MUSTARD GAS

The opening chapter of the 1925 Geneva Protocol banning chemical weapons opened with the following statement:

"Whereas the use in war of asphyxiating, poisonous, or other gases, and of all analogous liquids, materials, or devices, has been justly condemned by the general opinion of the civilized world ..."

Given that all weapons of war are relatively inhumane by their very nature, what was it about the chemical weapons covered in the 1925 treaty that made them considered beyond inhumane, but, "justly condemned by the general opinion of the civilized world"?

A World War I history site on the Web presented this report. "One nurse, Vera Brittain, wrote:

> ***'I wish those people who talk about going on with this war whatever it costs could see the soldiers suffering from mustard gas poisoning. Great mustard-colored blisters, blind eyes, all sticky and stuck together, always fighting for breath, with voices a mere whisper, saying that their throats are closing and they know they will choke.'"***

British soldiers blinded by mustard gas.

So what exactly is this grievous chemical weapon? Its chemical composition is relatively simple, a molecule of four elements, **$C_4H_8Cl_2S$.** These atoms form a short unbranched chain **$Cl\text{-}CH_2\text{-}CH_2\text{-}S\text{-}CH_2\text{-}CH_2\text{-}Cl$.** The first synthesis of mustard gas is often credited to Frederick Guthrie in 1860, although it may have been synthesized as early as 1822. Guthrie not only synthesized the compound but also experienced some of the toxic effects when the gas made contact with his skin.

Its name comes from impure forms of mustard gas, which has an odor resembling mustard. Its name is misleading. It's not a gas, but exists as a liquid at room temperature. In order to be used as a weapon, it has to be finely dispersed, usually by some sort of mortar or gun shell. Mustard gas does not occur naturally in the environment.

Mustard gas causes the skin to blister. Symptoms start with an immediate itching, which develops over the course of a day into deep blisters in the skin. The eyes become sore and eyelids swollen. Exposure to high concentrations can attack the corneas, resulting in blindness. Parts of the body that are moist, such as the eyes, nose, and lungs, are particularly susceptible to attack by the gas. If inhaled, it causes blistering in the lungs, which severely limits the amount of oxygen that the body can absorb. Minor amounts of lung damage can cause chronic health problems, but if too much damage occurs, death can result. Because mustard gas is a relatively nonpolar substance and only slightly soluble in water, washing it off can be difficult. Worse yet, the mustard gas will react with water to form a breakdown product called hemi-mustard, which is equally toxic. It also releases hydrochloric acid (HCl) as part of this reaction. The HCl has hazardous effects of its own.

So how does this relatively simple molecule have such a devastating effect on human tissues? Interestingly, the mechanism of the toxicity of mustard gas is not known with certainty. There are a number of hypotheses about how it works to cause injury. One suggests that the mustard gas reacts with DNA, causing breaks in the strands of DNA. This sets off a series of events in the cell leading to the release of enzymes that dissolve cell membranes and cause cell death. Another hypothesis suggests that the mustard gas inactivates a compound that is the major defense against attack by oxidation. In this scenario, mustard gas does not attack the cell; it is just that the cell is now vulnerable to the usual oxidative stress from reactive oxygen species. It also leads to inflammation.

First use

Mustard gas was not formally used as a weapon until 1917, during World War I. WWI was a turning point in the development of weapons of war. Technology was on the rise, and the war accelerated the development of many key technologies, including aircraft, communications, and weaponry. The war first saw use of chemical weapons in combat with the release of chlorine gas on a battlefield near Ypres, Belgium. Chlorine gas was a crude, but effective predecessor to mustard gas. Elemental chlorine is a greenish gas at room temperature. It is a very reactive substance. It attacked the respiratory tissue of the soldiers and caused slow painful death by asphyxiation. Two years later, in July 1917, the Germans were the first to use mustard gas on the battlefield. France and England soon followed by developing their own supplies.

The use of chemical weapons continued throughout the war. Death occurred in only about 1 percent of the people who were exposed to mustard gas. It was far more effective as an incapacitating agent, often taking soldiers out of action for the duration of the conflict. By the war's end, chemical weapons had killed some 100,000 people.

Fact: ***The first gas mask used by firemen, policemen, engineers, and later by U.S. soldiers during World War I was developed by an African American inventor, Garret A. Moran (1877–1963).***

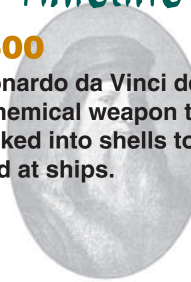
Chemical Weapons Timeline

??? B.C

Poison-tipped arrows.

600 B.C.

Assyrians poison wells with Rye Ergot—a fungal disease of rye—during the siege of Krissa. The fungus produces a hallucinogen related to LSD.



1500

Leonardo da Vinci devises a chemical weapon to be packed into shells to be fired at ships.

1899

Hague Declaration prohibits poison or poisoned arms, but isn't widely adopted.

1914–1918

Chemical weapons, including mustard gas, chlorine, and phosgene, are used during World War I, killing more than 90,000.

A call to ban

In 1925 the world reacted to the horrible use of these weapons and the Geneva Protocol was drafted, which called for the prohibition of chemical and biological weapons. The United States signed the treaty, but it was never ratified by Congress. The United States built its own arsenal of chemical weapons during World War II, as a hedge against the use of such weapons by Germany. Germany never did introduce them in combat, and the United States ended up with a large arsenal of surplus chemical weapons at the end of the war. During the Cold War, the United States continued to develop existing and new versions of biological and chemical weapons. Finally, in 1969, the United States renounced the use and development of all biological and chemical weapons of war. Six years later, in 1975, it finally ratified the Geneva Protocol and also the Biological and Toxin Weapons Convention of 1975. Since then, the main activity in the United States has been research on how to safely store and dispose of these weapons. The U.S. stock is located in seven military storage depots in various locations ranging from Johnston Atoll in the Pacific Ocean, to Aberdeen Proving Ground in Maryland.

Destroying stockpiles

Although mustard gas can be incinerated, the current favored method of disposal is by hydrolysis and neutralization.

Hydrolysis is a category of chemical reaction that literally means to break with water ("hydro" relates to water, "lysis" means to break). The water reacts with the mustard gas, adding –OH groups and eventually forming thiodiglycol and hydrochloric acid. Thiodiglycol is a common chemical found in pen ink and dyes. The hydrochloric acid is neutralized by adding sodium hydroxide, reacting to form sodium chloride and water.

Chemical Weapons

NERVE AGENTS **Tabun** **Sarin** **Soman** **VX (methylphosphonothioic acid)**	***Inhibit acetylcholinesterase and disrupt the central nervous system. Death is usually due to respiratory arrest.***
BLISTER AGENTS **Mustard gas, sulfur mustard, or Yperite** **Nitrogen mustard** **Lewisite**	***Burn and blister upon contact. They produce casualties and force opposing troops to wear full protective equipment, thus degrading fighting efficiency.***
CHOKING AGENTS **Phosgene** **Diphosgene** **Chlorine**	***Attack lung tissue, primarily causing pulmonary edema. Also known as lung damaging agents.***

Although the process is fairly straightforward chemically, there are safety issues in handling the dangerous substances to make sure that the workers are not exposed to hazardous materials.

The disposal of unwanted mustard gas has not always been so thoughtful or controlled. Most of the mustard gas found in Germany after WWII was dumped in the Baltic Sea. Polymerized pieces of the mustard gas occasionally show up on beaches and are mistaken for amber, the fossilized tree resin, leading to severe health problems.

More to do

Yet with all the efforts to ban and destroy chemical weapons, the final chapter has yet to be written. It has been used as recently as the 1980s, when Iraq employed it against Iranian solders and Kurdish villagers.

Work continues to ensure the abolition of chemical weapons of all types. The international community negotiated the Chemical Weapons Convention, which entered into force on April 29, 1997. The Chemical Weapons Convention is somewhat unique. Unlike previous treaties, it specifies stringent protocols for the inspection and verification of the ban. The Organization for the Prohibition of Chemical Weapons is the international agency charged with enforcing the treaty. To date, a total of 158 countries have signed on. Mustard gas is no longer produced by the United States, and the current stockpile, which is decades old, is slowly being destroyed.

Perhaps this can be the last chapter on inhuman materials that have earned every bit of their permanent ban from the civilized world.

Michael Tinnesand is the associate director for Academic Programs at ACS and formerly taught chemistry in Hillsboro, OR.

1980–1988
Iraq and Iran use chemical weapons during their 8-year war.

March 1988
Iraq uses mustard gas and nerve agents against Iraqi Kurds. An estimated 5000 civilians die in one attack.

1993
The Chemical Weapons Convention (CWC) is established. It prohibits the research and production of chemical agents such as Sarin and VX nerve gas.

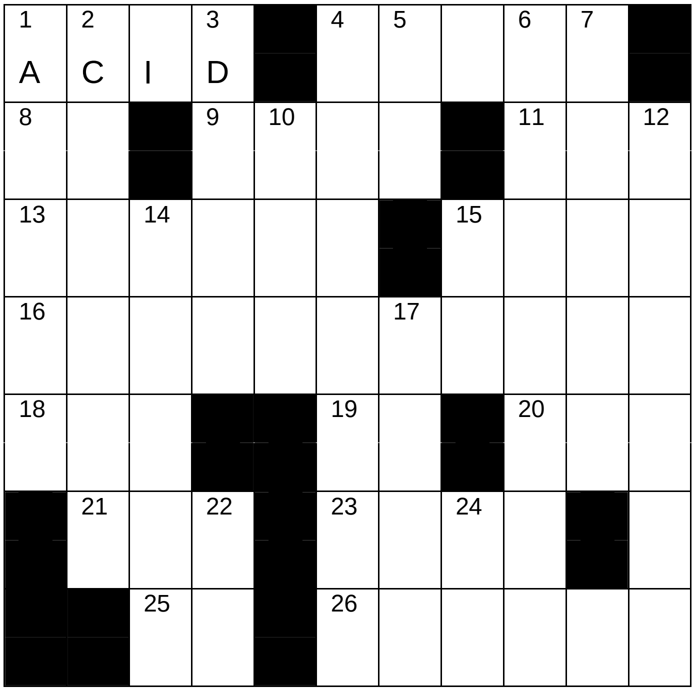
1995
Members of the Aum Shinrikyo cult release Sarin into the Tokyo underground rail system, killing 12 and injuring thousands.

April 2005 Teacher's Guide

"Mustard Gas"

Puzzle: Double Cross

We double your trouble by offering below two identical crossword grids. For each number, there are two clues in random order; it's up to you to decide which answer goes in which grid. Roughly half the clues are "scientific" . To get you started we have filled in 1 across in both grids. Two-letter answers clued by atomic information will be the symbol of an element. Don't get "double-crossed" as you tackle this puzzle !!



ACROSS

1 Proton donor
Proton acceptor

4 Dialect, regional usage
Narcotic from poppies

8 Chemistry Nobel winner in 1939 (initials)
Has 68 protons

9 SI prefix for 10^{-9}
Mythical monster, ex.Shrek

11 Nickname for the sun
Spoil, especially if organic

13 System where pH < 7
Indian tribe in SW USA

15 SI prefix for 10^{3}
___drama, eventful play

16 Forms at cathode in electrolysis of brine
Forms at anode in electrolysis of brine (both are two words)

18 Largest internet provider
___-Haw, country music show

19 Group 16, period 5
The radioactive halogen

20 Cheer at a bull fight
Tax-collecting federal agency

21 In basketball , wish, nothing but ___
Carpet

23 As opposed to odd
Unthreaded fastener for wood joints

25 Element name that honors great Russian chemist
Metalloid abundant in sand

26 Felt, experienced
PbO, CO, and NO_2, for ex

DOWN

1 Particle, symbol He^{2+}
Shorefront swimming place

2 William Tell, for example
Child's coloring marker

3 Stern, sullen
Prefix for energy <u>into</u> a system

4 Moves to action, rouses
A spice used in cooking

5 Gym class (initials)
First (and last) note on scale

6 Roots, sources
Apply Au foil when gilding (two words)

7 1 mole solute / kg of solvent
1 mole solute / L of solution

10 78 % N_2, 21 % O_2.
Sedan model type

12 Thrown, pitched
As opposed to winners

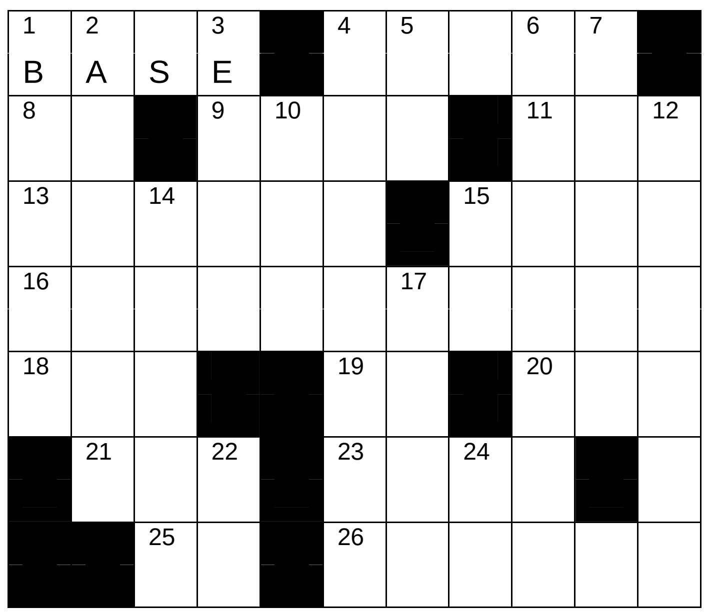
14 Car engine is on, but in neutral
Part of the intestines

15 Energy due to motion (initials)
In +7 or +4 state, a good oxidizer

17 Movie actress ____ Campbell
Form 1040 done via the intenet (hyphenated)

22 Seventh note on the scale
Lanthanide with half-filled 4f subshell

24 XVI ÷ VIII
Measure of attraction for an electron pair (initials)



Puzzle Answers: Double Cross

1 A	2 C	I	3 D	■	4 O	5 P	I	6 U	7 M	■
8 L	R	■	9 O	10 G	R	E	■	11 S	O	12 L
13 P	A	14 I	U	T	E	■	15 M	E	L	O
16 H	Y	D	R	O	G	17 E	N	G	A	S
18 A	O	L	■	■	19 A	T	■	20 O	L	E
■	21 N	E	22 T	■	23 N	A	24 I	L	■	R
■	■	25 S	I	■	26 O	X	I	D	E	S

1 B	2 A	S	3 E	■	4 I	5 D	I	6 O	7 M	■
8 E	R	■	9 N	10 A	N	O	■	11 R	O	12 T
13 A	C	14 I	D	I	C	■	15 K	I	L	O
16 C	H	L	O	R	I	17 N	E	G	A	S
18 H	E	E	■	■	19 T	E	■	20 I	R	S
■	21 R	U	22 G	■	23 E	V	24 E	N	■	E
■	■	25 M	D	■	26 S	E	N	S	E	D

Student Questions

Mustard Gas

1. What is the chemical formula and chemical structure of mustard gas?
2. Why is this material called mustard gas, and what is misleading about its name? What must be done in order to use mustard gas as a weapon?
3. Describe some of the effects of exposure to mustard gas.
4. What happens if you try to wash mustard gas off your body with water?
5. What is the mechanism by which mustard gas produces its damaging effects?
6. What gas was the first to be used as a weapon during WWI? Where was it used, and what effects did it have on the soldiers who were exposed to it?
7. Describe the most common procedure used to dispose of mustard gas.
8. What is the Chemical Weapons Convention? When did it go into force, and what is unique about its provisions?

Answers to Student Questions

Mustard Gas

1. What is the chemical formula and chemical structure of mustard gas?
   The chemical formula for mustard gas is $C_4H_8Cl_2S$. The chemical structure is $Cl\text{-}CH_2\text{-}CH_2\text{-}S\text{-}CH_2CH_2\text{-}Cl$.

2. Why is this material called mustard gas, and what is misleading about its name? What must be done in order to use mustard gas as a weapon?

   It is called mustard gas because impure forms of the gas have an odor that resembles that of mustard. The name is somewhat misleading because at room temperature the substance is actually a liquid, not a gas. In order to be used as a weapon, it must be finely dispersed. This is typically done by using some sort of mortar or gun shell.

3. Describe some of the effects of exposure to mustard gas. Which parts of the body are most susceptible to attack?

   The first symptom is itching. Over the course of a day, deep blisters form on the skin. Eyes can become sore and eyelids swollen. If a person is exposed to sufficiently high concentrations, the corneas can be damaged to the extent that blindness results. Moist parts of the body like the eyes, nose and lungs are especially susceptible to attack. If inhaled, it causes blistering in the lungs. If the damage is minor, chronic health problems may result, but if the damage is more extensive, it can even result in death.

4. What happens if you try to wash mustard gas off your body with water?

   First, it is difficult to wash off, since mustard gas is nonpolar and therefore only slightly soluble in water. More significantly, it reacts with water to form a breakdown product called hemi-mustard, which is equally toxic, and in addition forms hydrochloric acid, HCl, another toxic material.

5. What is the mechanism by which mustard gas produces its damaging effects?

   We are not sure. One hypothesis is that mustard gas reacts with DNA and causes breaks in the DNA strands. This causes a series of events in the cell that lead to the release of enzymes that dissolve cell membranes and cause cell death. A second hypothesis states that mustard gas inactivates a compound that is the major defense against attack by oxidation. In this scenario the cell itself is not actually attacked, but the cell is now vulnerable to the usual oxidative stress from reactive oxygen species. It also leads to inflammation.

6. What gas was the first to be used as a weapon during WWI? Where was it used, and what effects did it have on the soldiers who were exposed to it?

   The first gas to be used in combat was chlorine. It was used on a battlefield near Ypres, Belgium. It attacked the respiratory system of soldiers who were exposed, causing a slow painful death by asphyxiation.

7. Describe the most common procedure used to dispose of mustard gas.

   The favored method is hydrolysis and neutralization. Mustard gas is reacted with water. The water adds –OH groups, eventually forming thiodiglycol and hydrochloric acid. The hydrochloric acid is neutralized by sodium hydroxide, reacting to form sodium chloride and water.

8. What is the Chemical Weapons Convention? When did it go into force, and what is unique about its provisions?

   The Chemical Weapons Convention is a treaty designed to prevent the use of chemical weapons. It went into force on April 29, 1997. It is unique in that it specifies stringent protocols for inspection and verification of the ban.

Content Reading Guide

National Science Education Content Standard Addressed As a result of activities in grades 9-12, all students should develop understanding	**Going for Platinum**	**Biodiesel**	**Battling Zits!**	**Mustard Gas**	**Antimatter**
Science as Inquiry Standard A: about scientific inquiry.	✔	✔	✔	✔	✔
Physical Science Standard B: of the structure and properties of matter.	✔	✔	✔	✔	✔
Physical Science Standard B: of chemical reactions.	✔	✔	✔	✔	
Physical Science Standard B: of conservation of energy and increase in disorder					✔
Physical Science Standard B: of the interaction of energy and matter.		✔	✔		✔
Life Science Standard C: of matter, energy, and organization in living systems.		✔			
Earth & Space Science Standard D: of geochemical cycles.		✔			
Science and Technology Standard E: about science and technology.	✔	✔	✔	✔	✔
Science in Personal and Social Perspectives Standard F: of personal and community health.	✔	✔	✔	✔	✔
Science in Personal and Social Perspectives Standard F: of natural resources.		✔			
Science in Personal and Social Perspectives Standard F: of environmental quality.	✔	✔			
Science in Personal and Social Perspectives Standard F: of natural and human-induced hazards.	✔		✔	✔	
Science in Personal and Social Perspectives Standard F: of science and technology in local, national, and global challenges.	✔	✔	✔	✔	✔
History and Nature of Science Standard G: of science as a human endeavor.		✔	✔	✔	✔
History and Nature of Science Standard G: of the nature of scientific knowledge.	✔	✔		✔	✔
History and Nature of Science Standard G: of historical perspectives.	✔			✔	✔

Anticipation Guides

Anticipation guides help engage students by activating prior knowledge and stimulating student interest before reading. If class time permits, discuss their responses to each statement before reading each article. As they read, students should look for evidence supporting or refuting their initial responses.

Directions for all Anticipation Guides: In the first column, write “A” or “D” indicating your agreement or disagreement with each statement. As you read, compare your opinions with information from the article and complete the second column. In the space under each statement, cite information from the article that supports or refutes your original ideas.

Mustard Gas

Me	Text	Statement
		1. Mustard gas is a naturally occurring compound made of only four elements.
		2. Mustard gas is a liquid at room temperature.
		3. Mustard gas is easily washed off with water.
		4. Mustard gas first used as a chemical weapon in World War I.
		5. Mustard gas kills most people who are exposed to it.
		6. The United States has biological and chemical weapons in storage, waiting for disposal.
		7. Most of the mustard gas found in Germany after World War II was disposed of by hydrolysis, followed by neutralization.
		8. In the 1500s, Leonardo da Vinci was opposed to the use of chemical weapons.
		9. Chemical weapons may disrupt the nervous system, cause severe blisters, or attack lung tissue.

Reading Strategies

These content frames and organizers are provided to help students locate and analyze information from the articles. Student understanding will be enhanced when they explore and evaluate the information themselves, with input from the teacher if students are struggling. If you use these reading strategies to evaluate student performance, you may want to develop a grading rubric such as the one below.

Score	Description	Evidence
4	Excellent	Complete; details provided; demonstrates deep understanding.
3	Good	Complete; few details provided; demonstrates some understanding.
2	Fair	Incomplete; few details provided; some misconceptions evident.
1	Poor	Very incomplete; no details provided; many misconceptions evident.
0	Not acceptable	So incomplete that no judgment can be made about student understanding

Mustard Gas

Chemical description	
Symptoms of exposure to mustard gas	
How it works	
Use of mustard gas in weapons	

Disposal of mustard gas	
Future of chemical weapons	

Mustard Gas

Background Information

More on the effects of exposure to mustard gas

Oddly enough, when one is exposed to a typical dose of mustard gas, more often than not there is actually a delay of perhaps several hours before the effects become pronounced. If exposed to the liquid form this delay is shortened. Very often no significant effects are felt for the first hour or so after exposure, although this is not always the case.

Generally within about 2-6 hours symptoms begin. These include nausea, fatigue, headache, eye inflammation accompanied by intense pain, lachrymation (excessive secretion of tears) , blepharospasm (spasmodic winking caused by the involuntary contraction of an eyelid muscle), photophobia (an abnormal sensitivity to or avoidance of light), and rhinorrhoea (excessive nasal discharge). The face and neck typically become very red, the throat becomes very sore, and there is an increased pulse and respiratory rate.

These symptoms continue to increase in severity over the next twenty hours or so and are accompanied by skin inflammation, followed by blister formation in the warmest areas of the body such as the genitals, the buttocks, the armpits and the inner thighs.

These conditions generally continue to become more severe for the 2^{nd} twenty-four hours. Blistering increases and worsens. Severe coughing begins, often producing mucus, pus and necrotic slough. There is intense itching of the skin with increased pigmentation.

If the degree of exposure is much higher than what is typical, convulsions followed by a coma and death can occur within an hour.

Mild exposure to small amounts (such as might be experienced by workers involved in the manufacture of the material) can produce delayed effects months and even years later. Respiratory problems are the most common delayed effect. In addition, workers involved in mustard gas production have a higher incidence of cancer, influenza, pneumonia and chronic respiratory disease.

One American study involving 7,000 cases of exposure to mustard gas showed the following areas to be those most typically affected.

Eyes----------------------86.1%
Respiratory tract-------75.3%
Genitals------------------42.1%
Face----------------------26.6%
Armpits------------------12.5%
Arms---------------------11.7%
Legs----------------------11.4%
Abdominal regions-----6.4%
Hands---------------------4.3%
Feet-----------------------1.5%

Chemical and Biological Weapons Timeline Events

The article sidebar lists some of the significant events in the development and use of chemical weapons. Some additional events, including what would be more correctly listed as the use of biological weapons are:

5^{th} Century BC—During the war between Athens and Sparta, the Spartan forces besieging an Athenian city placed lighted mixtures of wood, pitch and sulfur under the walls of the city. They hoped that the noxious fumes would incapacitate the Athenians, but the attempt was not highly successful.

1346 AD—A battle had been raging around the town of Kaffa (Crimea, Russia). The town was under the control of Genoans from northern Italy, but Tartars from the east had been attempting, unsuccessfully, to retake the city for three years. The city was walled, highly defended, and self-sufficient.

This was the time of the bubonic plague. The plague struck the Tatar's ranks, but rather than providing victory for the Genoans, it led to their defeat. The Tartars had the rather ingenious idea of destroying their enemy by decimating them with plague, and they achieved this by catapulting infected corpses over the walls of the city. The technique proved successful and the Genoans were forced to surrender. There is some speculation that survivors fleeing the city were responsible for the spread of the disease from Asia to Europe and the subsequent death, over the next four years, of approximately 20,000,000 people.

1422—A similar thing occurred during the battle of Carolstein. Lithuanian soldiers adopted the same technique of hurling plague-infected bodies, and in addition they hurled about 2,000 cartloads of excrement over the walls of the castle they were putting under siege.

1500—Leonardo da Vinci—the chemical weapon he envisioned involved a mixture of sulfide or arsenic and verdigris (see *ChemMatters, Feb. 2003*). He wrote:

throw poison in the form of powder upon galleys. Chalk, fine sulfide of arsenic, and powdered verdegris may be thrown among enemy ships by means of small mangonels, (a military device used to hurl stones and other objects) *and all those who, as they breathe, inhale the powder into their lungs will become asphyxiated.*

Evidently it is not known whether the device was actually ever utilized.

1500s-1800s—During this period there are several episodes involving the use of smallpox to defeat an enemy. Conquistador Hernando Cortez used contaminated clothing to infect natives in his conquest of Peru. During the Indian wars in the United States it was a fairly common practice to try and induce smallpox into the Native American population by the use of contaminated blankets and handkerchiefs taken from hospitals. These were sometimes presented as "gifts."

1672—During the siege of the city of Groningen several different explosive and incendiary devices, some filled with belladonna (a poisonous herb) were used with the intention of producing noxious fumes.

1854—Lyon Playfair, a British chemist, proposed using a cacodyl cyanide artillery shell against enemy ships during the siege of Sevastopol. Although backed by Admiral Thomas Cochrane of the Royal Navy, the proposal was rejected by the British Ordinance Department as "bad a mode of warfare as poisoning the wells of the enemy." Playfair's response to their objection was used as a justification for the use of chemical warfare well into the next century.

There was no sense in this objection. It is considered a legitimate mode of warfare to fill shells with molten metal which scatters among the enemy, and produced the most frightful modes of death. Why a poisonous vapor which would kill men without suffering is to be considered illegitimate warfare is incomprehensible. War is destruction, and the more destructive it can be made with the least suffering the sooner will be ended that barbarous method of protecting national rights. No doubt in time chemistry will be used to lessen the suffering of combatants, and even of criminals condemned to death.

WWII—It is often stated that there was no use of chemical weapons during the 2nd World War. This is basically a valid statement, although they did see some very limited use and both sides certainly had amassed significant quantities of these kinds of weapons. Nazi Germany discovered the nerve agents tabun, sarin and soman. They developed large stockpiles of these and other agents, but although used in some limited contexts, these were never utilized on a large-scale basis. Evidently they interpreted the lack of discussion of these types of agents in Allies' scientific journals as evidence that they had actually developed the ability for their large scale use and the lack of journal articles was evidence that information regarding these agents was being suppressed.

In 1945, the Allies seized vast quantities of chemical weapons that had belonged to Germany. These included approximately 300,000 tons of mines, grenades, aerial bombs and artillery shells that were filled with mustard gas or other poisonous compounds.

Other gases used during WWI

Mustard gas and chlorine were hardly the only poisonous gases used during WWI. One comprehensive Website lists all of the following, along with the sides that used it, some of their effects, and the mode of delivery:

benzyl bromide

Germany, tearing, first used in 1915

bromoacetone

Both sides, tearing/fatal in concentration, first used in 1916

carbonyl chloride (phosgene)

Both sides, asphyxiant, fatal with delayed action, first used in 1915

chlorine

Both sides, asphyxiant, fatal in concentration, first used in 1915, cylinder release only

chloromethyl chloroformate

Both sides, tearing, first used in 1915, artillery shell

chloropicrin

Both sides, tearing, first used in 1916, artillery shell

cyanogen (cyanide) compounds

Allies, Austria, asphyxiant, fatal in concentration, first used in 1916, artillery shell

dichloromethyl ether

Germany, tearing, first used in 1918, artillery shell

dibromomethyl ethyl ketone

Germany, tearing, fatal in concentration, first used in 1916

diphenylchloroarsine

Germany, asphyxiant, fatal in concentration, (dust-could not be filtered), first used in 1917, artillery shell

diphenylcyanoarsine

Germany, more powerful replacement for diphenylchloroarsine, first used in 1918

ethyldichloroarsine

Germany, less powerful replacement for diphenylchloroarsine, first used in 1918, artillery shell

ethyl iodoacetate

British, tearing, first used in 1916

monobrommethyl ethyl ketone

Germany, more powerful replacement for bromoacetone, first used in 1916

trichloromethylchloroformate (diphosgene)

Both sides, asphyxiant, fatal with delayed action, first used in 1916

The Geneva Protocol of 1925—What did it actually prohibit?

The article mentions the Geneva Protocol of 1925 and presents some of the opening words. The complete protocol is:

TIAS 8061
PROTOCOL FOR THE PROHIBITION OF THE USE IN WAR OF ASPHYXIATING, POISONOUS OR OTHER GASES, AND OF BACTERIOLOGICAL METHODS OF WARFARE
ENTRY INTO FORCE: 8 February 1928

The undersigned Plenipotentiaries, in the name of their respective governments:

Whereas the use in war of asphyxiating, poisonous or other gases, and of all analogous liquids, materials or devices, has been justly condemned by the general opinion of the civilised world; and Whereas the prohibition of such use has been declared in Treaties to which the majority of Powers of the world are Parties; and To the end that this prohibition shall be universally accepted as a part of International Law, binding alike the conscience and the practice of nations;

Declare:

That the High Contracting Parties, so far as they are not already Parties to Treaties prohibiting such use, accept this prohibition, agree to extend this prohibition to the use of bacteriological methods of warfare and agree to be bound as between themselves according to the terms of this declaration.

The High Contracting Parties will exert every effort to induce other States to accede to the present Protocol. Such accession will be notified to the Government of the French Republic, and by the latter to all signatories and acceding Powers, and will take effect on the date of the notification by the Government of the French Republic.

The present Protocol, of which the English and French texts are both authentic, shall be ratified as soon as possible. It shall bear today's date.

The ratifications of the present Protocol shall be addressed to the Government of the French Republic, which will at once notify the deposit of such ratification to each of the signatory and acceding Powers.

The instruments of ratification of and accession to the present Protocol will remain deposited in the archives of the Government of the French Republic.

The present Protocol will come into force for each signatory Power as from the date of deposit of its ratification, and, from that moment, each Power will be bound as regards other Powers which have already deposited their ratifications.

In witness whereof the Plenipotentiaries have signed the present Protocol.

Done at Geneva in a single copy, the seventeenth day of June, One Thousand Nine Hundred and Twenty-Five.

The Biological and Toxin Weapons Convention of 1975

This is a much more comprehensive and involved document. If you would like to obtain more information regarding the history of this document or perhaps read the document itself, some good Websites include:

http://www.state.gov/t/ac/trt/4718.htm

http://www.pbs.org/wgbh/nova/bioterror/bwc.html

The Chemical Weapons Convention (CWC) and the Organization for the Prohibition of Chemical Weapons (OPCW)

Once again, the following Websites may prove very useful.

There is an official United States Chemical Weapons Convention Website at:

http://www.cwc.gov/

Other useful Websites include:

http://www.cwc.gov/treaty/cwcIndex_html

http://www.un.org/Depts/dda/WMD/cwc/

http://www.fas.org/nuke/control/cwc/

Mustard gas from WWII still poses a risk at sea

After the Second World War, shells that were leaking mustard gas were dumped into the Baltic sea. While that probably seems like a completely irresponsible act of bad judgment, during that time ecological concerns were not that common, and in fact, it was generally believed that dumping materials such as this into the seabed was actually one of the safest methods of disposal. It turns out that contact with sea water alters mustard gas's normal liquid state. It becomes very viscous and can even transform into a solid material. It is thought that significant quantities of this form of mustard gas remain at the bottom of the Baltic sea even today and pose a risk. Eleven fishermen have suffered from exposure to this mustard gas. Their symptoms included highly inflamed skin, including blisters and painful inflammations of the eyes producing transient blindness. Two of the fisherman also suffered pulmonary edema.

Connections to Chemistry Concepts

More about mustard gas

As stated in the article, the structure of mustard gas is

CH_2CH_2Cl
/
S
\
CH_2CH_2Cl

Mustard gas is classified as a *thioether.* Ethers are organic compounds with the general formula R-O-R', where R and R' represent hydrocarbon chains. "Thio" indicates that the oxygen atom in a regular ether molecule has been substituted by a sulfur atom. It goes under more than one chemical name. Included among them are 1,1-thio-*bis*-[2-chloroethane], 2,2'-dichlorodiethyl sulfide and *bis*-(2-chloroethyl)-sulfide.

It is also referred to as *sulfur mustard*, Yperite, *H*, *HT*, *HD*, and *Kampstoff Lost*. The last name is derived from two men who developed a process for mass-producing the substance for war use at the German company Bayer AG. Their names were Lommel and Steinkopf.

Mustard gas can be synthesized in more than one way. One common method is to react thiodiglycol (see below) with thionyl chloride:

$S(CH_2CH_2OH)_2 + 2\ SOCl_2$ -------> $S(CH_2CH_2Cl)_2 + 2\ SO_2 + 2\ HCl$

The Material Safety Data Sheet (MSDS) for mustard gas can be found at:

http://www.castleviewuk.com/Frameless/Safe/msds/ex/MSDS_mustard.htm

The article states that mustard gas, being nonpolar, is only slightly soluble in water, making it difficult to wash off. But more significantly, it reacts with water to form "hemi-mustard" and hydrochloric acid. The hemi-mustard is thiodiglycol, and is a widely used material (for example, in inks). The equation for this reaction is:

$S(CH_2CH_2Cl)_2 + HOH$ ------> $ClCH_2CH_2SCH_2CH_2OH + HCl$

How does mustard gas produce its terrible effects?

As the article states, we are not certain, but there are some ideas. Mustard gas is an alkylating agent. This means that it has a strong tendency to bind covalently to nucleophilic molecules (molecules that typically contain an atom(s) with unshared pairs of electrons) such as DNA, RNA, proteins and components of cell membranes. It is thought that mustard gas causes cross linking of DNA strands, which results in disruption of their function. It can upset normal protein synthesis, resulting in cell death.

Possible Student Misconceptions

Students may assume that Germany was the only nation that utilized chemical weapons during WWI. This was not the case. Chemical weapons were used by both sides (see *Background Information*). They may also think that chemical weapons were never used during WWII because of the Geneva Protocol. While this is approximately true, it is not entirely the case (see *Background Information*).

Students may have only heard about the use of mustard gas and chlorine during WWI, and may therefore assume that these were the only two gases that were utilized. This is evidently not the case (see *Background Information*).

Because mustard gas reacts with water, students may reasonably conclude that mustard gas cannot persist in the environment because it would be destroyed as soon as it got wet. This is not the case. Mustard gas can persist in the soil because it becomes coated with a material that insulates it from surrounding moisture. If dumped in the ocean, it once again can be altered into a viscous liquid or even a solid and thus can persist for many decades.

Demonstrations and Lessons

1. Although the use of chemical and biological weapons has been condemned, and both the Geneva Protocol and the Biological and Toxin Weapons Convention of 1975 ban their use, these weapons are still being developed and have been used by multiple nations during the last few decades.

   What should be the position of the United States? Should we renounce the use of chemical or biological weapons under any circumstances? Is there really any practical difference between killing people with these kinds of weapons compared to bombing or shooting? Since some other nations may not follow suit, should we continue to develop these kinds of weapons despite our stated formal position?

This issue could make for a very heated, but hopefully educational classroom debate. Of course such a debate could easily just be an exchange of personal opinion, so if such a debate is held, some ground rules might be advisable. These might include having some facts and figures regarding the probable effects of the use of various types of weapons, the amount of "collateral damage" that might be expected from each, and the potentially uncontrollable aftermath connected to the use of various types of weapons, both on populations and the environment. In addition, historical events and their consequences might be cited to support one position or another.

2. The Geneva Protocol of 1925 is often cited as a document that prohibited the use of chemical and biological weapons. If you read the entire document (see *Background Information*), you may be struck by things such as the following:

   how brief the document is—the lack of detail
   the fact that the document in no way prohibits the manufacture of chemical or biological weapons, but rather only talks about their use in "warfare"
   there is no stipulation in regard to what kind of penalties of punishments will be attached to nations who violate the protocol

   Once again, a class discussion or informal debate might be held about the actual value of this document. Was it a "step in the right direction," or basically just a symbolic gesture with no real teeth or meaning?

3. Along a similar vein, a discussion or debate could be centered on the provisions, etc. of either the Biological and Toxin Weapons Convention of 1975 or the Chemical Weapons Convention (CWC) and the Organization for the Prohibition of Chemical Weapons (OPCW)

Connections to the Chemistry Curriculum

While this article obviously has connections to organic structures, etc., the pure chemistry connections are probably not as strong as in many other *ChemMatters* articles. But if your course includes a significant societal content, such as is sometimes the case in the *ChemCom* curriculum, then this article could be a focal point for some very relevant and thoughtful discussions.

Suggestions for Student Projects

1. The article itself contains a brief timeline regarding the use of chemical warfare. In addition, the *Background Information* section of this Teacher's Guide adds several more examples of the use of chemical and biological agents. These listings, however, represent only a small fraction of the number of examples of both the use of chemical and biological weapons as well as the many cases where their use during a particular conflict was debated, but not realized. Students could prepare a more thorough report on this very controversial topic. Alternately, they could take one or two particular incidents and expand on them. What agents were debated or actually utilized? What arguments were presented to justify or condemn their use? For example, there is evidence that although they were never actually used, Churchill argued for the use of mustard gas against the population of Mesopotamia in 1920, and while there was only limited use of chemical agents by the Axis during WWII (see *Background Information*), such agents existed. Why weren't they used?

   Other possible topics include:

   Chemical warfare during the Cold War

   The "V" series of nerve agents, VE, VG, VM, and VX

   The development of binary weapons—weapons in which the weapon is only loaded with the precursors to the actual chemical agent and the chemical agent is only created just prior to the use of the weapon.

2. There have been several international efforts to draft documents dealing with chemical and biological warfare, such as the Geneva Protocol of 1925, the Biological and Toxin Weapons Convention of 1975 and the Chemical Weapons Convention. What do these documents really say? How strong are they in their prohibitions? What penalties are connected to noncompliance? How do these documents compare to each other? Investigating the actual content and real effect(s) that these documents have had and may

have on preventing the use of chemical and biological weapons could make for an excellent student report. See also *Demonstrations and Lessons*.

Anticipating Student Questions

Does mustard gas have anything to do with mustard?

No.

How deadly is mustard gas compared to more modern chemical weapons, such as nerve gases?

Mustard gas is less deadly than nerve gases and it would take a much larger quantity of mustard gas to kill the same number of people. On the other hand, mustard gas is capable of producing more lasting injuries if the person survives.

What is the antidote for mustard gas exposure?

There is no antidote. Symptoms are typically treated with antibiotics, painkillers, skin dressings and other therapies. In some cases eye operations, skin grafts or treatments for chronic respiratory conditions such as emphysema may be required.

Is there a preventive medicine that can be taken if there is a danger of exposure to mustard gas?

No.

Websites for Additional Information and Ideas

A very comprehensive site for all kinds of information about mustard gas, its properties, its effect, etc. is:

http://www.inchem.org/documents/pims/chemical/mustardg.htm

A good site for structural and other information on several kinds of chemical warfare agents:

http://groups.msn.com/CellNEWS/chemweapons.msnw

Some good Websites dealing with the historical use of chemical and biological weapons are:

http://www.fortworthgov.org/health/threats/bio_history1.asp

http://www.hq.usace.army.mil/history/NBC%20Warfare%20History.htm

http://dsc.discovery.com/anthology/spotlight/bioterror/history/history2.html

http://library.thinkquest.org/27393/dreamwvr/print/timeline.htm?tqskip1=1

http://www.lsic.ucla.edu/classes/mimg/robinson/micro12/m12webnotes/Biowarfare/warfare.html
To view actual newspaper stories printed at the time that chlorine gas was used during WWI, go to:

http://www.lsic.ucla.edu/classes/mimg/robinson/micro12/m12webnotes/Biowarfare/chlorgas.html