

ALTERNATIVE DETOXIFICATION TECHNOLOGIES FOR CHEMICAL WEAPONS

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INTRODUCTION

Biological and chemical weapons have a long history. Two thousand years ago the Greeks and Romans used human and animal corpses to poison wells. In mediaeval times, corpses of plague victims were thrown over the walls of besieged cities. The British distributed blankets infected with smallpox to native North Americans. In modern times, research into tularemia, brucellosis anthrax and yellow fever, together with agents of plant diseases resulted in large stockpiles of biological weapons. These weapons were the subject of the 1972 Biological Weapons Convention and the US stockpile was destroyed between 1971-1972 (Murphy *et al.* 1984). Nonetheless, as pointed out by Wright (1990) military involvement in genetic engineering and biotechnology increased through the 1980's, raising concerns about the future integrity of the Convention.

The development of biological and chemical weapons has always been closely associated. The 1914-18 conflict in Europe led to the first large scale testing of chemical weapons beginning with chlorine and phosgene and progressing to the "designer" vesicants mustard and Lewisite. By the end of the war chemical weapons had caused over 1 million casualties of which some 10% were fatal. Refining such weapons continued over the next four decades. The highly toxic organophosphorus acetylcholinesterase inhibitors "Tabun" and "Sarin" were first produced in Germany in 1936 while "VX" production began in 1961 in the United States (Murphy *et al.* 1984).

With each development, the toxicity of chemical agents increased. The weaknesses of the 1874 Brussels Convention and the 1899 Hague Declaration had been exposed by the events of the 1914-18 war. Subsequent to this conflict, chemical agents were deployed in a number of smaller regional conflicts. Responding to the widespread revulsion and horror of civilian populations following the use of chemical weapons between 1914-18, the Geneva Protocol was signed by nearly 40 nations in 1925. Several breaches, however, of the protocol took place in regional conflicts and in addition chemical weapons research continued unabated. Substantial stockpiles of these weapons were built up after the 1939-45 global conflict, principally by the United States, the Soviet Union and France (Murphy *et al.* 1984; OTA 1992; Carnes & Watson 1989) using expertise originally developed in Germany.

The signing of the Chemical Weapons Convention in January 1993 followed some twenty years of negotiations and commits signatory nations to stop development of further chemical weapons, decommissioning manufacturing plants, and to the destruction of existing stockpiles of chemical agents. As such, it completes an international regime outlawing the production and use of chemical and biological weapons.

DESTRUCTION OF CHEMICAL WEAPONS: THE JACADS PROGRAMME AND BEYOND

The destruction of chemical weapons has become a topic of intense debate. In the past, obsolete chemical agents have been disposed

of by a variety of routes. At the end of the 1939-1945 conflict, the Allies disposed of the German stockpile in an extensive sea dumping operation in the Baltic and North Sea. Other stockpiles were dumped elsewhere at sea and suspected dumpsites exist in the waters of the Atlantic, the Irish Sea and off the Australian, Canadian and Hebridean coasts. The total quantities of mustard gas dumped are estimated to be around 240,000 tonnes, together with unknown quantities of the nerve agents Tabun, Sarin and Soman (see: Knightley 1992). Belated international recognition that sea dumping was not an environmentally sound practice led to the development of incineration facilities for the treatment of chemical agents.

Manley (1990) describes the solid/liquid incinerator used by the UK Chemical Defence Establishment, Porton Down, for combusting small quantities of recovered munitions largely containing vesicants. Components of this plant were moved from their original location at the UK Nancekuke production facility in the South West of England. The expertise of the Chemical Defence Establishment was brought to bear on destruction of the Iraqi stockpile of agents after the Gulf conflict. Again incineration was the technique used (NRC 1993). Anecdotal evidence also exists of a transportable incinerator used by the Dutch government to treat stocks of mustard agent in Indonesia.

The most ambitious project to treat chemical agents using an incinerator was initiated by the United States following a 1985 direction to the Army by Congress to destroy the stockpile of unitary chemical weapons. Construction began on a prototype facility on Johnston Atoll in the Pacific Ocean, with the intention of transferring the evolved technology to eight sites in the continental US (Carnes & Watson 1989). One of these facilities is nearing completion at the Tooele Army Depot, Utah (NRC 1993). Greenpeace began registering concerns about the proposed operation in 1983. Greenpeace (1989) produced the first in a series of critiques of the Johnston Atoll operation, based on evidence of operational and environmental problems with incinerators used to treat hazardous waste (see also: Costner & Thornton 1990). The JACADS project is currently running considerably over budget, has exceeded the time projected for completion and has not yet proven itself capable of sustained, trouble free operation.

Widespread (and growing) local, national and international opposition to the JACADS facility and those planned for the continental US led to the US Office of Technology Assessment conducting a limited review of alternative technologies for dealing with the chemical weapons stockpile (OTA 1992). The OTA document noted that the Army faced legal, social and technical problems in successfully completing its current programme. The project is running considerably over budget and the JACADS facility demonstration required by Congress as a prerequisite to the full demilitarisation programme has not been successfully completed to date (see Picardi *et al.* 1991; OTA 1992).

The OTA (1992) review document followed a comprehensive review of alternative destruction technologies published by Greenpeace (Picardi *et al.* 1991). The US Army has also requested the US

National Research Council (NRC) Committee on Review and Evaluation of the Army Chemical Stockpile Disposal Program to reexamine the status of incineration. In addition, the NRC also formed a further Committee on Alternative Chemical Demilitarization Technologies to evaluate applicable technologies. This Committee sponsored a technology workshop in Washington in March 1992 and has recently reported on its deliberations (NRC 1993). The report is a first step in a three stage national advisory process. The Committee on Review and Evaluation of the Army Chemical Stockpile Disposal Program will use the information to develop recommendations for the Army which in turn will formulate its own proposals to be put before the US Congress.

The NRC (1993) document does not go as far as to recommend suitable alternative technologies, but observes that a wide variety of possible modifications to the existing baseline technology represented by the JACADS system are possible. These range from simply replacing one of the existing components to complete substitution of all combustion based components. It is estimated that new components are likely to require between 5 and 12 years for development and demonstration. Significantly, the report also notes that initial weapons disassembly and agent treatment would meet the terms of the international treaty and eliminate the risks of catastrophic agent release during continued storage pending the development of an alternative to the baseline technology.

Many of the alternative technologies reviewed by the NRC (1993) were considered in the earlier review by Picardi et al. (1991). The rationale behind this study was the identification of technologies which could conceivably be designed to operate in a closed configuration with total control over process effluents. This consideration was also regarded as important in the OTA (1992) report. NRC (1993) suggest that the risk of toxic air emissions can be virtually eliminated for all technologies. They indicate that waste gas storage and subsequent analysis and certification could be used together with methods to reduce the volume of gases generated.

ALTERNATIVE DESTRUCTION METHODS IN PERSPECTIVE

Much of the research relevant to alternative detoxification technologies was initiated in response to problems with conventional hazardous industrial wastes. In particular, those streams containing the environmentally problematical halogenated hydrocarbons have come under considerable scrutiny. Despite this focus, many of the technologies could be adapted to detoxify chemical weapon agents. The nature of the aggregated waste stream from chemical munitions means that a combination of technologies may be required to effectively treat all stockpile components. Potential technologies, some of which have been developed to the pilot plant stage and which could meet the primary requirement of closed configuration operation fall into four broad categories: biological methods, chemical processes, photochemical processes and electrochemical processes. The NRC (1993) review categorises technologies on the basis of operating temperature, pressure and

whether the reactions take place in a gas or liquid phase, but the broad methodological categorisation above still applies.

a) Biological processes

Biological treatment has a long history as the most widely applied method for the treatment of sewage effluents. Microorganisms can be isolated or selected to degrade a diverse array of chemicals and some of these have been employed in operating systems to treat chlorinated solvents and phenols (Boyer et al 1988, Krumme & Boyd, 1988). The wide potential application of such techniques is the subject of several general reviews (Visscher & Brinkman 1989, Ghosal et al 1985, Alexander 1981). Most biological systems are anaerobic and utilise either monocultures of specifically chosen species (Oldenhuis et al 1989a) or consortia of naturally occurring bacteria taken from contaminated areas (Neilson et al 1988, Dean-Ross 1989 and Genthner et al 1989a & b).

Degradation of the less toxic and persistent chemicals has frequently been achieved, for example, the alkanes (Onodera & Ogasawara 1989) and the chlorinated solvents (Boyer et al 1988, Oldenhuis et al, 1989b Galli & McCarty 1989, Mayer et al 1988, Vogel & McCarty 1985). Other chemicals and classes of chemicals for which degrading microorganisms have been identified include chloroguaiacols, chloroveratroles, chlorocatechols (Neilson et al 1987), chlorobenzenes (Bosma et al 1988), substituted benzenes (Goulding et al 1988), pentachlorophenol (Topp & Hanson 1990), 2,4-D (Kelly et al 1989) and dioxin (Klecka & Gibson 1980). Some groups of species, notably *Pseudomonas* spp. and fungal species such as white rot fungus, have been found to have potential for degradation of a range of chemicals and are the subject of considerable research.

Pseudomonas spp. have been found to break down chlorobenzenes (Haigler et al 1988, Spain & Nishino 1987), chlorotoluene (Haigler & Spain 1989), lindane (Imai et al 1989) and PCBs (Parsons & Sijm 1988). The fungus *Aspergillus niger* is reported to be able to degrade the lower chlorinated technical mixtures of PCBs (Dmochewitz & Ballschmitter 1988). The white rot fungus *Phanerochaete chrysosporium* can degrade DDT (Bumpus and Aust 1987) crystal violet (Bumpus & Brock 1988) and pentachlorophenol (Mileski et al 1988). The enzyme employed by the fungus is a ligninase, and this has been extracted from the fungus and used to oxidise PAHs and dioxins (Hammel et al 1986). This is an alternate method to adding pollutants to a culture of the appropriate microorganisms, although less flexible because natural selection in a pollutant-exposed culture will continually be improving microorganism resistance and catabolic capabilities. It has the advantage that extremely toxic materials can still be processed.

There are some important caveats in the use of biological methods. The degradation products in many cases have not been characterised. Moreover, not all compounds are fully broken down and metabolites such as trichloroethylene, dichloroethylene or vinyl chloride can accumulate (Vogel & McCarty 1985, Oldenhuis et al 1989b). Sholz-Muramatsu et al (1988) and Gibson & Suflita (1986) also note the difficulties of degrading a leachate of

complex character as compared with the simple mixtures used in the majority of laboratory studies. Organophosphate chemical agents would need to be diluted to 5-10% aqueous solutions for biological processing, while mustard agents are not thought likely to be amenable to this type of process. Nonetheless, NRC (1993) note that biological processes for the direct detoxification of GB and VX could be developed as could processes utilising microbial consortia to treat effluent streams from detoxification and partial oxidation. On the basis of the work reported by Committee Member James Wild at MOSCON on biological methods and the overview by NRC (1993), this would seem to be a highly promising route for the treatment of the organophosphate nerve agents given that an appropriate scale-up can be achieved.

b) Photochemical processes

In photochemical reactions the requisite energy is provided by photons of light. This is a natural route of degradation which takes place, often extremely slowly, in the atmosphere (Bunce *et al* 1989) and aquatic systems (Choudry & Webster, 1988 & 1989; Dulin *et al* 1986). This type of reaction has been investigated for a wide variety of compounds, using different light sources and catalysts.

For example, in static experimental systems, Wang & Tan (1988) report photolysis of chlorinated solvents in a platinum-catalysed system using natural sunlight as the energy source. Brominated and bromochlorinated dioxins and furans have been degraded by natural sunlight or artificial light either in hydrocarbon solution or as dispersed films (Buser 1988). Campanella *et al* (1989) have used iodine doped membranes of polyphenylacetylene to catalyse the breakdown of monochlorophenols and butylcellosolve. Stallard *et al* (1988) achieved dechlorination of PCBs using visible light and a common dye, methylene blue, to promote the substitution of chlorine in the PCB molecule with hydrogen from a source such as propane.

Gamma-radiation has also been used as the energy source for the breakdown of pollutants. Gehringer *et al* (1988) used gamma-irradiation combined with ozone to remove trichloroethylene and tetrachloroethylene from drinking water. Similarly, UV light, which has only slightly less energy, has been used to dehydrochlorinate environmentally intractable chemicals (Exner *et al* 1982). A potentially powerful catalyst for photodegradation of toxic organics is sodium borohydride. Using irradiation from low pressure mercury lamps researchers have shown that it is possible to degrade PCBs (Epling *et al* 1988a), PBBs (Epling *et al* 1987) and chlorotoluenes (Epling & Florio 1986). As with titanium dioxide-catalysed reactions, degradation can in some cases be accelerated by the addition of enhancers (Epling *et al* 1988b).

Researchers have also been investigating the use of sunlight with titanium dioxide as a catalyst. The pollutant in aqueous solution with suspended titanium dioxide particles is passed through glass tubes exposed to concentrated sunlight. The sunlight, concentrated by a mirror trough system, excites the titanium dioxide to release electrons which combine with dissolved oxygen and other

oxidants in the water to provide strongly oxidising hydroxide radicals and superoxide ions. This has proved effective for the destruction of trichloroethylene at low concentrations in water (Pacheco *et al* 1990), and these researchers cite the method as capable also of completely oxidising chemicals such as chlorinated solvents, PCBs, dioxins, pesticides and dyes. In some cases it has been found that the addition of sensitisers as well as the titanium dioxide catalyst can enhance the degradation of the less reactive substances such as the PCBs (Menassa *et al* 1988). A pilot plant, operating a flow-through system is currently in operation in the United States (Pacheco *et al* 1990) although this may be curtailed due to lack of funding.

Curiously, given the great potential for the use of catalysed photochemical reactions on dilute waste streams and the capacity for tailoring such technology to specific concentrated waste streams, the NRC (1993) restricts discussion to oxidising agents plus UV light. It is stated that the committee found no information on the treatment of concentrated organic wastes. Picardi *et al.* (1991) reported on a number of solar based techniques under development which seemed to have promise for the processing of such materials but which appear to have fallen victim to cutbacks in research funding.

c) Chemical processing

i) Low temperature processes

The literature on chemical processing is somewhat less extensive than for biological or photochemical processes. Chemical processing requires a high degree of waste specific process development. For intractable chlorinated waste, liquid sodium is highly effective but is expensive and has handling difficulties associated with it. Sodium sulphite, for example, is widely used as a mild dechlorinating agent (Fam & Senstrom 1988); in the case of non-chlorinated wastes, simple oxidising or reducing agents may be able to detoxify them effectively. In many cases of chemical processing the detoxifying agent is destroyed in the process. Alternatively, toxic reaction end products may be formed. It is therefore more difficult to adapt chemical methods to the closed system which would be necessary to achieve total destruction of toxic agents with zero discharge. A major advantage, however, is that many of these processes take place at low temperature and low pressure, thus minimising the risk of catastrophic releases of chemical agent.

The use of chemical processing for chemical warfare agents is relatively advanced following the Army's extensive experience with such techniques prior to the decision being made to develop incineration (see: Durst *et al.* 1988) and experience with field decontamination methods for agents (Trapp 1985). As noted by the NRC (1993) the organophosphorus nerve agents can be hydrolysed using sodium hydroxide in water or in ethanol. Acid catalysed hydrolysis also appears to be possible, while ethanolamine can be used as a reagent to form products of lower toxicity. Reaction of VX agent with aqueous sodium hydroxide creates a highly toxic intermediate. Hydrolysis is also possible for treatment of

mustards, but such reactions are complicated by the extreme insolubility of these agents. Reformation of active agent from the hydrolysis of GB agent in the reaction mixture is now thought to be an analytical artefact. Further processing of the reaction residues of hydrolysis reactions, however, would be needed.

Other chemical methods exist which could possibly find application in the treatment of explosives and other munition associated chemicals as well as the agents themselves. Alkali metal polyethylene glycolate complexes (APEGs) are a group of compounds capable of dehalogenating PCBs, working most efficiently at 60-100°C. It has been suggested that these could be used to decontaminate soils, though toxicity of the reaction products of the APEG and the need for a nonpolar solvent may preclude this. However, a modified reagent, APEGM, has been developed which does not have these solvation problems (Kornel & Rogers 1985). The reaction takes place in solution of the reagent itself. Toxicity of remaining reagent still needs to be assessed before it could be used *in situ*.

Ruthenium tetroxide is a very strong oxidising agent which has been used for applications such as the destruction of dioxins (Ayres *et al* 1985). Ruthenium tetroxide or the hydrated dioxide or trichloride may be applied either on its own or with a secondary oxidant such as potassium permanganate or sodium hypochlorite. In the latter case, it is the secondary oxidant which is consumed. This process is very vigorous and capable of destroying most classes of organic compounds at room temperature.

ii) Processes at elevated temperature

Molten salts have been suggested as oxidising agents for a wide range of wastes (Tyner *et al* 1990). Potassium and sodium nitrates heated to 500°C become very strongly oxidising. The major reaction products would be carbon dioxide and water vapour, and liberated halogens would precipitate out as sodium or potassium halides. Similarly any metals in the feedstock could be separated as simple salts. One advantage of this proposed method over some other chemical methods is that the nitrate reagent can be regenerated by the injection of oxygen and does not have to be discarded. NRC (1993) suggest that sodium carbonate melt would have a wide range of application ranging from pure agent to the explosive and propellant components with pure oxygen used instead of air to minimise gas effluent volume. Disadvantages include the possibility of superheated vapour explosions and the requirement for disposal of large quantities of salt residue from the process if it cannot be regenerated.

Molten metal technology and plasma-arc systems are reviewed by Picardi *et al.* (1991) and NRC (1993). In both cases, Picardi *et al.* (1991) considered that the processes offered no significant advantage over incineration in terms of their commitment to atmospheric discharges and the use of combustion based post process systems for waste gas clean up. This view is broadly confirmed by the NRC (1993) review which points out the need for careful control of operational parameters of molten metal systems

to avoid superheated vapour explosions. The effect of corrosive products on refractory linings requires evaluation. Similarly, the waste streams from plasma-arc technology are considered by the NRC to be essentially the same as those from incineration and moreover would require a substantial commitment to design, development and demonstration programmes.

Corrosion is also regarded as a potential problem in the operation of wet air oxidation (WAO) supercritical water (SCWO) and catalytic oxidation processes. Wet air oxidation, in addition, is probably limited to the treatment of dilute residues. Supercritical water oxidation has a number of advantages, some common to wet air oxidation. The systems lend themselves well to closed configuration operation. SCWO will require development to deal with the handling of salts likely to precipitate in the system. Both WAO and SCWO are at an advanced stage of development.

Finally, the Synthetica Steam Detoxifier consists of a series of processes integrated into an overall equipment package. The NRC (1993) review discusses this process and points out a number of advantages, disadvantages and development needs. The operation of the technology is also discussed in depth by Picardi *et al.* (1991).

d) Electrochemical processes

The electrochemical destruction of wastes has so far only been investigated by a few groups of workers. The energy necessary to break down the chemicals is supplied as electricity. The electric power is used to generate highly reactive moieties which break down the added waste.

In one process, for example, the current reduces dissolved oxygen to superoxide ion which then attacks the waste molecules by nucleophilic substitution (Sugimoto *et al* 1988). In another (Steele 1989), the current is used to generate strongly oxidising silver II ions which then react with water to form species such as hydroxide radicals which oxidise the waste. NRC (1993) devote considerable space to the evaluation of this process for agent destruction and conclude that while it may be applicable both to initial detoxification and subsequent complete oxidation, a considerable development and testing programme should be anticipated.

DISCUSSION

The reviews carried out by Picardi *et al.* (1991) and NRC (1993) have identified a wide range of alternative technologies for the destruction of the United States chemical stockpile. In particular, technologies which can be designed to run in a closed configuration with total control over process effluents could be realised over a time period ranging from 5-12 years for development and research. After appropriate development some of these processes could be tailored to the requirements of all constituents of the chemical munitions waste-stream. NRC (1993) points out that options include the possibility of partial or complete substitution of the combustion based JACADS system. It is

clear therefore that the continued use of the baseline system in some capacity has not been ruled out.

While stopping short of actually recommending an alternative system, the NRC (1993) outline two basic strategies for demilitarisation of the chemical agent stockpile. These are designed to satisfy treaty obligations while at the same time eliminating the risk of agent release and significantly reducing the commitment to aerial discharges. The first strategy of onsite disassembly and agent detoxification to allow transport or continued storage of residues is cited as having the major disadvantage of a relatively long development lead time although it could use the low temperature liquid phase detoxification systems reviewed. The second strategy involves conversion of agent and disassembled weapons to leave non-toxic residues and decontaminated metal. This involves the use of liquid phase detoxification and either components of the existing baseline technology or an alternative such as WAO or SCWO.

Significantly, NRC (1993) directs considerable discussion at the possibility of containing gaseous emissions from agent destruction. Further, the document notes that the Army and the NRC are together reviewing the possibility of using activated charcoal filters as part of the existing baseline technology. As an "end-of-pipe" solution this carries with it a continuing commitment to high volumes of gaseous effluent and does not resolve concerns about process and operational control of the baseline system. This solution does not satisfy the primary criterion for the selected technology: that it must operate as a closed configuration technology with containment (rather than passive capture) of all process effluents.

In conclusion, the NRC (1993) review, by identifying alternative chemical agent destruction technologies has created an important opportunity to re-evaluate the role of the current incineration baseline technology. The incineration based process under development at JACADS has substantially exceeded budget and time projections, largely due to mechanical and process unreliability. In particular, the NRC review makes it clear that alternatives which could satisfy the original mandate that agents be treated in an environmentally sound manner already exist. Some are at an advanced stage of development. From an environmental perspective it would be unacceptable if the review simply led to attempts to modify the JACADS technology using "end-of-pipe" solutions. The fundamental and varied problems with this installation require fundamental and progressive solutions. Closed configuration alternative processes which meet international treaty requirements are clearly possible and accordingly, they should be developed on a "fast-track" basis.

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