

5. PRODUCTION, IMPORT/EXPORT, USE, AND DISPOSAL

5.1 PRODUCTION

Sulfur mustard is a synthetic organic compound. It was first manufactured in 1822 by the action of ethene on sulfur monochloride or dichloride. Since then, the methods of manufacture have been refined, although they have not been changed substantially. Three main processes have been used. The Germans produced sulfur mustard using the Meyer process, which involved treating ethylene with hypochlorous acid followed by sodium sulfide, yielding β,β' -dihydroxy-methyl sulfide. This in turn was heated with hydrochloric acid, which produced sulfur mustard. In the United States, sulfur mustard was formerly made using the Levenstein process in which ethylene was reacted with sulphur monochloride at 30–35 °C. Sulfur mustard produced by this process contains 62–64% distilled sulfur mustard (or HD) (Munro et al. 1999). This process produces a complex mixture that includes constituents that are more toxic than sulfur mustard itself (Rosenblatt et al. 1975). The most recent process used in the United States involved the formation of bis-(2-hydroxyethyl)-thioether from ethylene oxide and hydrogen sulfide; this was then reacted with hydrochloric acid to form sulfur mustard (Franke 1967; IARC 1975; Rosenblatt et al. 1975). Sulfur mustard produced by this process contains 89% HD (Munro et al. 1999).

Sulfur mustard was manufactured in large quantities during World Wars I and II, but has not been manufactured on an industrial basis in the United States since 1968 (NRC 1994). Stockpiles of sulfur mustard are stored in 1-ton containers and/or chemical munitions at Blue Grass Army Depot in Kentucky, Anniston Army Depot in Alabama, Umatilla Depot Activity in Oregon, Pine Bluff Arsenal in Arkansas, Tooele Army Depot in Utah, Pueblo Army Depot Activity in Colorado, and Aberdeen Proving Grounds in Maryland. Stockpiles of sulfur mustard were also located at the U.S. territory of Johnston Atoll in the North Pacific Ocean. Destruction of sulfur mustard at this location was completed in 2000. Sulfur mustard may also be found at non-stockpile locations in various containers, buried chemical munitions, and at former production facilities. These are currently 45 non-stockpile locations with sulfur mustard across the United States and in the U.S. Virgin Islands as shown in Figure 5-1 (NRC 1996, 2000). Sulfur mustard is probably still being made for laboratory experiments on a small scale.

Information about other mustard agents, such as nitrogen mustard (HN), thickened mustard (HT), and lewisite, are not included in this document (see Chapter 4).

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Figure 5-1. Locations of Sulfur Mustard Stockpile and Non-stockpile Sites in the United States^a



Source: OA 2000, 2002 (★) = Stockpile sites; (○) = Non-stockpile sites

- | | | |
|---|---|---|
| AL | GA | NE |
| Anniston Army Depot (★) | Ft. Gillem (○) | Nebraska Ordnance Plant (○) |
| Ft McClellan (○) | Manchester (○) | NV |
| Camp Sibert (○) | HI | Hawthorne Army Ammunition Plant (○) |
| Huntsville Arsenal (○) | Kipapa Ammunition Storage Site (○) | NJ |
| Redstone Arsenal (○) | Schofield Barracks (○) | Raritan Arsenal (○) |
| Theodore Naval Ammunition Magazine (○) – not shown on map | IL | OH |
| AK | Savanna Army Depot Activity (○) | Ravenna Army Ammunition Plant (○) |
| Adak (○) | IN | OR |
| Chicagoff Harbor (○) | Camp Atterbury (○) | Umatilla Depot Activity (★) |
| Gerstle River Test Center (○) | Naval Weapons Support Center (○) | SC |
| AZ | KS | Charleston Army Depot (○) |
| Navajo Depot Activity (○) | Marysville (○) | Naval Weapons Center (○)–not shown on map |
| Yuma Proving Ground (○) | KY | SD |
| AR | Blue Grass Army Depot (★) | Black Hills Ordnance Depot (○) |
| Pine Bluff Arsenal (★) | LA | TN |
| CA | Ft Polk (○) | Defense Depot Memphis (○) |
| Ft Ord (○) | Concord Spur (○) | TX |
| Edwards AFB (○) | MD | Ft Hood (○) |
| CO | Edgewood Area- Aberdeen Proving Grounds (★) | Camp Stanley Storage Activity (○) |
| Rocky Mountain Arsenal (○) | MS | Camp Bullis (○) |
| Pueblo Army Depot Activity (★) | Camp Shelby (○) | UT |
| FL | Columbus Army Airfield (○) | Dugway Proving Grounds (○) |
| Brooksville Army Air Base (○) | Horne Island (○) | Defense Depot Ogden (○) |
| Drew Field (○) | NC | Tooele Army Depot (★) |
| MacDill AFB (○) | Laurinburg-Maxton Army Air Base (○) | VI |
| Withlacoochee (○) | | Ft. Segarra (St. Thomas) (○) |
| Dry Tortuga Keys (○) | | Other |
| Zephyr Hills Gunner Range (○) | | Johnston Atoll (S. Pacific)(★) |

Source: NRC 1996, 2000

^apost office state abbreviations used

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5.2 IMPORT/EXPORT

Sulfur mustard is not imported into or exported from the United States.

5.3 USE

The principal use of sulfur mustard was as a vesicant chemical warfare agent. The Germans first used it against the British during World War I during the battle of Flanders, near Ypres, Belgium, in 1917 (Franke 1967; Rosenblatt et al. 1975). It was used by the Allies in 1918 and by the Italians in Ethiopia in 1936. It has also been used recently in the Iran-Iraq War in 1984–1988 and by Iraq against its Kurdish minority in Halabjah in 1988 (Black et al. 1993b; Budiansky 1984).

Attempts have been made to use sulfur mustard as an antineoplastic agent, although this has not met with much success due to its high toxicity. A similar product, nitrogen mustard, has been successfully employed as an anticancer agent (IARC 1975). Sulfur mustard has provided a useful model in biological studies concerning the behavior of alkylating agents (IARC 1975). Sulfur mustard has also been used medicinally to control hyperproliferation of psoratic keratinocytes (SBCCOM 1999).

5.4 DISPOSAL

For the past several decades, the United States has stored its stockpile of sulfur mustard at eight Army facilities under a policy of total containment (Colburn 1978). The total quantity of sulfur mustard (i.e., H, HD, and HT) in the original stockpile was 17,358 tons (34,716,945 pounds) (DOA 2000). The stockpile consists of both munitions and 1-ton containers of bulk agent (see Table 5-1; DOA 2000, 2002; NRC 1994). In addition to sulfur mustard, munitions may contain energetics (e.g., explosives and propellants). Public Law (PL) 99-145 (as amended by PL 100-456) and PL 104-484 (October 23, 1992) requires the Army to destroy the U.S. stockpile of all lethal unitary chemical agents and munitions by December 31, 2004 (DOA 1988; NRC 1994). Some chemical-warfare agents and related material, referred to as non-stockpile chemical material (NSCM), were not included in the stockpile inventory, but were subsequently added to the chemical demilitarization program in HR 101-822, which accompanied

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Table 5-1. Original Stockpile Quantities of Sulfur Mustard as Munitions and Bulk Agents

Chemical munitions or bulk agent	APG	ANAD	BAD	JAP ^b	PBA	PUDA	TEAD ^c	UMDA
HD								
105-mm projectile		68,500		140		1,138,760	5,860	
155-mm projectile		206,420	181,260	66,340		3,504,780		
4.2-inch mortar		452,160		116,294		460,340		
M60 projectile				261,960				
Ton container	3,249,740	185,080		116,294	188,400		11,383,420	
H								
155-mm projectile							639,540	
Ton container								4,679,040
HT								
4.2-inch mortar		1,064,600				118,220	363,020	
Ton container					6,249,100			
Total	3,249,740	1,976,760	181,260	578,705	6,437,500	5,222,100	12,391,840	4,679,040
Percent of total sulfur mustard stockpile	9.4	5.7	0.5	1.7	18.5	15.0	35.7	13.5

^aQuantities of agent reported in pounds. Original stockpile quantities reflect amounts before the onset of Chemical Stockpile Disposal Program. Quantities do not include non-stockpile amounts of sulfur mustard. Up-to-date information about stockpile destruction is available at <http://www-pmcd.apgea.army.mil/>.

^bAs of the year 2000, the entire stockpile of sulfur mustard at JAP has been destroyed.

^cAs of November 1, 2002, 44% of the agent and 81% of the munitions at TEAD have been destroyed (exact percentage of sulfur mustard destruction is unspecified)

ANAD = Anniston Army Depot, Alabama; APG = Aberdeen Proving Ground, Maryland; BAD = Blue Grass Army Depot, Kentucky; H = undistilled sulfur mustard; HD = distilled sulfur mustard; HT = 60% sulfur mustard + 40% Agent T; JAP = Johnston Atoll, Pacific Ocean; PBA = Pine Bluff Arsenal, Arkansas; PUDA = Pueblo Depot Activity, Colorado; TEAD = Tooele Depot, Utah; UMDA = Umatilla Depot Activity, Oregon

Source: DOA 2000, 2002

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the 1991 Defense Appropriations Act. NSCM includes lethal wastes from past disposal efforts, unserviceable munitions, chemically contaminated containers, chemical-production facilities, newly located chemical munitions, and known sites containing significant quantities of buried chemical weapons and waste (NRC 2000).

As part of the Chemical Stockpile Disposal Program (CSDP) mandated by Congress, the Army currently uses the “baseline system” for destruction of munitions and bulk agents containing sulfur mustard (NRC 1994). The “baseline system” consists of several steps: (1) storage, transportation, and unloading of munitions and containers, (2) disassembly and draining, (3) agent destruction, (4) energetics destruction, (5) metal parts decontamination, and (6) dunnage (i.e., other contaminated materials) disposal (NRC 1994). Munitions are currently stored and monitored in vented igloos; bulk containers are stored in the open or in monitored warehouses. The munitions or bulk sulfur mustard are transported to the on-site disposal facility and unloaded. Munitions are disassembled, drained of sulfur mustard, and separated into streams of bulk liquid agent, metal parts, energetics, and dunnage, all of which contain different amounts of sulfur mustard. Liquid agents from drained munitions and bulk containers are fed into a primary incinerator preheated to an operating temperature of 2,700 °F (1,480 °C). Exhaust gases from the primary incinerator are fed into a secondary incinerator at a temperature of 2,200 °F (1,200 °C) for 2 seconds, after which 99.9999% of the agent is destroyed (DOA 2000). The gaseous effluents then flow into pollution abatement system before release into the atmosphere. Energetic materials are burned in a counterflow rotary kiln and then heated on a discharge conveyor at 1,000 °F (540 °C); the solid waste produced is nonhazardous and may be shipped for land disposal. Discharged gases pass through a secondary incinerator and a pollution abatement system, and then are released to the atmosphere. Metal parts are heated to 1,000 °F for 15 minutes in a fuel-fired metal parts furnace; the heat-treated metal parts are then released as scrap metal. Gases discharged pass through a secondary incinerator and a pollution abatement system, and then are released to the atmosphere. Dunnage generated during the entire process may be either incinerated (with pollution abatement) or shipped for land disposal as hazardous waste. At all steps, monitoring for chemical agents is performed to detect concentrations of the agent well below those that present an immediate threat to personnel or the surrounding population. There are no measurable sulfur mustard effluents leaving the baseline system facilities under normal operating conditions (MacNaughton 2001). At present, Johnston Atoll is the first site to destroy its portion of the chemical agent and munitions stockpile in the United States. Incineration of sulfur mustard is currently underway at Tooele, Utah. Construction of baseline system facilities near Umatilla, Oregon and Anniston, Alabama are completed with operational testing in progress at these facilities. As of late 2002,

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a baseline system facility at Pine Bluff, Arkansas is near completion with operational testing to be conducted afterwards.

To address growing public concern over incineration, in 1992, Congress directed the Army to evaluate alternative disposal methods that might be significantly safer and more cost effective than the baseline system (NRC 1994). Two alternatives were accepted by the Army for further development: (1) stand-alone neutralization followed by incineration and (2) neutralization followed by bio-treatment (NRC 1996). Neutralization of sulfur mustard is achieved by hydrolysis with hot water (90 °C) and vigorous mixing. This process reduces the sulfur mustard concentrations to levels <200 ppb and selectively converts 90% of the sulfur mustard to thiodiglycol and hydrochloric acid (Currie et al. 1977; May 1998; NRC 1996). Once the reaction is complete, a base (e.g., sodium hydroxide or lime) is added to neutralize the acid and adjust the pH of the hydrolysate (i.e., product of hydrolysis). The dilute processing of sulfur mustard and the addition of base after completion of the neutralization reaction are designed to minimize the production of unwanted byproducts during reaction (NRC 1996). Hydrolysis has been used effectively to detoxify over 700 tons of sulfur mustard located at a Canadian defense facility in Cornwall, Ontario (Currie et al. 1977). After hydrolysis, the hydrolysate can either be incinerated using the baseline system or biotreated. Biotreatment requires adjusting the pH of the hydrolysate to neutral by adding sodium bicarbonate buffer and some nutrients. Bacteria oxidize thiodiglycol to carbon dioxide, water, and sulfate with high efficiency. During the actual process, approximately 0.8 g of cell mass (dry weight) will be produced for every 1 g of organic carbon removed from solution. The biomass is further oxidized through aerobic digestion, and then dried and disposed of at a commercial water treatment facility. Any volatile organic compounds (VOCs) that are present are condensed and the resulting condensate is removed by direct photodegradation and photooxidation by OH radicals. The treated bioresidue is then filtered, dried, and sent to landfill (May 1998; NRC 1996). A chemical neutralization facility is currently being constructed at Aberdeen, Maryland, where sulfur mustard is stored only as bulk liquid in 1-ton containers (NRC 1994). The waste product from this facility will be transported to Dupont's Chambers Works Plant in Deepwater, New Jersey for final treatment at this chemical waste disposal facility. Chemical neutralization will also be used to destroy the sulfur mustard stockpile at Pueblo, Colorado. In November 2002, the Department of Defense selected neutralization followed by super critical water oxidation to destroy the chemical weapons stockpile at the Blue Grass Army Disposal in Kentucky (DOD 2003).