

A SHORT REVIEW OF THE TECHNOLOGIES FOR DESTRUCTION OF CHEMICAL WEAPONS

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ABSTRACT— *About 13% of the world's declared chemical agents are under process of destruction and 35 % or approximately 3 millions different type of munitions must be destroyed. The aim of this paper is to compare the different destruction technologies with the incineration (which is called baseline technology). It will cover the following: a) the principles of these alternatives; b) the possible applications; c) advantages and disadvantages. It will be worthwhile to say, though, this paper is not comprehensive. The major sources of this paper are open publications, Internet access.*

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Incineration technology has been adopted to destroy the Chemical weapons stockpile in the USA since the early 90s. However, this destruction method has been opposed since its start among many citizens or groups. In order to response to the public concern and the USA congress's request to demonstrate different destruction technologies, the army was tasked to test alternative technologies rather than the accepted baseline incineration.

The neutralization technology of chemical agents was tested at least in two destitution plants in the USA. In Russia, using ethanolamine tested the neutralization technology even earlier, though there have not been industry-scale operations due to economic reasons. A quite new technology called "silver II" was reported in the United Kingdom during the treatment of nuclear waste. Other technologies such as super critical water oxidation (SCWO), biodegradation, plasma arch, catalytic extraction process (CEP), and so on were widely discussed after Chemical Weapons convention entered in to force in the end of April 1997.

In order to achieve the complete destruction of chemical weapons, a technology package (a combination of several different destruction technologies) might be used.

For the chemical agent destruction, destruction technologies can be divided into three categories based on the operating temperatures [4]: low (0-200°C); medium (200-600°C); and high temperature (600-3500°C)

Based on the characteristics of the operation itself, the destruction technologies can be divided into the following categories: chemical methods such as neutralization or oxidation; biochemical methods; electrochemical method; pylorysis; etc.

Low temperature technologies include chemical detoxification (including neutralization), biodegradation, electrochemical oxidation, etc. Medium temperature technologies include wet air oxidation (WAO). supercritical water oxidation (SCWO); High temperature destruction technologies include plasma arc process, molten metal pyrolysis, hydro cracking process, catalytic fluidized-bed oxidation, molten salt oxidation, catalytic oxidation, etc.

As to the demilitarization of the chemical munitions, three technologies have been tested: a) baseline's disassembling technology; b) drilling, cutting (including high-pressure fluid jet cutting) and punching; c) cryofracture.

As to the chemical agents, who have been weaponized, a demilitarization technology is needed to first extract the agent from the chemical weapons before further treatment.

Although it is possible to completely destroy chemical weapons by one technology, a combination of different technologies may reach the best result of destruction given the reason that each and every technology has its own advantages and disadvantages.

1. Neutralization as a method for the destruction of chemical agents

The neutralization is a hydrolysis of chemical agents. The reaction of GB (Sarin, CAS:107-44-8), O-Isopropyl- methyl-phosphono-fluoridate, $\text{CH}_3\text{P}(\text{O})(\text{OC}_3\text{H}_7)\text{F}$ with aqueous NaOH solution is as follows:



It is reported that a small amount of catalyst ortho-iodosbenzoate salts can be used to accelerate reactions of structural analogs of GB with sodium hydroxide and only a small amount of excess NaOH can be used to balance the above equation [3, p. 112]. The products from the hydrolysis are only slightly hazardous and are suitable for shipment, storage, or further processing.

HD, Mustard gas, (Ipreet, mustard), Bis(2-chloroethyl)sulfide, $\text{S}(\text{CH}_2\text{CH}_2\text{Cl})_2$ can be neutralized with alkali in water very rapidly.



However the very low solubility of HD in water hampers the process. The inclusion of thickeners and the formation of gels and solid deposits during long storage also cause problem for the process. In order to increase the speed of this reaction, the HD agent particle size must first be reduced to $1\mu\text{m}$ in diameter so that a large surface area can be formed.

VX (O-Ethyl-S-2-diisopropylaminoethyl methyl phosphonothiolate), reacts with NaOH in water, but the resulting products are nearly as same toxic as VX. By adding hydrogen peroxide to aqueous NaOH, much low toxic product will be formed.

Neutralization can also occur in alcohol with alkali. The process is said to be suitable for the destruction of GB and HD. For VX there is some doubt of the forming of a new highly toxic chemical [3, p. 113].

GB can also react with ethanolamine to form products of lower toxicity, which are suitable for storage and further treatment. This method has been used in Russia.

Advantages and disadvantages of neutralization technology can be operated at low temperature (room temperature to 100°C) and atmospheric pressure. The processes are relatively simple and can be operated in batch mode. Applications of the methods:

Neutralization/biotreatment technology as the destruction technology for mustard, $\text{S}(\text{CH}_2\text{CH}_2\text{Cl})_2$ stockpile.

There are three major steps in this process [7]:

Step I - Steel containers are transferred from the Chemical Agent Storage Facility to the chemical demilitarization building. Each steel ton container is emptied by mechanically

punching two holes in the top section of the container. The liquid mustard agent is pumped out to an agent holding tank. The container is then cut in half and sprayed to bare metal with high-pressure hot water. The ton containers that store the agents also require extensive processing to ensure that any remaining chemical agent is destroyed. The ton container cleaning process is outlined below [6].

Step 2 - Liquid mustard agent from the agent-holding tank is fed into a tank containing hot water. Neutralization is performed by vigorously mixing the mustard agent and hot water, measuring 90° C. The mustard agent reacts with water to form a biodegradable liquid byproduct -hydrolysate.

Step 3 - During biotreatment, the hydrolysate is added to a mixture of ordinary sewage treatment bacteria. During the biotreatment process, the bacteria "digest" the thiodiglycol to form carbon dioxide and wet solids. The carbon dioxide is released into the atmosphere through carbon filters. The water from the solids is extracted and is non-toxic enough to be treated at the APG wastewater treatment facility. The dried solids are disposed of in a permitted landfill.

Neutralization followed by SCWO (Supercritical Water Oxidation) was chosen as the destruction technology for VX stored at the storage facility [5]. It begins by mechanically punching the thick walled steel ton containers and draining the VX. The drained containers will be cut in half and sprayed to bare metal with high-pressure hot water. After cleaning and agent free confirmation the containers will be shipped off-site to a steel recycling facility. The VX will be added to a neutralization reactor containing water and sodium hydroxide. The chemical reaction that occurs in the reactor destroys the VX and produces a liquid by-product called hydrolysate. The hydrolysate in the neutralization reactor will be pumped to a second reactor for further processing and agent-free confirmation before being sent to the SCWO unit. In the SCWO unit the total organic carbon content of the hydrolysate will be destroyed with greater than 99% destruction and removal efficiency.

2. Supercritical Water Oxidation (SCWO)

The principles of Supercritical Water Oxidation (SCWO), also known as Hydrothermal Oxidation, destroys toxic and hazardous organic wastes using an oxidant in water at temperatures and pressures above the critical point of water, 374°C and 218 at. At these conditions, the fluid properties of water change dramatically and organic materials and gases become highly soluble in water. Inorganic salts become completely insoluble under supercritical conditions. In SCWO process, dissolved organics, oxygen (or other oxidants), and water are reacted above the critical temperature and pressure of water.

The major advantages of the SCWO technology are as follows:

- Some troublesome components found in incineration process such as NO_x, dioxins are not found to be in the gas effluent;
- Oxygen is to be used instead of air, thus the volume of discharge gas is greatly reduced, and actually it can reduce theoretically to zero when CO₂ is removed as carbonate. The whole system can be treated as a closed system with no discharge of products until the analyses are complete;
- Up to 20% organic waste solution is particularly well suited for SCWO, therefore the process can be used to treat products from a prior aqueous treatment such as

neutralization.

Disadvantages of this technology are as follows:

- The formation of strong corrosive compounds during the reaction and the high-pressure condition requires that the reactor be specially designed and special construction material be used.
- Plugging problem will be another concern due to salt precipitation when discharge the products.

3. Silver II technology

The principle of this technology is based on the highly oxidizing nature of Silver (II) in a nitric acid solution. Ag (II) is one of the strongest oxidizing agents known: nitric acid also makes a great contribution to the oxidizing process. Normally the Silver II process is carried out at 90°C and at 8.0 M HNO₃, [2, p.39].

Silver (II) can oxidize all elements to their oxidation state if allowed to reach equilibrium. The anode reactions of Ag (II) for the normal chemical agents are as follows:

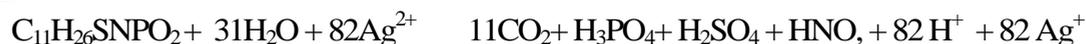
GB (Sarin):



HD (Mustard):



VX:



Silver II can also easily oxidize energetic materials; Actually Silver II can oxidize all elements to their highest oxidation state if allowed to reach equilibrium:



Silver (II) technology can be applied to destroy chemical agents on a standard industrial electrochemical cell.

Advantages of this technology are as follows:

- Because of the strong oxidizing capability of Ag (II), a wide range of organic chemicals can be completely treated;
- It can operate at very mild conditions as low temperature (90°C) and ambient atmosphere;
- Chlorinated dioxins won't be formed in this process. They can be formed in other technologies where the temperature reaches 180-400°C and where chlorine and hydrocarbons are present.[3, p.85];
- When the reaction is complete the final product (CO₂, CO, NO_x, etc.) are easy to deal with and little solid waste formed.

Disadvantage silver (II) technology are as follows:

- When treating mustard, AgCl (insoluble) will be formed and may precipitate out, which means more silver will be consumed to treat mustard;
- The silver (II) oxidized solution leaving the cell contains the mediating metal and

need separation and recycling;

- The strong oxidizing property of silver (II) makes it impossible to use a normal construction material, which is not glass lined or noble metal, coated;
- There exists a mechanical complexity which need to break material particles to a very small size so that they can be easily dissolved in nitric acid.

4. Catalytic Extraction Process Technology

The Catalytic Extraction Process (CEP) is conducted mainly within a molten metal bath at high temperature (1650°C) and low oxygen potential. In this process [2, p.26], CW feed material is injected into the molten metal bath along with oxygen and methane; the molecular entities in the feed material are decomposed by catalysis into their component elements. These elements dissolve in the metal and form intermediates by bonding chemically with the metal. Since this process is carried out at low oxygen potential and decomposes feed molecules to elements regardless of their starting molecular structure, the process provides neither pathways nor precursors for the formation of oxides of nitrogen or sulfur or the formation of dioxins and furans.

The technology has been well used in the steel industry. It has the potential to treat a variety of chemicals that can be in various physical forms. As to the destruction of chemical agents, more test and more careful designs have to be done. Experience in the steel industry primarily relate to the injection of gases for the purpose of changing the composition of the bath and a little escape of the gases from the bath causes no much concern rather than an economic loss. As to the CW agent, a complete reaction of injected gases with the bath must be achieved because of the residual level requirement of CW destruction.

5. Plasma arch technology

The principle electric arcs and discharges involve high-temperature, conductive gases (plasmas). Typically, an arc can be established between two conducting electrodes (e.g., graphite or metal) in a variety of atmospheres. The plasma is composed of molecules, atoms, ions, and electrons at temperatures of 1000°C to 20000°C depending on the current and voltage, the gaseous environment, and the pressure of the constricting gas.

Advantages of this technology are as follows:

- The startup and shutdown time is relatively short;
- The destruction time is pretty short and the system can be a closed one so that the waste gas can be released when the analysis satisfied;

Disadvantages of this technology are as follows:

- Non homogeneous temperature distributions, gas turbulence, and incomplete mixing may limit the absoluteness of the process [1, p.79].;
- Cooling water circulated through the plasma torch (to keep it from melting) is a potential danger to the downstream gas handling system, which can even lead to explosion in serious leak [1, p.82].
- Labor requirement is relatively high since it need frequently change the electrode [3, p. 160]

Though the technology has some industry applications, it has never been dealt with CW munitions therefore need more sophisticated research.

6. Gas-Phase Chemical Reduction Technology

The principle Gas-Phase Chemical Reduction (GPCR) Process is a patented technology developed by ECO LOGIC, Inc., of Rockwood, Ontario. The process uses hydrogen and steam at elevated temperatures (up to 850°C) and nominally atmospheric pressure to transform organic compounds into simpler substances which are either less toxic or convertible to less toxic materials such as methane, hydrogen chloride, and minor amounts of low molecular mass hydrocarbons. The chemistry by which GPCR destroys organic feed material is very complicated especially for chemical agents [1, p 102]. HD and VX contain a high proportion of heteroatoms (such as chlorine, phosphorus, sulphur, or nitrogen). The reaction products containing these heteroatoms will generate a large volume of inorganic process residuals.

Advantages are as follows:

- Mature technology especially for the treatment of chlorinated hydrocarbons in various matrices, operating commercially at sites worldwide;
- Closed-loop, therefore no uncontrolled emissions;
- Ability to hold and test all process outputs prior to reuse in system or off site disposal;
- Can process material in a variety of matrices including liquids, solids and soil.

Disadvantage:

- Elemental carbon (formed as soot) and high-carbon-content precursors such as aromatics and polycyclic organic compounds have to be dealt with in the downstream system;
- As a continuous process rather than a batch operation, the entire system (consists of a number of sequential operations) must be tightly integrated and controlled. Much more stringent safety requirement is needed.

7. Biochemical method for the destruction of CW agents

Study shows that many enzyme systems and some microbial cultures are able to hydrolyze nerve agents, particularly the P-F bond in GB and other G agents. There has been less study of V agents, but the organophosphorus hydrolase (OPH) enzyme cleaves the P-S bond to produce thiol and alkyl methylphosphonate derivatives. For HD, direct biodegradation is not possible because the agents deactivate both enzymes and cellular systems through alkylation of critical proteins and nucleic acids. On the other hand, thiodiglycol (TDG), the hydrolysis product from mustard agent is very susceptible to biological oxidation. Consequently, an integrated neutralization-biodegradation appears promising for mustard agent [4, p. 130]. As to the VX case, biodegradation of VX hydrolysate is not so well studied and the test is not so satisfied.

8. Cryofracture technology

General Atomics (GA) developed this technology. The principle is based on the property change of metal when it is cooled to liquid Ni temperature (-273°C). At such a low temperature, its structure becomes very brittle and easy to press to pieces. The robotics and hydraulic press are similar to hundreds used throughout industry. Based on this theory, the technology can dispose of every type of chemical munitions in the U.S. stockpile and most non-

U.S. types as well. After the cryofracture, the agents and energetics are taken out for further treatment by either 1) incineration in a modern rotary kiln with a state-of-the-art pollution abatement system or 2) an alternative destruction process such as neutralization followed by supercritical water oxidation.

9. Solvated Electron Technology (SET)

In general, the solvated electrons are attracted to the polar bond between carbon and a more electronegative species, such as chlorine, fluorine, phosphorous, sulphur, or oxygen. The result is cleavage of the covalent bond and release a gaseous alkane or alkene [1, p. 137],

The reaction of HD with SET solution is cleavage of the carbon-chlorine bond by a solvated electron to form sodium chloride. The initial reaction of GB in SET process via cleavage of the phosphorous-fluorine bond by an electron to form sodium fluoride. Unlike HD and GB, VX molecule does not have a strongly polar bond for the SET electron to attack. The possible initial reactions may be the cleavage of P-S bond, S-C bond or at both simultaneously.

SET solution can also react with the energetics; the reaction time is longer compared with chemical agents.

Conclusions

General conclusions can be made as following:

As each alternative destruction technology has its own advantages and disadvantages, a selection of an appropriate technology or technology package (consists of different technologies) can be made based on a series of factors, which may include:

- The type of the munitions (bulk containers or assembled munitions);
- CWC requirements such as time limit and irreversibility;
- Stability, reliability, robustness and maturity of the technology process;
- Environmental burden, safety and health effects of the technology;
- Economic concern, public acceptance to the technology, etc.

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