CHEMICAL WARFARE AGENTS TODAY

DR. DAVID NYAMAH; Dipl.-Chem.,Dr.rer.nat.
DEPARTMENT OF CHEMISTRY, UNIVERSITY OF SCIENCE & TECHNOLOGY, KUMASI.

ABSTRACT

On January 13, 1993, in Paris, 130 countries signed the Chemical Weapons Convention (CWC). The CWC will ban the development, production, acquisition, stockpiling, retention and direct or indirect transfer of Chemical Weapons (CW). It also prohibits the use or preparation for use of CW and the assistance, encouragement, or inducement of anyone else to engage in activities prohibited by the CWC. A chemical weapons system consists of several components. A chemical weapon carrier is usually required, e.g., an aircraft, in order to transport the ammunition to the target. CW ammunition, which may consist of a bomb or an artillery shell, contains the active chemical ingredient, the CW agent. About 70 different chemicals have been used or stockpiled as CW agents during the 20th century. Today, only a few of these are considered of interest owing to a number of demands that must be placed on a substance if it is to be of use as a CW agent. This paper gives a description of the major chemical warfare agents of interest today.

***KEYWORDS**: Chemical warfare agents, nerve agents, mustard agents, tear gases, hydrogen cyanide.*

INTRODUCTION

A United Nations report of 1968 defines chemical warfare agents as "....chemical substance, whether gaseous, liquid or solid, which might be employed because of their direct toxic effects on man, animals and plants ...". The Chemical Weapons Convention states that the term chemical weapons must cover not only toxic chemicals but also ammunition and equipment for their dispersal. Toxic chemicals are stated to be "...any chemical which, through its chemical effect on living processes, may cause death, temporary loss of performance, or permanent injury to people and animals". Plants are not mentioned in this context. However, it is expected that each signatory of the convention shall undertake not to use herbicides in warfare. A ban of this kind does not prevent herbicides being used for other purposes, e.g., in agriculture.

Toxins, i.e., poisons produced by living organisms and their synthetic equivalents, are classed as chemical warfare agents if they are used for military purposes. However, they have a special position since they are covered by the Biological and Toxin Weapon Convention of 1972. This convention bans the development, production and stockpiling of such substances not required for peaceful purposes. CW agents can be classified in many different ways. There are, for example, volatile substances, which mainly contaminate the air, or persistent substances, which are involatile and therefore mainly cover surface. CW agents mainly used against people may also be divided into lethal and incapacitating categories. A substance is classified as incapacitating if less than 1/100 of the lethal dose causes incapacitation, e.g., through nausea or visual problems. The limit between lethal and incapacitating substance is not absolute but refers to a statistical average. In comparison, it may be mentioned that the ratio for the nerve agents between the incapacitating and lethal dose is approximately 1/10. Chemical warfare agents are generally also classified according to their effect on the organism.

NERVE AGENTS

Among lethal CW agents, the nerve agents have had an entirely dominant role since the Second World War. Nerve agents acquired their name because they affect the transmission of nerve impulses in the nervous system. All nerve agents belong chemically to the group of organo-phosphorus compounds. They are stable and easily dispersed, highly toxic and have rapid effects both when absorbed through the skin and via respiration. Nerve agents can be manufactured by means of fairly simple chemical techniques. The raw materials are inexpensive and generally readily available.

In the early 1930's, German scientists observed that organo-phosphorus compounds could be poisonous. They produced a phosphorus compound with extremely high toxicity for the first time. This phosphorus compound, given the name tabun, was the first of the substances later referred to as nerve agents. A factory for production of the new CW agent was built and a total of 12,000 tonnes of tabun were produced during the years 1942 - 1945. Up to the end of the war, the Germans synthesized about 2,000

Dr. David Nyamah

new organo-phosphorus compounds, including sarin (1938). The third of the "classic" nerve agents, soman, was first produced in 1944. These three nerve agents are known as G-agents in the American nomenclature.

After the war, research was mainly concentrated on studies of the mechanisms of the nerve agents in order to discover more effective forms of protection against these new CW agents. The results of these efforts led, however, not only to better forms of protection but also to new types of agents closely related to the earlier ones. By the mid-1950's a group of more stable nerve agents had been developed, known as the V-agents in the American nomenclature. They are approximately ten-fold more poisonous than sarin and are thus among the most toxic substances ever synthesized. In the United States, the choice fell in 1958 on a substance known by its code name VX as suitable as a CW agent of the persistent type. Full-scale production of VX started in April 1961 but its structure was not published until 1972.

Physical and Chemical Properties

The most important nerve agents included in modern CW arsenals are:

1. Tabun, ethyl N,N-dimethylphosphoramidocyanidate, with the American denomination GA. This nerve agent is the easiest to manufacture. Consequently, it is more likely that developing countries start their CW arsenal with this nerve agent whereas industrialized countries consider tabun to be out-of-date and of limited use.

2. Sarin, isopropyl methylphosphonofluoridate, with the American denomination GB, a volatile substance mainly taken up through inhalation.

3. Soman, pinacolyl methylphosphonofluoridate, with the American denomination GD, a moderately volatile substance which can be taken up by inhalation or skin contact.

4. Cyclohexyl methylphosphonofluoridate, with the American denomination GF, a substance with low volatility which is taken up through skin contact and inhalation of the substance either as a gas or aerosol.

5. O-ethyl S-diisopropylaminoethyl methylphosphonothiolate, better known under the American denomination VX, a persistent substance which can remain on material, equipment and terrain for long periods. Uptake is mainly through the skin but also through inhalation of the substance as a gas or aerosol. The general formula for the nerve agents (see Table 1) is:

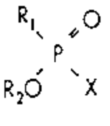


Table 1: Chemical Formula of Some Nerve Agents

Nerve agent	X	R_1	R_2
Tabun GA	-CN	$-N(CH_3)_2$	$-C_2H_5$
Sarin GB	-F	$-CH_3$	$-CH(CH_3)_2$
Soman GD	-F	$-CH_3$	$-CH(CH_3)C(CH_3)_3$
GF	-F	$-CH_3$	-cyclo-C_6H_{11}
VX	$-SCH_2CH_2N(CH(CH_3)_2)_2$	$-CH_3$	$-C_2H_5$

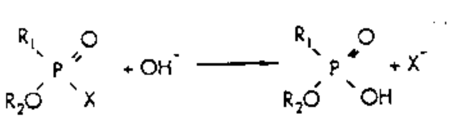
The same type of phosphorus compounds are used as, for example, insecticides. In the structure of insecticides P = O has generally been replaced by P = S and X consists of a less reactive group than in nerve agents.

All nerve agents in pure state are colourless liquids. Their volatility varies widely (Table 2). The consistency of VX may be likened to an involatile oil and is therefore classified as belonging to the group of persistent CW agents. Its effect is mainly through direct contact with the skin. Sarin is at the opposite extreme, being an easily volatile liquid (comparable with, e.g., water), and mainly taken up through the respiratory organs. The volatilities of soman, tabun and GF are between those of sarin and VX. By addition of a thickener it is possible for, e.g., soman, to be transferred from the category of volatile CW agents to the persistent agents. Sarin is very soluble in water whereas other nerve agents are sparingly soluble. VX has the unexpected property of being soluble in cold water but sparingly soluble in warm water (> 9.5°C).

Table 2: Physical Properties of Some Nerve Agents

	Tabun	Sarin	Soman	GF	VX
Molecular weight	162.1	140.1	182.2	180.2	267.4
Density, g/cm^3*	1.073	1.089	1.022	1.120	1.008
Boiling point, °C	247	147	167	92**	300
Melting point, °C	-50	-56	-42	<-30	-39
Vapour pres. mm Hg*	0.07	2.9	0.3	0.06	0.0007
Volatility, mg/m^3*	600	17,000	3,900	600	10
Solubility in water, %*	10	∞	2	2	3 (∞<9.5°C)
* = at 25 °C ** = at 10 mm Hg					

The most important chemical reactions of nerve agents take place directly at the phosphorus atom. The P - X bond is easily broken by nucleophilic reagents such as water or hydroxyl ions (alkali). In aqueous solution at neutral pH the nerve agents decompose slowly whereas the reaction is greatly accelerated following the addition of alkali. The result is a non-toxic phosphoric acid:



The formation of the non-toxic phosphoric acid is also accelerated by rise in temperature or by a catalyst (e.g., hypochlorite ions from bleaching powder). This hydrolysis forms the basis of most decontamination procedures utilizing decomposition. In general, it may be assumed that an area exposed to G-agents decontaminates itself within a few days. However, V-agents may remain on the ground for several weeks because of their greater stability with respect to water and their much lower volatility. At pH-levels between 7 and 10 large quantities of VX are transformed into an extremely non-volatile product of hydrolysis which is incapable of penetrating skin. The product is less toxic than VX but still there is a risk during decontamination.

The nucleophilic attack on the phosphorus atom also forms the basis of different types of colour reactions used in detecting nerve agents.

Binary Technology

In December 1989, the U. S. A. started to produce a completely new type of chemical ammunition. In this ammunition the nerve agent is generated by means of binary technology.

The chemical ammunition available hitherto can be described as unitary, which implies that it contains one active ready-to-use CW agent. Binary technology implies that the final stage in the synthesis of the nerve agent is moved from the factory into the warhead, which thus functions as a chemical reactor. Two initial substances which are stored in separate containers are mixed and allowed to react and form the nerve agent when the ammunition (bomb, projectile, grenade, etc.) is on its way towards the target. Until the actual moment of use, the ammunition contains only relatively non-toxic initial substances. It is therefore considered to be safer to manufacture, store, transport and, finally, destroy.

Binary components (precursors) for the three most common nerve agents (American code names are given in brackets) are the following:

Sarin (GB-2): methylphosphonyldifluoride (DF) + isopropanol. The isopropanol is included in a mixture (OPA) with isopropylamine which binds the hydrogen fluoride generated.

Soman (GD-2): methylphosphonyldifluoride (DF) + pinacolylalcohol.

VX - 2: O-ethyl O-2-diisopropylaminoethyl methylphosphonite (QL) + sulphur.

The production of binary weapons in the U. S. A. was terminated in 1990 as a result of negotiations with the former Soviet Union on an agreement on the destruction of large parts of CW stockpiles on both sides. However, the agreement did not include research and development of binary weapons

MUSTARD AGENTS

Mustard agents are usually classified as "blistering agents" owing to the similarity of the wounds caused by these substances resembling burns and blisters. However, since mustard agents also cause severe damage to the eyes, respiratory system and internal organs, they should preferably be described as "blistering and tissue-injuring agents". Normal mustard agent, bis-(2-chloroethyl)sulphide, reacts with a large number of biological molecules. The effect of mustard agent is delayed and the first symptoms do not occur until between 2 - 24 hours after exposure.

Mustard agent was produced for the first time in 1822 but its harmful effects were not discovered until 1860. Mustard agent was first used as a CW agent during the latter part of the First World War and caused lung and eye injuries to a very large number of soldiers. Many of them still suffered pain 30 - 40 years after they had been exposed, mainly as a result of injuries to the eyes and chronic respiratory disorders.

Towards the end of the Second World War a large number of soldiers and sailors were injured during a German attack on the Italian port of Bari. A cargoship loaded with mustard agent ammunition was hit and large amounts of mustard agent became mixed with the water. The victims swam around in the contaminated water but it was not realized until too late that a large number of people had been injured by mustard agent. The Bari incident served as a macabre illustration of the delayed effect of mustard agent.

During the war between Iran and Iraq in 1979 - 1988, Iraq used large quantities of chemical agents. About 5,000 Iranian soldiers have been reported killed, 10 - 20 per cent by mustard agent. In addition, there were 40,000 to 50,000 injured. A typical result of warfare with mustard agent is that the medical system is loaded with numerous injured who require long and demanding care.

Mustard agent is very simple to manufacture and can therefore be a "first choice" when a country decides to build up a capacity for chemical warfare.

Apart from mustard agent, there are also several other closely related compounds which have been considered as chemical weapons. During the 1930's, several reports were published on the synthesis of nitrogen mustard agent and its remarkable blistering effect. The mechanism of action and symptoms largely agree with those described for mustard agent. Germans and Americans started the military production of nitrogen mustard in 1941 and 1943, respectively, whereas the development in England was abandoned following an explosion. There is no verified use of nitrogen mustard agents as chemical weapons and their usefulness is restricted by these types of agents being unsuitable for storage.

Physical and Chemical Properties

In its pure state, mustard agent is colourless and almost odourless. The name was given to mustard agent as a result of an earlier production method which yielded an impure mustard-smelling product. Mustard agent is also claimed to have a characteristic smell similar to rotten onions. However, the sense of smell is dulled after only a few breaths so that the smell can no longer be distinguished. In addition, mustard agent can cause injury to the respiratory system in concentrations which are so low that the human sense of smell cannot distinguish them.

At room temperature, mustard agent is a liquid with low volatility and is very stable during storage. The melting-point for pure mustard agent is 14.4°C. In order to be able to effectively use mustard agent at lower temperatures, it has been mixed with lewisite in some types of ammunition in a ratio of 2 : 3. This mixture has a freezing-point of -26°C. During the Second World War, a form of mustard agent with high viscosity was manufactured by means of the addition of a polymer. This is the first known example of a thickened CW agent.

Mustard agent can easily be dissolved in most organic solvents but has negligible solubility in water. In aqueous solutions, mustard agent decomposes into non-poisonous products by means of hydrolysis. This reaction is catalyzed by alkali. However, only dissolved mustard agent reacts, which means that the decomposition proceeds very slowly. Bleaching-powder and chloramines, however, react violently with mustard agent, whereupon non-poisonous oxidation products are formed. Consequently, these substances are used for the decontamination of mustard agent.

The structural formulae for mustard agent and nitrogen mustard agent are as follows:

mustard agent: $S(CH_2CH_2Cl)_2$
Nitrogen mustard agent (HN3): $N(CH_2CH_2Cl)_3$

HYDROGEN CYANIDE

Hydrogen cyanide is usually included among the CW agents because of its ability to cause general poisoning. There is no confirmed information on this substance being used in chemical warfare. However, it has been reported that hydrogen cyanide was used by Iraq in the war against Iran and against the Kurds in northern Iraq during the 1980's. Hydrogen cyanide has high toxicity and in sufficient concentrations it rapidly leads to death (Table 3). During the Second World War, a form of hydrogen cyanide (Zyklon B) was used in the Nazi gas chambers.

Table 3: Relationship betwen concentration and effects when inhaling hydrogen cyanide

Concentration (mg/m^3)	Effect
300	Immediately lethal
200	Lethal after 10 minutes
150	Lethal after 30 minutes
120 - 150	Highly dangerous (fatal) after 30-60 min.
50 - 60	Endurable for 20 min. - 1h without effect
20 - 40	Light symptoms after several hours

At room temperature, hydrogen cyanide is a colourless liquid which boils at 26°C. The most important route of poisoning is through inhalation. Both gaseous and liquid hydrogen cyanide, as well as cyanide salts in solution, can also be taken up through the skin. Its high volatility probably makes hydrogen cyanide difficult to use in warfare since there are problems in achieving sufficient high concentrations outdoors. On the other hand, the concentration of hydrogen cyanide may rapidly reach lethal levels if it is released in confined spaces.

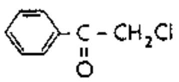
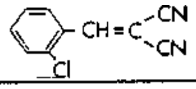
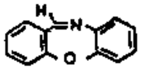
TEAR GASES

Tear gas is the common name for substances which, in low concentrations, cause pain in the eyes, flow of tears and difficulty in keeping the eyes open. Tear gases are used mainly in military exercises and in riot control, etc., but have also been used as CW agents. Irritating gases have been used in war since ancient times but it was not until after the Second World War that a more systematic search for effective substances was started.

Among a long series of substances, three have become of greater importance than the others. They are effective and cause low risks when used. These substances are chloroacetophenone (codename CN), ortho-chlorobenzylidene-malononitrile (codename CS) and dibenz(b,f)-1,4-oxazepine (codename CR) (see Table 4). CN was formerly the most widely used tear gas. Today, CS has largely replaced CN and is probably the most widely used tear gas internationally. CR is used only to a minor extent.

At room temperature, these tear gases are white solid substances. They are stable when heated and have low vapour pressure. Consequently, they are generally dispersed as aerosols. All of them have low solubility in water but can be dissolved in several organic solvents. Hydrolysis of CN is very slow in water solution, also when alkali is added. CS is rapidly hydrolyzed in water solution (half-life at pH 7 is about 15 min. at room temperature) and extremely rapid when alkali is added (half-life at pH 9 is

Table 4: Chemical formulae for the three most common tear gases

Code-name	CN	CS	CR
Chemical name	Chloroaceto phenone	Orto-chlorobenzyl-idene-malononitrile	Dibens(b,f)-1,4-oxazepine
Chemical formula			

about 1 min.). CR is hydrolyzed only to a negligible extent in water solution. CN and CR are, thus, difficult to decompose under practical conditions, whereas CS can easily be inactivated by means of a water solution. Skin is suitably decontaminated by thorough washing with soap and water. CS is then decomposed whereas CN and CR are only removed. Decontamination of material after contamination with CS can be done with a 5 - 10% soda solution or 2% alkaline solution. If this type of decontamination cannot be accomplished (e.g., contaminated rooms and furniture), then the only other means is by intensive air exchange - preferably with hot air.

In contrast to human beings, animals generally have low sensitivity to tear gases. Dogs and horses can therefore be used by police for riot control even when tear gas is used.

ARSINES

Among the arsenal of chemical weapons can be found mustard agent mixed with lewisite which is an aliphatic arsenic compound, 2-chlorovinyldichloroarsine. Pure lewisite is a colourless liquid. Solubility in water is approximately the same as for mustard agent. Injuries caused by lewisite are similar to those caused by mustard agent. However, the mechanism of action for lewisite is different. From the diagnostic viewpoint, an important difference is that symptoms in lewisite poisoning are not delayed and the irritation effect occurs immediately.

Other arsenic-containing substances have also been of interest as CW agents. One example is adamsite, 10-chloro-5,10-dihydrophenarsazine, which is a nasal and throat-irritating powder.

PSYCHOTOMIMETIC AGENTS

This group of agents usually includes substances which, when administered in low doses (< 10 mg/m^3) cause conditions similar to psychotic disorders or other symptoms emanating from the central nervous system (loss of feeling, paralysis, rigidity, etc.). The effects are transitory and cause inability to make decisions and incapacitation. Several such substances may be used to achieve these objectives and only a few examples are given here.

During the 1950's, studies were made of substances such as glycolic acid esters (glycolates). Particular interest was paid to 3- quinuclidinylbenzilate, BZ. BZ causes poisoning at doses of 0.5 - 5 mg. Peripheral symptoms such as distended pupils, deteriorated short-distance vision, dry mouth and palpitations occur after about 30 minutes. A serious effect of poisoning with BZ is an increased body temperature. Deterioration in the level of consciousness, hallucinations and coma occur subsequently.

Incapacitating after-effects may remain 1 - 3 weeks after the poisoning. Since the effect of glycolates was found to be difficult to predict, interest in continued research into this type of substance gradually decreased.

HERBICIDES

In military contexts, herbicides have been used for two purposes: to disrupt food supplies by destroying crops and to defoliate vegetation in order to complicate the enemy's means of protecting himself or to provide a clear field of fire.

A number of commercial herbicides can be used in military connection. Phenoxy acids is a collective name for a group of defoliating herbicides which were used in, e.g., the Vietnam War. They are similar to the growth hormone of plants and kill them by initiating uncontrollable growth.

More recent types of herbicides are triazines and sulphonylurea. Triazines work through inhibiting the photosynthesis.

Herbicides usually have a relatively low acute toxicity to animals and humans.

TOXINS

Toxins are effective and specific poisons produced by living organisms. They usually consist of an amino acid chain which can vary in molecular weight between a couple of hundred (peptides) and one hundred thousand (proteins). They may also be low-molecular weight organic compounds. Toxins are produced by numerous organisms, e.g., bacteria, fungi, algae and plants. Many of them are extremely poisonous, with a toxicity that is several orders of magnitude greater than the nerve agents.

Toxins started to attract military interest already during the first half of the present century. At that time, it was difficult to manufacture sufficient large amounts of toxins which caused interest to decrease. In the late 1970's, there was a rapid development of gene technology together with biotechnology. This led to the threat from toxins as CW agents again arising. Now it became possible to produce greater amounts of many toxins more easily, in some cases even synthetically.

Toxins are still considered to be less suitable for dispersal on a large scale. Nonetheless, they could be used for sabotage or in especially designed inputs, e.g., against key persons. Since toxins have low volatility, they are dispersed as aerosols and then taken up foremost through inhalation. The new microencapsulation technology, which is easy to use, makes it possible to protect unstable toxins when dispersed.

Most toxins are unstable in alkaline water solutions and are thus easily destroyed by means of normal decontamination methods.

A few examples of toxins which may be used as chemical warfare agents are listed below. The trichothecenes, mycotoxins obtained from, e.g., Fusarium species, were alleged in the early 1980's to have been used as CW agents in Southeast Asia ("yellow rain"), but are of no military value today.

Bacterial Toxins

Botulinum toxin, produced by the bacteria *clostridium botulinum*, is the most poisonous substance known. The bacteria grows on, e.g., poorly preserved food and causes a severe form of food-poisoning (botulism). The toxin is a protein available in seven different forms, where the most poisonous is type A (molecular weight = 150,000 D). The lethal dose to man has been estimated to about one microgram if ingested and even less if inhaled.

Not all toxins have a lethal outcome. One of those classified in the incapacitating group is staphylococcus enterotoxin type B (SEB), which is produced by *staphylococcus aureus* bacteria. SEB is the toxin which is most commonly found to have caused food poisoning.

Many toxins are produced by marine organisms. One such example is saxotoxin, which is synthesized by a type of blue-green algae (cyanobacteria). These algae provide food for different shellfish, e.g., mussels. The mussels themselves are not influenced by the poison, but human beings who later eat the mussels may become seriously ill. Saxitoxin attacks the nervous system and has a paralyzing effect, but causes no symptoms in the gastrointestinal tract. The development of the illness is extremely rapid and at high doses death may occur within less than 15 minutes. Saxitoxin is a small molecule with a molecular weight of 370 D. It is not sensitive to heat but is destroyed by oxygen.

Plant Toxins

The seeds of the castor oil plant can be used to extract a mixture of poisonous proteins, ricin. One of these has also been produced by *Escherichia* coli bacteria to which the ricin gene has been transferred.

Ricin became of interest as a CW agent at an early stage as it is relatively easy to produce in large quantities. In 1978, it was used in the "umbrella murder" in London where a ricin-treated bullet was used to shoot a Bulgarian defector who died within a day. Ricin has approximately the same toxicity as saxitoxin.

POTENTIAL CW AGENTS

Development of new types of CW agents is probably restricted to highly industrialized states. One category of substances which may become of particular importance is based on biotechnology. The borderline between BW and CW agents has started to lose importance as a result of the rapid development in biotechnology. Biotechnology has enabled the large scale production of new types of substances. Toxic compounds of natural origin which were earlier difficult to produce, e.g., toxins and bioregulators, can now be produced in large quantities. Many of these substances exceed the toxicity of nerve agents by several orders of magnitude.

Biotechnology has also offered opportunity to produce bacteria, viruses, etc., in modified form. The gene material of microorganisms can be modified so that new bacteria or viruses are created, against which man has no immune defence. In addition, the bacteria can be changed so that they themselves can produce toxins while they multiply in the body. In comparison with pure toxin, only a very small dose of bacteria is then needed to achieve full effect.

There are large opportunities to further develop weapons based on biotechnology. After studies of structure-activity relationships for certain toxins and substances produced within the body, it is possible to develop modified and even more active substances. Improved knowledge of receptors on the cell surface, for example as a result of cancer research, will make it possible to target toxic substances to selected organs.

Weapons based on biotechnology today are probably still within the research or developmental stages. In the long-term, they may become a serious threat. Factors supporting this are that such substances:

- are active in very low concentrations,
- can cause poisoning which is difficult to diagnose and treat,
- can be completely broken down within the body,
- usually lack antidotes for medical protection and treatment,
- are difficult to detect in the environment.

Factors suggesting that their use may not arise are:

- their range of use is limited, e.g., to sabotage,
- suitable substances are rapidly broken down by the enzyme system in the gastro-intestinal tract and lungs,
- exposure via the airways can probably easily be stopped by use of respiratory protective equipment.

CONCLUSION

Chemical Weapons are almost as old as war itself. There is evidence that poisonous substances were used in warfare during antiquity. However, it was not until the First

World War that chemical weapons were first used on a large scale. Subsequently, chemical research and technology have created CW agents for use in many different weapon systems and which have become fully integrated components of security policy doctrines and military tactics.

Negotiations have been concluded to ban totally chemical weapons. However, several important technical questions still remain to be solved. The most important deals with how verification can be made that a ban is being respected, e.g., inspections by independent control groups. Destruction of the vast quantities of CW agents stored in the U. S. A. and Russia involve major problems and will require at least ten years to complete.

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