hydrolysis is (Demek et al. 1970):

$$\log k_2 = 9.8507 - (1985.4/T[K])$$

This gives a value of 1,543 M⁻¹min⁻¹ at 25°C. Hence, the estimated rate constant at pH 10 is 0.1543, and the half-life is approximately 4.5 min. At higher pH levels, the half-life would be proportionately lower. When large amounts of sarin are added to distilled water, the observed hydrolysis rate constant first decreases, but it increases again once the pH has dropped through the minimum reaction rate range and acid catalysis begins to take effect.

Hydrolysis of sarin can also be affected by a catalyst in the reaction process. The hydrolysis of sarin is catalyzed (especially under alkaline conditions) by metal ions, such as calcium, magnesium, cupric, cerous, and manganous (Demek et al. 1970; Epstein and Rosenblatt 1958). Catalyzed hydrolysis by the strongly nucleophilic anion of hypochlorous acid is especially pronounced (Epstein et al. 1956). At a temperature of 25°C, with the K_a of HOCl = 4 × 10⁻⁸, the second-order rate constant is about 600 M⁻¹ s⁻¹, and the activation energy is 11.4 kcal/mol. The hydrogen peroxide anion-facilitated hydrolysis reaction involves a two-stage process, in which two moles of hydrogen peroxide are consumed and oxygen is one of the products (Larsson 1958). At a temperature of 25°C, with the K_a of H₂O₂ = 2.92 × 10⁻¹², the second-order rate constant is 1,340 M⁻¹ s⁻¹, and the activation energy is about 7.6 kcal/mol.

B.4 VX

VX is much more persistent than sarin because of its low vapor pressure and low evaporation rate, which is about 1/1,500 that of water (Headquarters, Department of the Army et al. 1990). Nevertheless, studies have estimated conservatively that 90% of VX applied to soil would be lost in 15 days (Small 1983). Historically, VX was handled at RMA only in the vicinity of the Toxic Storage Yard, where the M55 VX-filled rockets were demilitarized. If any VX still

remains in the soil at RMA, the volume of the affected soil is likely to be relatively small, compared to the volume of other RMA soil requiring decontamination.

VX should degrade at the soil surface in a matter of weeks; it might take longer to evaporate or decompose deep within the ground (Carpenter and Hill 1988; Small 1983). Because the decomposition of VX would be largely by means of hydrolysis, it can be expected that the highly vesicant bis(diisopropylaminoethyl) disulfide (EA 4196) would be formed by the facile air oxidation of the VX hydrolysis product diisopropylaminoethanethiol (Epstein et al. 1974). A second product, S-diisopropylaminoethyl methylphosphonothioic acid (EA 2192), which is stable in terms of hydrolysis and almost as toxic as VX, would also be formed. Both compounds, but especially the latter, should be fairly water-soluble and thus tend to migrate toward the water table. A third type of toxic material, the pyrophosphonate ester, $\text{CH}_3\text{P}(\text{O})(\text{OC}_2\text{H}_5)\text{-O-P}(\text{O})(\text{OC}_2\text{H}_5)\text{-CH}_3$, should be hydrolyzable and degrade in the environment sooner than EA 4196 or EA 2192 (Epstein et al. 1973; Yang et al. 1990).

Although VX contamination has been shown to degrade relatively quickly, the cholinesterase inhibitors from the decomposition products have been persistent in soils. In tests on loss rates for VX at 0.01% loading for fairly dry soils, the VX content decreased to 10% of the initial value (range about 3 to 30%) after one week. However, toxic cholinesterase inhibitors can form as decomposition products (Epstein et al. 1973). The most common cholinesterase inhibitor is pyrophosphonate ester, which has an acute intravenous toxicity to rabbits of 0.089 mg/kg, compared with 0.008 mg/kg for VX (Yang et al. 1990). Compounds were extracted from Carroll Island soil that contained anticholinesterase activity as late as three months after the VX was applied to the soil. The persistence of these cholinesterase inhibitors should be considered because of their toxicity.

VX hydrolysis rates are generally slower than those of sarin. At a pH of 10 and temperature of 25°C, the half-life in water is 2432 min (converting data from Epstein et al. 1974), compared with approximately 4.5 min for sarin. At a pH of 5 and temperature of 25°C, the half-life was reported as 2,342 h, compared with 160 h for sarin (Clark 1989).

The two types of catalytic hydrolysis to which VX is subject are water-catalyzed and hydroxyl ion-catalyzed hydrolysis. VX is not subject to acid-catalyzed hydrolysis, as the sarin is. Water-catalyzed hydrolysis below pH 7 and alkaline hydrolysis above pH 10 result in P-S cleavage, to give ethyl methylphosphonic acid and diisopropylaminoethanethiol (DESH). Complex mixtures of hydrolysis products are formed in the pH range 7-10; these involve ethoxy cleavage from the phosphorus, as well as C-S and P-S cleavage at the sulfur (Epstein et al. 1974). Studies by Yang et al. (1990) have shown that considerable ethoxy cleavage occurs even in 2 N sodium hydroxide. Some of the hydrolysis products are believed to be toxic. Bis(diisopropylaminoethyl) disulfide (EA 4196), formed by air oxidation of the primary cleavage product DESH, is said to be a powerful vesicant, comparable to mustard gas (Small 1983). The product of ethoxy cleavage, S-diisopropylaminoethyl methylphosphonothioic acid (EA 2192), is stable in terms of hydrolysis and almost as toxic as VX (Sage and Howard 1989). The difference in toxicity is shown by comparing the acute intravenous toxicity to rabbits: 0.017 mg/kg for EA 2192 vs. 0.008 mg/kg for VX (Yang et al. 1990).

B.5 References

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Appendix C:

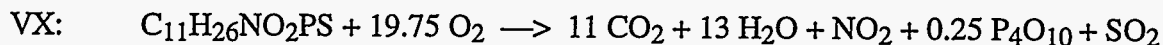
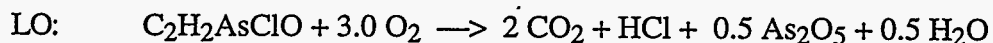
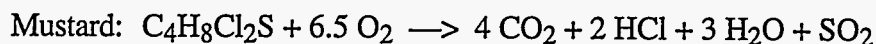
**Reactions of Significance in Chemical
Detoxification of Contaminants**

Appendix C:

Reactions of Significance in Chemical Detoxification of Contaminants

C.1 Combustion

Combustion or incineration, the burning or rapid oxidation of a compound in the presence of oxygen, results in the complete breakdown of the compound. Afterburning, commonly used in combination with thermal desorption, is also combustion. The following equations are the assumed reactions of the agents of concern. All carbon is assumed to be converted to CO₂, nitrogen to NO₂, phosphorus to P₄O₁₀, sulfur to SO₂, fluorine to HF, chlorine to HCl, and hydrogen (if not converted to HF or HCl) to H₂O:

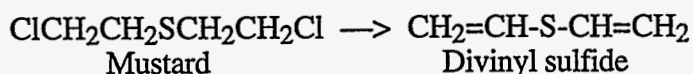


When these reactions go to completion, some of the products — NO₂, HCl, HF, and SO₂ — are common air pollutants requiring the use of air pollution control devices, such as air scrubbing. Others, such as P₄O₁₀ and As₂O₅, can also be removed from air by scrubbing. Carbon in exhaust gases is often partly in the form of carbon monoxide, coming from the fuel used to aid incineration or afterburning as well as from the pollutants; carbon monoxide emissions must be controlled so as not to exceed permitted levels. It should be noted that the toxicity of As₂O₅, with arsenic in the +5 valence state, is considered to be less than that of As₂O₃, where arsenic is in the +3 valence state; therefore, sufficient oxygen is required to support complete combustion to As₂O₅.

C.2 Hydrolysis, Alcoholysis, and Related Reactions

C.2.1 Mustard

Mustard reacts very rapidly with strong bases and other highly reactive nucleophiles, provided they are dissolved in the same phase. Thus, for example, mustard is completely converted by DS2, a very alkaline solution of 2% sodium hydroxide in 28% 2-methoxyethanol/70% diethylenetriamine (Yang et al. 1992), to the relatively harmless divinyl sulfide within one minute at room temperature by an elimination reaction (Yang et al. 1992):

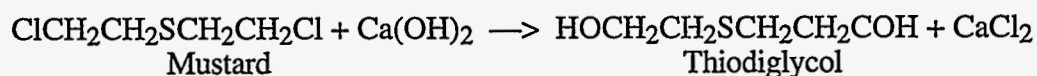


When water is added to DS2, the reaction becomes one of slow displacement, rather than rapid elimination (Yang et al. 1992), forming such products as S(CH₂CH₂-NH-CH₂CH₂-NH-CH₂CH₂-NH₂)₂.

Preliminary data indicate that mustard dissolves in, and can be detoxified by, the solution of a strong base (alkoxide) in the biodegradable solvent N-ethyl-2-pyrrolidinone (Yang et al. 1992).

Mustard is reported to hydrolyze rapidly to the extent that it can be reacted with an aqueous solution; unfortunately, its water solubility and rate of solution are very low. When a polar organic solvent is mixed with water to solubilize mustard, the diminished polarity of the medium greatly reduces the hydrolysis rate. The presence of chloride ion (including that initially formed in the reaction) inhibits the reaction significantly (Yang et al. 1992).

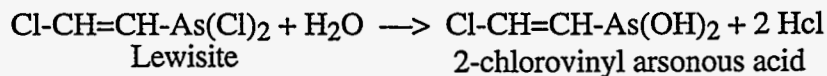
In aqueous hydrolysis, formation of a troublesome, and still toxic, oligomeric sulfonium salt can be avoided if a strong nucleophile is present in the water; hydroxide ion (e.g., in sodium hydroxide or calcium hydroxide) fulfills this role (National Research Council 1993). Calcium hydroxide is reported to have been used at 90-100°C to convert 125-gal batches of mustard to thiodiglycol "in an apparatus not much more complicated than a tub" (National Research Council 1993):



Aqueous sodium hydroxide (about 5%) should also be effective at 90°C, according to William T. Beaudry of the Edgewood Research, Development, and Engineering Center (ERDEC) (Beaudry 1993).

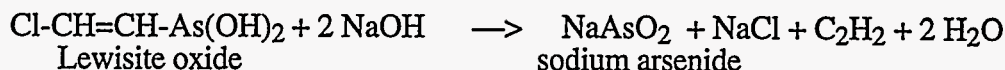
C.2.2 Lewisite and Lewisite Oxide

The hydrolysis of lewisite (L) is extremely rapid, so that even recently released lewisite would have almost instantly been converted to lewisite oxide (LO) on contact with soil moisture:



As discussed in Appendix B, Section B.2, LO is actually a complex and variable mixture. Its susceptibility to cleavage by base, with the formation (to a considerable extent) of acetylene and sodium arsenite, is sufficient to allow that reaction to be the basis for the analysis of lewisite in soil. The soil is extracted with water containing ascorbic acid and the aqueous extract mixed with one fifth its volume of 4% sodium hydroxide at ambient temperature; very soon after addition of

the sodium hydroxide, acetylene-containing air in the headspace above the liquid mixture may be drawn off to analyze chromatographically (Program Manager, Rocky Mountain Arsenal 1993). As inferred from the discussion in Appendix B, Section B.2, only the *trans*- compound would react rapidly under these conditions; higher temperature, and perhaps a higher concentration of sodium hydroxide, might be required for the *cis*- isomer to react, giving some acetylene and some vinyl chloride. The reaction stoichiometry for the predominant *trans*- isomer reaction may be expressed as:

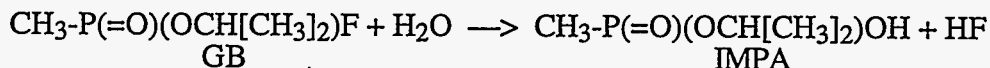


Although hydrolysis and cleavage reactions eliminate the characteristic toxic properties of lewisite and LO, they introduce the toxicity and carcinogenicity of sodium arsenite.

According to Paul Bossle of ERDEC (Bossle 1994), LO is not readily soluble in water. However, dissolution can be enhanced with a trace of HCl in solution.

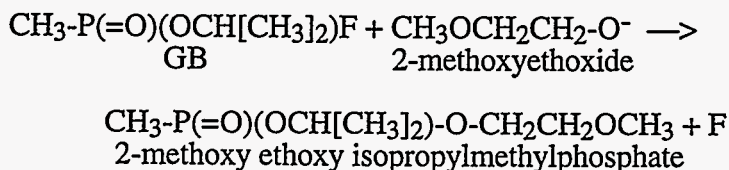
C.2.3 Sarin

Sarin (GB) is infinitely miscible with water. When dissolved in water at 25°C, it can complete its hydrolysis reaction within a few weeks at most, forming such relatively innocuous products (in trace amounts) as isopropyl methylphosphonic acid (IMPA) and hydrofluoric acid:



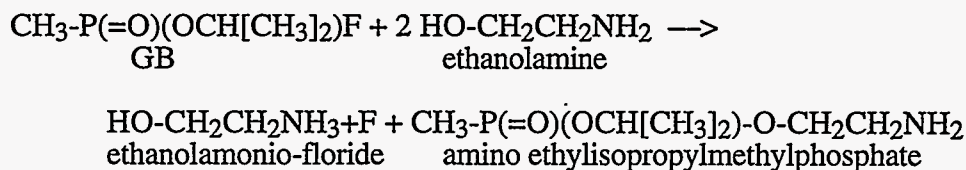
In acidic or — especially — in basic aqueous solution, the reaction rate whereby fluoride ion is cleaved from sarin is considerably enhanced. As discussed in Appendix B, Section B.3, the hydrolysis reaction is catalyzed by various nucleophilic reagents (for example, hypochlorite ion). Base-catalyzed hydrolysis, however, remains the simplest means of detoxifying sarin.

Several basic solutions have been tested on sarin for detoxification. The U.S. Army decontaminating agent DS2 contains the strong base 2-methoxyethoxide. A large part of the sarin exposed to this solution would initially be converted to a theoretically innocuous ester product, as follows:



The ester could eventually be cleaved to a phosphonic acid by the hydroxide ion that is present. A closely related alkaline decontaminant is potassium hydroxide in 2-methoxyethanol, the active ingredient in the proprietary DeChlor/KGME process (National Research Council 1993). With

sarin, it should form the same ester as that described in the preceding paragraph for DS2. Canada has used methyl alcoholic potassium hydroxide to hydrolyze sarin (National Research Council 1993), presumably with some initial formation of the methyl isopropyl ester. Preliminary data indicate that sarin, as well as mustard, can be detoxified by a strong base (alkoxide) in the biodegradable N-ethyl-2-pyrrolidinone (Yang et al. 1992). The Soviet Union used ethanolamine to detoxify sarin, in an apparently clean reaction, to form the ester:

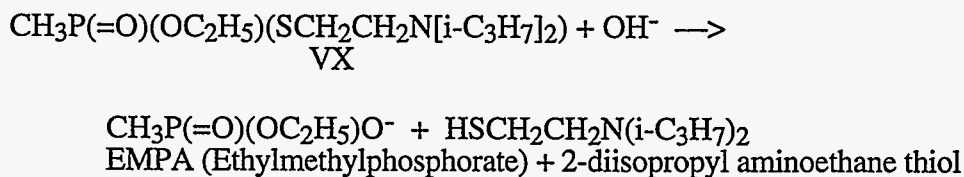


Advantages of this process are that (1) sarin's volatility is much reduced when it is dissolved in ethanolamine, and (2) corrosion of the process equipment is minimal (National Research Council 1993).

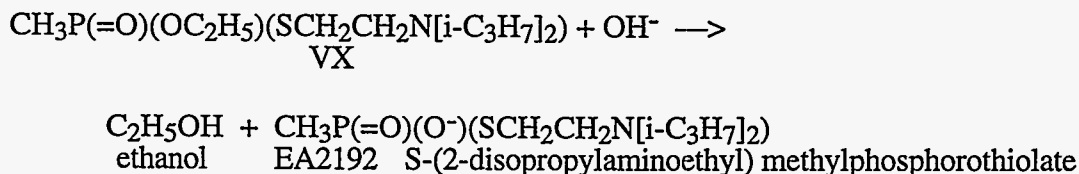
C.2.4 VX

VX hydrolysis is relatively slow and complex. Both protonated and unprotonated VX react with hydroxide ion. Above pH 10, reaction with unprotonated VX predominates, with a second order rate constant of about $30 \text{ M}^{-1} \text{ hr}^{-1}$ and $K_a = 2.5 \times 10^{-9}$ at 25°C . Typical half-lives (Epstein et al. 1974) are 15 h at pH 11; 2.5 h at pH 12; 17 min at pH 12.9; and 3 min at pH 13.5.

At pH levels high enough for hydrolysis to be considered as a practical means of detoxification (at 25°C), two sets of reactions predominate (Yang et al. 1992):



and



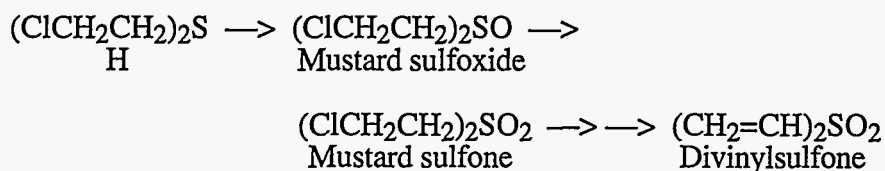
In the first of these reactions, the second (thiol) product is easily air-oxidized, especially under basic conditions, to produce the disulfide known as EA 4196. In the second reaction, the phosphorus-containing product (EA 2192) comprises roughly one fourth of the phosphorus-containing starting material and is about half as toxic a cholinesterase inhibitor as VX; furthermore, it is quite stable.

Preliminary data indicate that VX, as well as mustard and sarin, can be transformed by a strong base (alkoxide) in the biodegradable N-ethyl-2-pyrrolidinone (Yang et al. 1992). Concerns about the reaction products, however, still remain.

C.3 Oxidation

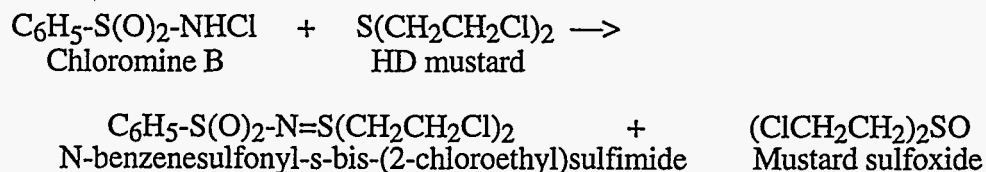
C.3.1 Mustard (H)

The interaction of mustard with strong and otherwise reactive oxidants, as with nucleophiles, is limited by the low solubility of mustard in water (Yang et al. 1992; National Research Council 1993). Such reactions appear to progress through a series of stages involving oxidation on the sulfur and elimination of HCl, giving considerably less vesicant products (Yang et al. 1992):



The first decontaminants used were calcium hypochlorite-containing "bleaching" powders and, to a lesser extent, potassium permanganate. The reactions of chemical agents with excess bleach are so vigorous that neat agents can be converted to less toxic products at the liquid-solid (bleaching powder) interface in a few minutes; solubilization of the agent in the same medium as the bleach is not required (Yang et al. 1992). According to the National Research Council (1993), "a water solution of sodium hypochlorite, although good for decontamination of thin-layered spills, can make such poor contact with bulk mustard that very little reaction occurs."

A slight variation on the above theme is seen in the reaction of the skin decontaminant Chloramine B with mustard to give nonvesicant products:



The identification of a medium in which hypochlorite is soluble and stable and mustard is soluble has apparently been achieved in the newly developed Decontaminating Agent: Multipurpose (DAM), consisting of 4 wt% calcium hypochlorite in an equal-volume mixture of water with N-cyclohexyl-2-pyrrolidinone, a solvent that is considered biodegradable. DAM is said to detoxify mustard, as well as VX and sarin (Yang et al. 1992).

Although uncatalyzed hydrogen peroxide (in the aqueous N-hexyl-2-pyrrolidinone medium) reacts only slowly with mustard, such peroxy compounds as m-chloroperoxybenzoic

acid and magnesium monoperoxyphthalate are effective against mustard — but fairly expensive. The first of these was reported to give the sulfoxide, $(\text{ClCH}_2\text{CH}_2)_2\text{SO}$ (VX), and the sulfone, $(\text{ClCH}_2\text{CH}_2)_2\text{SO}_2$, at a rate "too fast to measure." Oxone, a commercial mixture of the peroxy compound KHSO_5 with KHSO_4 and K_2SO_4 in 2:1:1 proportions, is suitably reactive. In a solution of 0.05 M mustard, 0.1 M Oxone, and 15 vol % N-methyl-2-pyrrolidinone (necessary to dissolve the mustard), the mustard was oxidized immediately to the sulfoxide, $(\text{ClCH}_2\text{CH}_2)_2\text{SO}$. The sulfoxide was converted completely to the sulfone, $(\text{ClCH}_2\text{CH}_2)_2\text{SO}_2$, in less than an hour (Yang et al. 1992; National Research Council 1993).

As an alternative to the use of solvents to bring mustard and oxidants into the same phase, emulsification can be used to increase the reactive surfaces between phases. This has been done with the tetrachloroethylene-containing microemulsion mixtures, C8 and MCB (the latter with Fichlor, an added organochlorinating agent). These organochlorinating emulsions will not be discussed in detail because the presence of a volatile organochlorine compound makes them environmentally objectionable.

C.3.2 Lewisite and Lewisite Oxide

Oxidations of lewisite or LO have not been investigated in terms of decontamination. However, oxidation of lewisite or LO from the +3 to the +5 valence state, namely from Cl-CH=CH-As(OH)_2 to $\text{Cl-CH=CH-As(O)(OH)}_2$, has been accomplished with chlorine or hydrogen peroxide in an aqueous medium (Hewett 1948). Irradiation in an open dish with a mercury vapor lamp also converted the *trans*-isomer of lewisite to the arsonic acid, though the conditions under which this took place are unclear (Hewett 1948). In related chemistry, calcium hypochlorite was used to oxidize potassium arsenite in the soil to the arsenate salt (Dragun 1988), effecting conversion of arsenic from the +3 to the +5 valence state. Such oxidations are generally believed to decrease the toxicity of trivalent arsenic compounds. However, there is no toxicological information to confirm this specifically for lewisite and LO. Finally, the reverse reaction, from pentavalent to trivalent (L), is easy to carry out (for example, by iodine-catalyzed sulfur dioxide reduction) (Hewett 1948).

C.3.3 Sarin

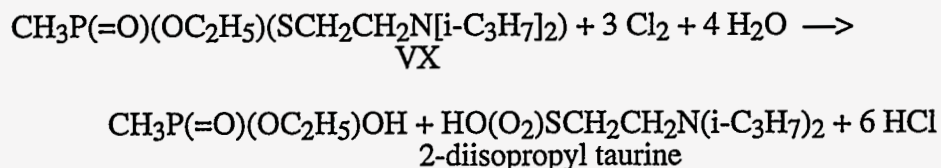
Sarin is not oxidized by decontaminants. The mediated electrochemical oxidation (MEO) process (National Research Council 1993), although theoretically able to mineralize sarin, could probably not be applied to contaminants in soil, because (1) the substance to be oxidized would have to be in a fluid reasonably close to the electrodes, (2) silver ion is required for the process, and (3) the oxidation would be nonselective.

The oxidative decontaminant DAM is said to be effective against sarin (Yang et al. 1990); this could be attributed to the ability of hypochlorite ion to catalyze the hydrolysis of sarin, rather than oxidize it.

C.3.4 VX

The oxidation of VX at room temperature as a means for its decontamination can give rise to a variety of products. All, it would seem, are less toxic than the parent compound.

Past development of decontamination procedures has placed emphasis on the use of chlorine-based oxidants. When hypochlorites are used under basic conditions, more than 10 mol of active chlorine is required to oxidize 1 mol of VX, though neither the precise stoichiometry nor the products have been determined (Yang et al. 1992). It is likely that the focal point for initial attack is the tertiary nitrogen, and that the molecule fragments in a manner similar to that described for typical oxidative fragmentations (Dennis et al. 1967). Under acidic conditions, the reaction is much cleaner, involving oxidation at the sulfur, followed by hydrolysis of the sulfur-phosphorus bond to give ethyl methylphosphonic acid and N,N-diisopropylethanesulfonic acid:

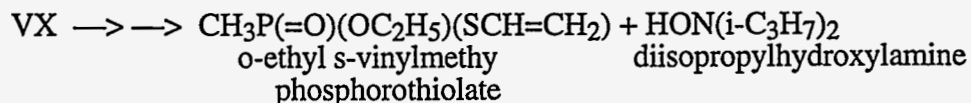


The reaction is written as occurring between VX and the chlorine molecule, because this is the simplest way to explain the increase in rate with decreasing pH. Under acidic conditions, the tertiary amine nitrogen is protonated, and thus protected from attack by active chlorine. (As a decontaminant, chlorine gas would be highly effective but extremely reactive and corrosive.) The active chlorine required for the preceding reaction may be supplied in the form of an N-chloro compound, such as acidified "Fichlor" (sodium N,N-dichloroisocyanurate).

As discussed above, the newly developed DAM consists of 4 wt% calcium hypochlorite in an equal-volume mixture of water and the biodegradable N-cyclohexyl-2-pyrrolidinone. DAM is said to detoxify VX, as well as mustard and sarin (Yang et al. 1992).

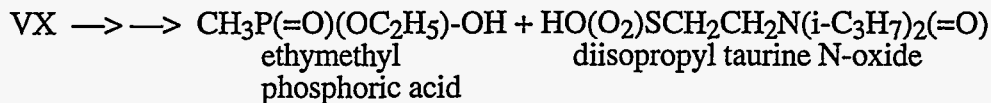
Chlorine dioxide in aqueous solution at high pH detoxifies VX more rapidly than hypochlorite. The products of this reaction have not been determined, however (Epstein 1993).

VX is oxidized rapidly by equimolar m-chloroperoxybenzoic acid in aqueous t-butyl alcohol to the N-oxide, which then slowly decomposes to O-ethyl S-vinyl methylphosphonothiolate and diisopropylhydroxylamine (Yang et al. 1990):

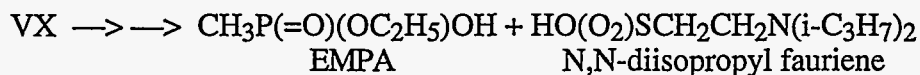


Under similar conditions, but with a sufficient excess of the oxidant, the above-mentioned N-oxide intermediate is next oxidized at the sulfur, followed by rapid hydrolytic cleavage to form

ethyl methylphosphonic acid and the N-oxide of N,N-diisopropylethanesulfonic acid (Yang et al. 1990):



Oxone (defined in Section C.3.1), the active ingredient of which is peroxysulfuric acid, cannot attack the protonated nitrogen of VX to form the N-oxide under acidic conditions, but instead oxidizes the sulfur, giving ethyl methylphosphonic acid and N,N-diisopropylaminoethanesulfonic acid:



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Appendix D:
Toxicological Properties of Contaminants

Appendix D:

Toxicological Properties of Contaminants

D.1 Mustard

Mustard (H) is a vesicant (blister agent), as well as an alkylating agent that produces cytotoxic effects on the hematopoietic (blood-forming) tissues; its primary effects are on the skin and eyes, though it is also quite toxic by inhalation or ingestion (Edgewood Arsenal 1974).

In acute (one-episode) exposures to mustard vapors, the eyes are especially sensitive. Symptoms of mild exposure (after a latent period) consist of tearing and a sensation of "sand" in the eyes, with the conjunctiva and lids becoming swollen and fluid-filled. Higher exposures bring on blepharospasm (inability to keep the eyes open), blurring of vision, mucoserous discharge, and other symptoms of ocular irritation. At the highest exposures, there is also headache, deep ocular pain, ulceration, necrosis, and dense corneal opacification. Convalescence can take as much as several months (Edgewood Arsenal 1974).

Acute skin exposure to mustard is first manifested several hours after exposure by gradual reddening of the skin, as if by sunburn, accompanied by itching and mild burning. This is followed by blistering; pinpoint lesions form, enlarge, and coalesce to large translucent yellowish blisters. If the blisters do not rupture, they are resorbed in about a week. Mustard burns of the skin are usually followed by a persistent brown pigmentation except at the site of vesication, which may be depigmented (Edgewood Arsenal 1974). In addition to surface effects, high levels of mustard vapor would be absorbed through the skin into the body to cause systemic effects. These may include anorexia, nausea, vomiting, depression, and fever (Edgewood Arsenal 1974). Respiratory-tract lesions caused by acute exposure to mustard develop slowly over several days. Symptoms begin with hoarseness, which may progress to aphonia, cough, fever, and dyspnea. Incidence of bronchopneumonia is high. Convalescence is slow, and coughing may persist a month or longer (Edgewood Arsenal 1974). Ingestion of food or water contaminated with liquid mustard produces nausea, vomiting, pain, diarrhea, and prostration (Edgewood Arsenal 1974).

Chronic skin exposure may lead to hypersensitivity of the skin to mustard. Sensitization is followed by a more rapid onset of symptoms upon re-exposure to low levels of mustard, as well as by the development of a dermatitis similar to that from poison ivy (Edgewood Arsenal 1974). Exposures of munitions plant workers to mustard for periods of three weeks to six months led these persons to seek treatment for respiratory distress. Typically, a worker developed some or all of the following symptoms: red eyes, photophobia, lacrymation, impaired vision, blepharospasm, loss of taste and smell, nose bleed, sore throat, chest pain, wheezing, and dyspnea (Panel on Cholinesterase Reactivator Chemicals et al. 1984). It was also stated that exposure to mustard at

constant low concentrations led to lingering bronchitis, bronchial asthma, hoarseness, aphonia, and hypersensitivity to smoke, dust, and fumes (Panel on Cholinesterase Reactivator Chemicals et al. 1984). The eyes of workers chronically exposed to low levels of mustard for over two months showed low-grade conjunctival infection, reduced corneal sensitivity, and staining or pigmentation of the corneal epithelium (Edgewood Arsenal 1974).

Mustard is a carcinogen in animals and humans, as well as a mutagen (Panel on Cholinesterase Reactivator Chemicals et al. 1984). An upper bound (95% confidence limit) unit cancer risk of $8.5 \times 10^{-2} \mu\text{g}/\text{m}^3$ has been calculated for mustard (Koppikar et al. 1991).

D.2 Lewisite and Lewisite Oxide

Unlike mustard, where the effects can be delayed for several hours, lewisite (L) irritates skin immediately on contact, is instantly irritating to the eyes, and is also toxic on inhalation. The burning sensation on the skin gradually increases, but remains bearable (if not too extensive); the skin becomes red and blisters form. Healing can take up to a few weeks (Goldman and Dacre 1989). Serious injury by lewisite vapor to the eyes may sometimes be avoided, owing to the almost immediate, searing sensations. These sensations cause the lids to close and alert the victim to the need for precautionary measures, one of which is the timely administration of the antidote, British anti-lewisite (BAL) (Goldman and Dacre 1989). There is no information to indicate how irritating or damaging lewisite oxide (LO) would be to the eyes, or whether intraocular exposure is a reasonable pathway for systemic penetration by LO.

The systemic effects of lewisite include pulmonary edema, diarrhea, restlessness, weakness, subnormal temperature, low blood pressure, interference with kidney function, and hemoconcentration caused by loss of fluid from the bloodstream. In nonfatal cases, hemolysis of erythrocytes has occurred, with a resultant hemolytic anemia. The excretion of oxidized products into the bile by the liver produces local necrosis of that organ, necrosis of the mucosa of the biliary passages with periobiliary hemorrhages, and some injury to the intestinal mucosa (Edgewood Arsenal 1974; Safety Office, U.S. Army Chemical Research, Development, and Engineering Center [CRDEC] various dates; Goldman and Dacre 1989). It is reasonable to assume that LO, absorbed by inhalation or ingestion of dust, would have similar systemic effects, although the pulmonary effects might be somewhat less severe than those from inhalation of lewisite. It is not certain whether immediate irritation to the eyes would occur as a result of exposure to LO.

LO has not been studied to any extent for toxicological effects. To assume that lewisite toxicological data could apply to LO would be misleading. Properties such as volatility and (in the case of lewisite) hydrolysis (which produces HCl) are quite different between the two. As to comparisons of the abilities of these two substances to penetrate skin sufficiently to cause blistering, the statement has been made (Headquarters, Department of the Army et al. 1990) that, "when humidity is high, lewisite hydrolyzes so rapidly that it is difficult to maintain a concentration sufficient to blister bare skin." This may be evidence that the danger of absorption of LO through the skin may be negligible. Inhalation of dust containing LO would be the most probable exposure route for that substance. The data indicate that the systemic toxicity of lewisite is considerably less

via the dermal route than by inhalation (CRDEC various dates); this suggests that a large portion of lewisite gets trapped in the upper layers of the skin as LO and may act locally but does not reach the circulatory system.

Chronic exposure to lewisite can cause sensitization and chronic lung impairment (CRDEC various dates). Despite statements to the contrary (e.g., in Material Safety Data Sheets¹ [CRDEC various dates]), there is no evidence that lewisite (or LO) — or any other organic arsenical — might be carcinogenic, mutagenic, or teratogenic (Goldman and Dacre 1989).

The toxicity of both lewisite and LO may be attributed to an increase in capillary permeability to plasma proteins. That effect appears to be associated with the ability of lewisite to interfere with such enzymes as pyruvate oxidase by binding with enzyme thiol groups (Goldman and Dacre 1989).

D.3 Sarin

Sarin (sarin), a nerve agent, exerts its physiological effects through its powerful inhibition of the enzyme acetylcholinesterase (AChE), which is required for nerve and muscle function in multicellular animals. Normally, AChE prevents accumulation of acetylcholine after its release as a chemical messenger in the nervous system. AChE inhibition adversely affects skeletal muscle, parasympathetic end organ, and central nervous system operation. Individuals poisoned by sarin may show the following symptoms (Edgewood Arsenal 1974; Headquarters, Department of the Army et al. 1990):

- Difficulty in breathing, tightness of chest
- Dimness of vision and pinpointing of the eye pupils
- Drooling and excessive sweating
- Nausea
- Vomiting, cramps, and loss of bladder/bowel control
- Twitching, jerking, and staggering
- Headache, confusion, drowsiness, coma, and convulsion

The number and severity of symptoms depend on the quantity and route of entry of the nerve agent into the body. When the agent is inhaled, a prominent symptom is pinpointing of the pupils and dimness of vision. However, if exposure to the nerve agent has been through the skin

¹ Each "safety sheet" is actually a packet of sheets, normally consisting of ten sections. An individual information packet has been prepared for each chemical of interest to CRDEC; such "safety sheets" are updated at irregular intervals.

or by ingestion, the pupils may be normal or only slightly reduced in size. In this event, diagnosis of nerve agent poisoning, can not be relied upon as the sole symptom for its effects on the pupils (Headquarters, Department of the Army et al. 1990).

Exposure through the eyes produces a very rapid onset of symptoms (usually in less than two to three minutes). Liquid in the eyes kills nearly as rapidly as respiratory exposure. Symptoms from skin absorption appear more slowly. Skin absorption, if great enough to cause death, may occur in one to two hours. Most of the sarin applied as a liquid to skin will evaporate if not covered. Very small skin dosages sometimes cause local sweating and tremors, but few other effects. Nerve agents are cumulative poisons. Repeated exposure to low concentrations, if not too far apart, will produce symptoms (Headquarters, Department of the Army et al. 1990).

If a victim recovers from acute sarin poisoning, recovery will be complete unless anoxia and convulsions have gone unchecked so long that irreversible central nervous system changes have occurred (Headquarters, Department of the Army et al. 1990).

A review of the histories of human volunteers exposed to anticholinesterase agents (i.e., nerve agents) concluded that, "no evidence has been developed (to date) that any of the anticholinesterase test compounds surveyed carries long-range adverse human health effects in the doses used.... Exposures to low doses of OP [organophosphorus] compounds have been reported (but not confirmed) to produce subtle changes in EEG, sleep pattern, and behavior that persist for at least a year" (Panel on Anticholinesterase Chemicals and Panel on Anticholinergic Chemicals 1982).

D.4 VX

VX, a nerve agent, exerts its physiological effects through its powerful inhibition of the enzyme acetylcholinesterase (AChE), which is required for nerve and muscle function in multicellular animals. (VX is considered a more potent agent than sarin [Lewis 1992].) Normally, AChE prevents accumulation of acetylcholine after its release as a chemical messenger in the nervous system. AChE inhibition adversely affects skeletal muscle, parasympathetic end organ, and central nervous system operation. As with sarin, individuals poisoned by VX may show the following symptoms (Edgewood Arsenal 1974; Headquarters, Department of the Army et al. 1990):

- Difficulty in breathing, tightness of chest
- Dimness of vision and pinpointing of the eye pupils
- Drooling and excessive sweating
- Nausea
- Vomiting, cramps, and loss of bladder/bowel control

- Twitching, jerking, and staggering
- Headache, confusion, drowsiness, coma, and convulsion

The number and severity of symptoms depend on the quantity and route of entry of VX into the body. When the agent is inhaled, a prominent symptom is pinpointing of the pupils of the eyes and dimness of vision because of the reduced amount of light entering. However, if exposure to VX has been through the skin or by ingestion, pupils may be normal or only slightly reduced in size. In this event, diagnosis must rely on the symptoms of nerve agent poisoning other than its effects on the pupils (Headquarters, Department of the Army et al. 1990).

Exposure through the eyes produces a very rapid onset of symptoms (usually in less than two to three minutes). Liquid in the eyes kills nearly as rapidly as respiratory exposure. Symptoms appear more slowly from skin absorption, which is a very important route of entry for VX. Skin absorption, if great enough to cause death, may occur in one to two hours. Very small skin dosages sometimes cause local sweating and tremors but few other effects. VX is a cumulative poison. Repeated exposure to low concentrations, if not too far apart, will produce symptoms (Headquarters, Department of the Army et al. 1990).

If a victim recovers from acute VX poisoning, the recovery will be complete unless irreversible central nervous system damage has occurred due to unchecked anoxia and convulsions (Headquarters, Department of the Army et al. 1990).

Because VX has such a low volatility, liquid droplets on the skin do not evaporate, as do uncovered droplets of sarin; this is one reason why effective percutaneous absorption can take place. Indeed, by this route, VX is estimated to be more than 100 times as toxic to humans as sarin (Edgewood Arsenal 1974).

A review of the histories of human volunteers exposed to anticholinesterase agents (i.e., nerve agents) concluded that, "no evidence has been developed (to date) that any of the anticholinesterase test compounds surveyed carries long-range adverse human health effects in the doses used.... Exposures to low doses of OP [organophosphorus] compounds have been reported (but not confirmed) to produce subtle changes in EEG, sleep pattern, and behavior that persist for at least a year" (Panel on Anticholinesterase Chemicals and Panel on Anticholinergic Chemicals 1982).

D.5 Chemical Agent Exposure Criteria

Criteria for worker safety are presented in the literature mainly in the form of air concentration levels, even though the toxicants addressed may also present hazards by dermal penetration. The most respectable criteria are those developed by the Occupational Safety and Health Administration (OSHA) and the American Conference of Governmental Industrial Hygienists (ACGIH); these two organizations work together rather closely, so that they differ only

rarely in assigned values and cover almost the same set of compounds. OSHA presents most values as Permissible Exposure Limits (PELs) and ACGIH issues Threshold Limit Values (TLVs). In Table D.1, one OSHA PEL has been cited. Because PELs were unavailable for the other contaminants, the Army's Airborne Exposure Limits (AELs) are quoted, except that an adjusted value was used for LO. LO has a lower molecular weight than lewisite, with arguably the same systemic effects; hence, the AEL for lewisite (see Table D.1) was adjusted accordingly to give a suggested AEL of 0.002 mg/m³ for LO.

TABLE D.1 Workplace Exposure Criteria

Compound	Type of Criterion	Source	Criterion (mg/m ³)
Mustard	AEL	a	0.003
Lewisite	AEL	a	0.003
LO	Suggested AEL	b	0.002
Sarin	AEL	a	1 × 10 ⁻⁴
VX	AEL	a	1 × 10 ⁻⁵

^a CRDEC various dates.

^b See explanation in text.

D.6 References

CRDEC: see Safety Office, U.S. Army Chemical Research, Development, and Engineering Center.

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Appendix E:
Preliminary Pollutant Limit Values

Appendix E:

Preliminary Pollutant Limit Values

The U.S. Army has developed Preliminary Pollutant Limit Values (PPLVs) for 60 chemicals of concern likely to be found on RMA property. Included in this list are several of the chemical agents and breakdown products. The PPLV methodology, which has been used by the Army at numerous Army properties throughout the country, provides an estimation of the maximum allowable soil concentrations for three direct exposure pathways for humans, soil ingestion, soil skin contact, and soil particle inhalation, as well as one indirect exposure pathway, vapor inhalation. PPLVs were established for each chemical of concern. Values were determined by using such variables as the concentration of the chemical in the soil, human intake rates, and chemical properties and behaviors, such as the partition coefficient specific to the exposure pathway under consideration. Exposure pathways were developed based on the potential use of the Arsenal land following cleanup. Future land uses include a nature preserve, wildlife refuge, and recreational park.

Objectives for using PPLVs are (1) to identify areas where contamination levels pose a health risk to humans, based on the future land use; (2) to identify sites where chemical levels are low or not present, thereby excluding the area from cleanup; (3) to identify the contaminants of concern; and (4) to provide a basis for characterizing risk. PPLVs, however, may not be the only factor dictating remediation. Other factors include Applicable or Relevant and Appropriate Requirements (ARARs), detection limits, natural background concentrations, and restrictive use criteria in cases where the suitable technologies for meeting a desired response objective are not available.¹

¹ Ebasco Services, Inc., et al., 1989, *Exposure Assessment for Rocky Mountain Arsenal, Vol. IV, Preliminary Pollutant Limit Value (PPLV) Methodology, Version 2.1*, report RIC-89227R01, prepared for Program Manager, Rocky Mountain Arsenal, Commerce City, Colo., July.

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