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Development of Alternative Technologies for Chemical Demilitarisation:

Equivocal Commitment Equates with Slow Progress

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Kentucky Environmental Foundation (KEF) is a non-profit public corporation dedicated to educating citizens about environmental issues. Our primary mission is to improve access to information, promote communication and foster cooperation between government and citizens on matters concerning the environment.

KEF is the democratically-elected lead organization of the Chemical Weapons Working Group (CWWG), a coalition of grassroots organizations in the US, the Pacific and Russia who work toward safe disposal of chemical weapons.

I

Introduction

There is no doubt that development of a robust method for the demilitarisation of chemical weapons is a pressing need. Under the terms of the 1993 Chemical Weapons Convention, signatory states are obliged to achieve the comprehensive elimination of chemical weapon arsenals worldwide. Ultimately it seeks to establish a permanent injunction against chemical warfare by not only eliminating the weapons themselves, but also the facilities in which they are produced. It seeks also to address the problems associated with the chemical precursors to these weapons.

The 1993 Chemical Weapons Convention will enter into force 180 days after the 65th country deposits its instrument of ratification with the United Nations Secretary General. At present, the Convention is lacking a total of 2 signatures, including those of the US and Russia, which possess the greatest stockpiles. Once ratified, a signatory nation has 10 years within which to demilitarise and decommission its stockpiles and production facilities which may be extended to 15 years if exceptional technological problems are encountered.

There is, of course, an additional imperative to destroy these weapons. Many of the stockpiles of chemical agents are now old, in excess of forty years in some cases. While the agents themselves are still fully potent, the containment has begun to exhibit clear signs of aging. Both individual weapon elements (eg., M-55 rockets) and bulk containers are giving rise to concerns about the achievability of continued storage. An excellent review has recently been produced of the current situation pertaining to chemical munitions in the US and to a less comprehensive extent it also identifies some of the problems of historical dumping at sea and on land elsewhere (Koplow, 1995).

The potential difficulty in conforming to the provisions of the 1993 Chemical Weapons Convention in the US appears, at first, somewhat surprising given the financial investment and time dedicated to the construction of a facility to carry out such a programme. Developmental work has been under way since at least 1972 at the Rocky Mountain Arsenal and since 1979 at Tooele, Utah. The experience gained in incineration techniques has been the basis for a prototype incineration facility located at Johnston Atoll in the Pacific. It is planned to replicate this technology at the eight facilities in the Continental US where elements of the chemical weapons stockpile are housed.

Despite this considerable development lead time and the rapidly increasing budget, the baseline incineration technology has consistently failed to prove itself. The demilitarisation programme is now running a long way behind schedule and substantially over budget (Kentucky Environmental Foundation, 1995).

II

Failures of the Baseline Technology (JACADS)

There has been a comprehensive failure of the baseline technology to meet prescribed operational standards. Based on four parallel incinerator plants, the Johnston Atoll Chemical Agent Disposal System (JACADS) facility has been dogged by technical problems and cost overruns. Failures include jamming of the Deactivation Furnace System (DFS) and the DFS Conveyor, damage to the DFS caused by explosives being processed (1990, 1992, 1994) and release of chemical agent (GB nerve agent) to the atmosphere in 1994. The facility has also been fined for operational violations, some 122,000 dollars US to date.

These incidents took place during the Operational Verification Testing of the facility, the prerequisite to transferring the technology to the Continental US. As it now stands, the US Department of Defense estimates that destruction of the US chemical weapons stockpile alone will now cost in the region of 12 billion dollars US (1996) against the US Army's original 1985 budget of 1.7 billion. The JACADS facility is projected to cost 1.3 billion dollars US against an original 1987 estimate of 233 million.

These, among other clear operational failures, have led to justifiable public concerns about the construction of similar facilities in the continental United States. In addition, the incineration technology itself has come increasingly into question since it is inherently an "open process" which in normal operation will emit toxic chemicals, with the problem being magnified substantially during any periods of abnormal or "upset" operations. The US Army, however, has consistently maintained that the baseline technology represents the current "state of the art" technology.

A further argument has been that this is the only single technical solution to the diverse array of chemical agents requiring treatment. Reinforcing this entrenched position is the more subtle factor of the perceived "window of opportunity" which exists to rid the planet of chemical weapons. In essence, the argument is that any inadequacies in the technology and consequent environmental impacts can be justified in terms of the end goal of demilitarisation of the chemical weapons stockpile. These arguments are demonstrably fallacious.

On the one hand a new generation of technologies are now becoming available for the detoxification of chemical agents. While admittedly none of these is entirely without environmental impact, the risks they pose to the wider environment and to human populations living in proximity to the sites in question are very much less than the open-ended poorly controlled incineration technology.

III

Alternatives in Perspective

On the basis of the cost overruns experienced in developing the baseline technology and the operational difficulties encountered, it is signally striking how few resources have been directed at developing alternative technologies and the degree to which opportunities have been missed. In response to the "window of opportunity" argument, Greenpeace International produced a review in 1991 detailing the availability of technologies which might have utility in addressing the chemical weapons stockpile (Picardi, et al., 1991). Then, as now, the organisation did not specifically endorse any of these technologies but merely indicated where possible alternative technological approaches might exist.

The review was conducted on the premise that a technology would prove suitable only if it was capable of operation in a closed configuration, with total control over the quality and timing of release of any process wastes and effluents. What emerged from the exercise was surprising. Far from incineration being the best available technology, it was obviously rapidly coming into competition with a diverse array of alternative technologies. Some of these were at an advanced state of development, capable of addressing the chemical weapons stockpile, and operable under closed conditions. Many of these technologies were undergoing substantial development programmes.

Subsequently, the US National Research Council (NRC), at the behest of the Army and the US Congress, initiated a study by the Committee on Alternative Chemical Demilitarisation Technologies. The report from this exercise, following a workshop in 1992, was published (NRC, 1993). This document effectively set the framework for the subsequent evaluation by the NRC Committee on Review and Evaluation of the Army Chemical Stockpile Disposal Program, which was reported to the Army in 1994 (NRC, 1993).

The conclusions of the Stockpile Committee were highly disappointing. Far from recommending the use and fast track development of alternative technologies it set a "watching brief" to monitor progress in the field and recommended that development of the baseline procedures should continue. It was considered that none of the alternative technologies reviewed through the process were mature enough to meet the Army's needs. Concessions were largely made in the area of "end-of-pipe" pollution abatement technologies. One of its proposals, for example, was that the baseline technology should be developed with a carbon filter system to treat stack gases. Significantly, however, the

Stockpile Committee recommended that four alternative technologies based upon chemical neutralisation and neutralisation followed by biodegradation should be aggressively investigated with a view to proceeding to pilot stage after October 1996. These processes are specific for bulk storage sites (Landry, 1996).

By late1995, the Army was soliciting details of other potential alternative technologies through the Commerce Business Daily journal in response to the watching brief it had been set by the Stockpile Committee. In mid-November 1995 three further potential alternatives had been identified, based upon manufacturers' submissions, as suitable for bulk storage sites. These were electrochemical oxidation, gas phase hydrogenization and molten metal technology. With the exception of the gas phase hydrogenization process, all these alternatives had been identified in the 1991 review commissioned by Greenpeace International (Picardi, et al., 1991). In terms of financing, only the neutralisation techniques are being researched as government financed projects. The others are joint industry/government initiatives.

IV

Current Status of Alternatives

The alternative technologies selected for further consideration by the Army are an extremely limited subset of those potentially available (Picardi, et al., 1991; NRC, 1993; Workshop Proceedings: Advances in Alternative Demilitarization Technologies, 1995; Australian Environmental Protection Agency, 1995). Currently, those selected are:

A) Chemical Neutralisation;
B) Chemical Neutralisation with Biodegradation;
C) The Silver II electrochemical process;
D) The Eco-Logic Gas phase hydrogenization process; and
E) M4 Environmental Molten Metal Process.

The basic process details of these are as follows.

A. CHEMICAL NEUTRALISATION

Chemical neutralisation of chemical warfare agents is relatively well understood and indeed has formed the basis for the demilitarisation programmes of several countries including Britain and France. Chemical neutralisation is applicable to all agent types, but different reactions are employed in each case. The basic mechanisms have been recently reviewed (Yang, 1995). The reactions involve simple reagents used at low temperature in water based medium. The simplest reagents are sodium or calcium hydroxide. Basic hydrogen peroxide solutions can also be used as can more complex reagents such as monoethanolamine. Oxidation reactions can be effected using aqueous bleach and this has formed a basis for battlefield decontamination procedures. Oxone, a mixture of potassium sulphur salts, and peroxydisulphate can both also serve as oxidising agents.

B. CHEMICAL NEUTRALISATION AND BIODEGRADATION

The processes here are the same as for stand-alone neutralisation processes, but the biodegradation step is added as a post neutralisation treatment step. Chemical neutralisation has a number of advantages, particularly low costs and use of common industrial chemicals. The major perceived disadvantage lies in the volumes of neutralised agent produced and the need to dispose of biological sludges from any biological treatment processes used. One significant advantage of neutralisation techniques, however, is that they provide a basis for a powerful interim solution to the stockpile problem and such methods, suitably configured, could deal with whole munitions, by opening them by drilling whilst immersed in a bath of the neutralising chemical. The energetic components, freed of chemical agents, could then be processed by other techniques.

The terms of the 1993 Chemical Weapons Convention could be met by using neutralisation techniques. These could be developed fairly rapidly on the basis of the considerable research carried out on such methods in the US before the programme was largely abandoned in favour of incineration (Picardi, et al., 1991). The process could also provide the key to the problem of continued storage. Neutralised agent could be stored pending suitable technology to process the residues further. Costs are estimated at around 20% of the cost of the baseline technology. The technology could be demonstrated within two years at pilot plant level and in full operation within five.

A perceived difficulty with neutralisation techniques is the volume of neutralised material likely to arise from them which will necessitate further processing.

C. THE SILVER II ELECTROCHEMICAL PROCESS

This technology has been developed by AEA Technology as a means of destroying solvents used in the processing of radioactive material. The technology is based around electrochemical cells normally used for the production of chlorine. In this application, the cell is filled with silver nitrate dissolved in nitric acid in the anode compartment and nitric acid in the cathode compartment. Passage of an electric current through the cell generates divalent silver ions which act as an oxidising agent towards materials in the waste stream. The waste is progressively added to the anode solution.

The method has been used successfully to demonstrate the destruction of a wide range of organic substances including explosive energetics and a variety of chemical agents. Significantly, the ability of the system to deal with whole munitions, modelled on the M55 rocket has also been demonstrated. A further advantage to this system is that it potentially can be deployed in a mobile configuration to allow the problem of sea-dumped and buried munitions to be addressed on site (Batey, et al., 1995). The overall costs are around 30% of the current estimate of demilitarisation through incineration, and working systems could be demonstrated within one-three years.

D. THE ECO-LOGIC GAS-PHASE REDUCTION PROCESS

This technology, which has a wide spectrum of potential applications, depends upon the gas-phase reduction reaction of hydrogen with organic wastes to produce methane gas. This can be compressed and stored subject to a satisfactory analysis before re-use in the process. It operates in a closed-loop recirculating mode. Commercial scale versions of the process are currently in operation, notably in Australia where it has been applied to the destruction of pesticide wastes. It has not yet been demonstrated on energetics or on the chemical agents themselves, but it may be practicable to treat whole munitions in a suitably configured device (Casten, 1995). Currently validation of the system using VX and HD agent is underway and the applicability to energetics is the subject of research under contract to the US Navy.

The system is not totally without emissions. There is still a commitment to the disposal of grit material from the reactor and sludge and decant water blowdown from the gas stream scrubber. This scrubber system may also be used to recover hydrochloric acid from chlorinated waste streams. The metal component of wastes cannot, of course be destroyed and any use of this technology in the demilitarisation programme will have to make provision for onward treatment of the residues to deal with these substances present in various components of the munitions. Add-on technology in the form of a Thermal Desorption Unit (TDU) heated by molten metal may partially alleviate this problem.

Volatile metals are likely to dissolve in the molten metal bath. In US Environmental Agency (USEPA) tests, the TDU did not perform according to specification due to the "clumping" of soil under treatment, but this aspect is apparently being modified (USEPA, 1994) and is of limited application to munitions components. Recent communications from the manufacturer (Chisholm, personal comment) suggest that the problems have been eliminated by extensive redesign to produce a Thermal Reduction Mill. A full scale commercial scale unit is currently under construction. In any case, this component is stated not to be relevant to the chemical weapons stockpile. Importantly, however, the release of materials to atmosphere can be conducted in a controlled manner, after analysis. Moreover, since the process is conducted in a hydrogen atmosphere, it is claimed that chlorinated dioxin and furan production is impossible.

E. M4 MOLTEN METAL PROCESS

The M4 Molten Metal Catalytic Extraction Process is claimed to be able to operate with no process emissions with the exception of introduced inert materials. Essentially, the materials are introduced into a bath of molten metal held at a temperature 2400-3200F. The technology originated from the steel industry where it was observed that molten metal has both solvent properties and catalytic capacity, effecting a rapid breakdown of complex organic molecules. By feeding proprietary chemicals into the bath together with the waste, materials can be reconfigured into usable products. The end product gases evolved in the form of hydrogen and carbon monoxide (syngas) can be used as a fuel resource or as a feedstock for the production of chemicals such as methanol. A ceramic end product can be skimmed off the top of the bath, while metal by-products remain as a ferroalloy which can be blended with scrap material to produce, for example, stainless and tool steels (Valenti, 1996).

The claim that there are no process emissions needs some verification for this technology. The synthesis gas produced from the reaction chamber is claimed to be suitable as fuel in heating and boiler plant. Nonetheless, if chlorinated compounds are present in the waste feed, then this will lead to the production of hydrogen chloride, which in turn could react with organic fragments to form further chemical species. When processing chlorinated feedstocks, hydrochloric acid has been recovered as a commercial grade chemical. Total organic carbon in the acid was not detected at the somewhat high detection limit of 40mg/l. Analysis for chlorinated dioxins and dibenzofurans gave results below a detection limit of 0.1ng Nm3 TCDD Toxic Equivalents (Abraham, personal comment). The reducing environment in which the process takes place will tend to prevent the formation of chlorinated dioxins and furans together with NOx and SOx. This aspect is one which will need to be evaluated in further detail although the system configured for treating chemical agent will be designed around three process retention tanks, where the syngas product can be retained and tested for unconverted agent prior to use.

V

Overview of Selected Alternatives: The Development Perspective

The alternative technologies currently under review by the Army appear to largely fulfil the criteria that such technologies must meet to be acceptable. All are non-incineration technologies, capable of operation in closed configuration and with full control over process emissions. Undoubtedly, in each case a number of questions remain to be resolved concerning their full environmental impact, and these aspects of operation should be fully investigated as part of the research and development programmes now under way. In particular, the various claims of emissions performance need to be comprehensively verified. Nonetheless, these alternatives appear to offer much better process performance and control than can be achieved by the baseline technology.

As noted above, however, the selected technologies represent an extremely limited subset of those potentially available to address the problem. Among those which have previously identified, but which have apparently been excluded from consideration as potential "fast track" developments at this stage are the following.

A) Biodegradation using bacteria or bacterially derived enzymes to breakdown organophosphorus nerve agents.

B) Supercritical Water Oxidation using water at medium temperature under a high pressure.

C) Molten Salt Process which works on a similar principle to molten metal but using fused salts.

D) Wet Air Oxidation which can be used to oxidise chemical agent by air or oxygen under increased pressure.

E) Steam Gasification which uses steam at medium temperature and pressure to detoxify agents and convert them to gaseous products.

F) Photochemical processes which use ultraviolet light or sunlight to degrade chemical agents

In fact, Supercritical Water Oxidation and Photochemical Processing, together with electron beam bombardment have been identified as potential follow-up processes to neutralisation alone and coupled with biodegradation.

Comparison of the technologies under evaluation with those which appear to have been totally or partially excluded raises some important considerations concerning the financing of research and development costs. Of the technologies being considered, the neutralisation techniques are undergoing research at the expense of the US Government. The development costs of the other three are being borne by private industry, with some help provided at the proof of principle stage by the US Army. This latter is largely a low cost facilitation role. The three technologies (Silver II, ECO-LOGIC and M4 Molten Metal) are already at an advanced stage of development due to the considerable research support already made by industry and other governments.

Two important points arise from this.

1) The three selected external technologies have widespread generalised application to a variety of waste-streams in a variety of industrial sectors. This general applicability undoubtedly explains their relatively advanced development since they can attract funding relatively easily.

2) Potentially effective methods for specific elements of the stockpile such as enzymic or bacterial degradation, because of their highly specific applications, would have been unable to attract research and development funding from the private sector. This is a consequence of their lack of generalised application. Added to this is the fact that the chemical agent inventory represents a very specialised detoxification task and will necessitate the development of specialised handling and containment procedures.

Overall, these factors conspire to create a highly uneven commercial playing field and an environment in which lack of financial commitment to the development of alternatives is hardly likely to progress at the maximum possible rate.

It is clear that the development of alternative technologies has proceeded extremely quickly where commercial incentives exist to do so. Many of the technologies identified in the 1991 Greenpeace Review (Picardi, et al., 1991) have reached pilot or commercial scale operation from the concept or bench scale stage in 1996. Yet others such as the ECO-LOGIC process have developed since this review. Yet the US Army Programme has signally failed to develop or prove either the baseline technologies or any alternatives to it despite a clear mandate to examine such possibilities. In the meantime, despite widespread opposition and highly condemnatory reports relating to finances from Government agencies, substantial resources have continued to be poured into the baseline technology system.

This indicates that a modified approach is likely to prove more fruitful in fulfilling the international and domestic imperatives to demilitarise and detoxify the chemical agents in the US stockpile. At the outset, it must be recognised that a "fast track" approach to the configuration of potential alternative technologies to the chemical agents problem is a vital prerequisite of success. In turn, in a climate of resource limitation it means that the baseline

technology would probably be better abandoned and the resources placed in the alternatives sector creating a levelled playing field. Accordingly, the major elements of a modified strategy could be:

A) Abandonment of the existing baseline technology;

B) Neutralisation of problematic stocks of agent currently prone to leakage and storage of neutralisation products as a priority;

C) Campaign approach to the neutralisation of other stocks of agent contingent upon development of other technologies;

D) Redirection of existing funding and resources into fast track approach to development of at least the three private sector alternatives selected; and

E) Immediate resourcing to optimise the configuration of the identified alternatives to address the chemical agents stockpile.

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