

Selected Chemical Weapon Destruction Techniques

CHEMICAL NEUTRALIZATION: THE ARMY'S EXPERIENCE

In a 1969 report, the National Research Council (NRC) recommended chemical neutralization for the destruction of the chemical weapons (CW) agent GB and incineration for mustard agents H and HD. After research and development work on chemical neutralization at the Chemical Agent Munitions Disposal System (CAMDS) (Tooele, Utah) and Rocky Mountain Arsenal (Denver, Colorado) in the 1970s, the Army concluded that incineration was the best method for the destruction of all chemical weapons. The NRC Committee on Chemical Weapons Disposal has recently been asked by the Army to reevaluate incineration and alternatives for CW disposal.

Chemical Neutralization of Nerve Agents

Most of the Army's experience with large-scale chemical neutralization of chemical weapons was with the organophosphorus ester agent GB. This agent was successfully neutralized using aqueous sodium hydroxide on a scale compatible with destruction of the current U.S. CW stockpile. Approximately 8.4 million pounds of GB-taken from underground storage tanks, GB ton containers, M139 bomblets (Honest John Warhead), M34 cluster bombs, M55 rockets, and 155/105-mm projectiles, were neutralized at Rocky Mountain Arsenal from 1974 to 1976 and at CAMDS between 1979 and 1982. By weight, this represents 17 percent of the 25,000 tons of agent to be destroyed in the current program.

GB is stable at neutral pH but is hydrolyzed rapidly at alkaline pH. The half-life of GB at 300 C in aqueous solution is 146 hours at pH 7 (neutral conditions) but decreases to 0.4 hour at pH 9 (alkaline conditions) (1). Presumably at higher pH and temperature, the hydrolysis rate would be even more rapid. The suggestion has been made that the addition of a catalyst could speed up this hydrolysis reaction even more (2).

As part of the Army's program, after GB neutralization was determined to be complete, the resulting brine was evaporated by spray drying and the salts were packed into drums for disposal. There were some problems with the spray-drying process, including the possibility that GB might re-form under certain conditions. This re-formation could be successfully avoided by adjusting the pH and brine flow rate, and by reducing the operating temperature (1).

Difficulties were also encountered in confirming that the brine was agent-free. Particularly at the CAMDS

facility, minute quantities of agent were detected in the brine. At Rocky Mountain Arsenal the neutralization brine was considered agent-free if a 5 percent excess sodium hydroxide level was achieved. At CAMDS a more strict criterion was used of less than 20 parts per billion (ppb) agent (the Army's soldier drinking water standard). Difficulties in certifying this level of destruction at CAMDS may have come from occlusion of GB in rust or other particulate, formation of GB during analysis, or false positives resulting from some unidentified interference in the complex neutralization mixture (1). Agent emissions at the facility during brine spraying at Rocky Mountain Arsenal often exceeded the action level (0.0003 milligram per cubic meter (mg/m^3)) and occasionally the shutdown level (0.003 mg/m^3). These levels were promulgated by the Department of Health and Human Services (DHHS) and the Army's Surgeon General. However, perimeter monitors showed that the emission standard for the general population was not exceeded (1).

After being drained of GB, the empty munition bodies were moved to a deactivation furnace where explosives and propellants were incinerated and metal parts thermally decontaminated, i.e., incinerated. Empty ton containers were similarly incinerated in separate furnaces. Thus, "chemical neutralization" actually applied only to the drained agent and treatment of the remaining waste depended on incineration. However, disposal of the M34 cluster bomblets and ton containers used a caustic (aqueous sodium hydroxide) wash to treat the drained container by neutralizing any residual agent. For some reason—possibly a lack of confidence in the efficacy of this process—the caustic wash treatment was also followed by thermal decontamination (incineration).

From 1979 to 1981, 13,951 M55 rockets containing GB (2.9 percent of the current M55 rocket stockpile) were destroyed by this combined chemical neutralization/incineration process (1). The Army also reported problems with re-formation of GB during the brine drying process, although it is not clear why the corrective actions described above were not applied to solve the problem in this instance. The reaction was also reported to take longer than expected. Adding excess sodium hydroxide to accelerate the reaction created a larger amount of salt for disposal. Given the intrinsically rapid hydrolysis rate of GB under alkaline conditions (corresponding to a short half life), the apparent slow reaction encountered in this situation may have been due to problems associated with the large scale of the demonstration such as complete and thorough mixing of the organic material with the aqueous sodium hydroxide.

Although the agent VX, which is structurally similar to GB, can also be chemically neutralized, this was never demonstrated by the Army on a large scale. Acid chlorinolysis (chlorination in an aqueous acidic medium followed by caustic neutralization) rather than alkaline hydrolysis was suggested by the Army as the best method for chemical destruction of VX (1). However, VX was shown to be neutralized on a small scale by hydrolysis with sodium hydroxide. The problems encountered with the neutralization of GB led the Army to abandon plans to test the large-scale neutralization of VX. The Army indicated that a poor water volubility, mixing problems, and the presence of a "bis" impurity (with unspecified susceptibility to alkaline hydrolysis) made alkaline hydrolysis of VX difficult (1). As with GB, neutralization was apparently intended only for the liquid chemical agent. Incineration was to be used for destruction of the explosives and propellant components, and for thermal decontamination of munition cavities and metal parts. In addition, lack of a reliable low-level monitoring capability for VX in the neutralization brine at the time of the Army's research program led it to conclude that DHHS would never approve chemical hydrolysis (1).

Chemical Neutralization of Mustard Agents

Mustard agent has also been shown in the Army's research to be hydrolyzed under alkaline conditions on a small scale, although only slowly at ambient temperature. The corresponding reaction rates with alkaline hydrolysis at elevated temperature were not reported. The products of mustard hydrolysis with sodium hydroxide were not identified and their toxicities were not assessed. Alkaline hydrolysis of mustard agents on a pilot-plant scale was reported, using the base monomethanolamine instead of sodium hydroxide, to produce a homogeneous nontoxic organic waste. Calcium hypochlorite slurry or aqueous bleach (sodium hypochlorite) was used to oxidize rather than hydrolyze mustard agents, but there was "uncertainty about the completeness of the reaction" (1).

Summary of the Army's Neutralization Process Experience

In the Army's summary of its experience with chemical neutralization, the following reasons were given for abandoning the process in favor of incineration (1):

1. ***The perceived complexity of neutralization compared to incineration.*** Caustic reactants used for chemical neutralization had to be handled safely in bulk quantities. However, many industrial large-scale processes routinely use such caustic agents, e.g., the manufacture of soap. The major safety issue in handling chemical weapons will always be the agents themselves.
2. ***The sensitivity of neutralization to a number of variables that could slow the reaction and possibly***

lead to re-formation of the agent. In some situations, the rate of neutralization in large-scale tests of chemical agents was much slower than had been predicted. Very large amounts of impurities in certain grades of mustard agent also made neutralization difficult to monitor adequately. However, it is not clear that the problems encountered with "industrial scale-up" of chemical neutralization are insurmountable, and the scale of a chemical neutralization program is similar to or smaller than that of industrial large-scale processes.

3. ***The quantity and nature of the waste produced by neutralization are more problematic than those produced by incineration.*** Calculations by the Army indicated that 1 pound of GB will produce 1.5 pounds of salt, compared to a salt yield of 1.4 pounds from incineration. In practice, the excess caustic added to speed up the reaction led to 2.6 pounds at Rocky Mountain and 3 to 6 pounds at CAMDS of salt per pound of agent hydrolyzed. The Army speculated that the sometimes heterogeneous form of some agents (partially gelled, mixed with solid particles such as rust) may have contributed to the variation in results obtained with chemical neutralization. These types of technical problems encountered in the transformation of industrial processes from bench-scale demonstrations may not be insurmountable given sufficient motivation to reach a solution. Also, it has been argued that producing larger amounts of salts from neutralization may be relatively more acceptable than some of the perceived problems of incineration, such as the formation of dioxins.
4. ***The capital and operating costs of chemical neutralization were estimated to be higher than those of incineration (1).*** This cost comparison might have to be considerably revised now in light of the unanticipated cost increases in the Army's incineration program, which are due in part to technical problems encountered by the Army after 1987 (3).
5. ***The analytical problems encountered in certifying that the waste materials of chemical neutralization were agent-free.*** This must be compared to the analytical problems faced in demonstrating that incineration products of incomplete combustion (PICs) are dioxin or agent-free, etc.

After reviewing the Army's experience with chemical neutralization and incineration of chemical weapons, the NRC in 1984 supported the Army's decision to abandon chemical neutralization in favor of incineration. In light of the current political opposition to incineration, and after considerably more experience with this technology, it is not clear that the same endorsement would be made today. In principle, with appropriate conditions, alkaline hydrolysis could be a means to chemically neutralize the CW agents GB, VX, and mustards. Problems encountered

with alkaline hydrolysis of all types of CW agents might today appear to be surmountable in view of new techniques as well as increased pressure to exploit existing techniques for use with CW destruction. The NRC's Committee on Review and Evaluation of the Army Chemical Stockpile Disposal Program and Committee on Alternative Chemical Demilitarization Technologies, were recently requested by the Army to reevaluate incineration and alternatives for CW disposal.

SUPERCRITICAL WATER OXIDATION

Supercritical water refers to water that has been heated and pressurized to a transition point between gas and liquid phases, and thus has some of the properties of both. In the supercritical phase the solvent properties of water change, and organic materials becomes soluble, whereas inorganic salts become insoluble and tend to precipitate (4). Organic materials in solution with supercritical water can be oxidized by oxygen introduced from air. This is a broad-spectrum oxidation procedure for organic compounds, and at elevated temperature (4000 C), even refractory compounds such as coal are oxidized (5). Supercritical water oxidation (SCWO) is similar to incineration in that it involves oxidation of organic compounds to carbon dioxide and inorganic acids or salts. However, SCWO operates at much lower temperatures than incineration. SCWO is under commercial development as a general technology for the destruction of many different organic hazardous materials, and the destruction of CW agents would at most constitute only a small portion of its use.

SCWO may have certain advantages over incineration for the oxidation of organic waste. Compared to incineration, SCWO has no requirement for a large airflow. SCWO carries out oxidation at lower temperature, and the reaction medium (water) can be contained until it is tested to be safe. A major selling point of this technology is that potential PICs are entrained in solution rather than emitted in stack gases. The apparently superior control of emissions is an attractive feature of SCWO technology. The effluents from SCWO, in contrast to exhaust stack gases from incineration, may be collected, analyzed, and even recycled to achieve more complete destruction.

In discussions with Modell Corp. and General Atomics, two companies that are involved in the development of SCWO for CW agent destruction, it was apparent that currently there are both advantages and limitations with this technology. Modell has completed the initial phase of a research program on the use of SCWO for the treatment of CW agents (5). It has successfully demonstrated for the Defense Advanced Research Project Agency (DARPA) the destruction of "simulants" (analogs) of GB, VX, and HB on a bench scale. Modell achieved "destruction and

removal efficiencies" (DREs) of 99.99999 percent and has proposed, but not begun, a demonstration of the technology for DARPA with actual agents. Although Modell has not yet worked with actual CW agents, it has demonstrated the oxidation of some explosive materials such as the effluent from TNT manufacture ('red water').

The formation and environmental release of dioxin, a concern in the incineration of organic materials, may not be significant for SCWO. Modell has demonstrated that the dioxin congener (TCDD) was oxidized to below detectable levels when introduced at 500 parts per million (ppm). The Modell technology has also been demonstrated to work for the destruction of dioxin in pulp mill waste streams. Wood, when suitably pulverized and converted to a flowable form, can also be treated.

Gaseous effluents from SCWO are carbon dioxide and oxygen with traces of carbon monoxide (10 to 15 ppm with optimized operation). In Modell's process, these effluent gases are expanded and cooled; the carbon dioxide is solidified and removed, and the oxygen is recycled through the system. This process might be considered a "closed" system in comparison with incineration. Oxidation of organic materials containing hetero atoms such as fluorine, chlorine, sulfur, or phosphorus produces the corresponding hydrofluoric, hydrochloric, sulfuric, and phosphoric mineral acids in solution. These can be neutralized, precipitated from the SCWO reactor water solution, and removed from the SCWO reaction vessel.

Although Modell believes that its SCWO technology could be developed for the Army's CW destruction program, it has been unable to interest the Army in this work. From Modell's perspective, the Army's commitment to incineration technology has led it to dismiss viable alternatives such as SCWO. On the other hand, the U.S. Department of Energy (DOE) has apparently expressed an interest in using the technology to treat radioactive mixed waste. In general, Modell considers that the greatest commercial opportunities and market for this technology are not in CW destruction but in other areas of organic waste disposal. The Modell Corp. is currently operating a bench-scale SCWO facility with a capacity of 30 gallons per day and hopes soon to construct an SCWO facility in Germany with a capacity of 5 to 10 tons a day. Modell estimates a cost of \$200 per ton for sludge disposal.

General Atomics' (GA) engineers who are involved with SCWO development are considerably more cautious about the future uses of this technology for hazardous waste and CW agent disposal (6). Although a wide range of organic compounds have been shown by GA to be oxidized by SCWO technology on a bench scale, it has never been demonstrated with actual CW agents. GA is currently under contract to DARPA and the Office of

Naval Research to perform the necessary research and build a prototype SCWO system that would be capable of processing relatively small amounts of chemical agents, propellants, and other U.S. Department of Defense wastes. SCWO as it is presently conceived is not designed to handle solid CW agent disposal waste forms such as drained munitions or dunnage. The research program, which will be conducted with support from the University of Texas, the IIT Research Institute (Chicago, Illinois), and EcoWaste Technologies (Austin, Texas), will initially focus on two areas of importance—corrosion and solids handling. Corrosion with SCWO is a significant issue especially because of the mineral acids formed from the oxidation of compounds containing fluorine, chlorine, sulfur, and phosphorus hetero atoms. The handling of solids, such as the salts formed and precipitated during SCWO, will require careful attention because such inorganic salts can become sticky under SCWO conditions and could foul the walls of the reactor.

The DARPA contract calls for a 15-month research phase to address these and other issues and to develop data, initially on simulants and then on actual CW agents. Concurrently, a 3+-year pilot-plant development effort is planned to lead to the construction and testing of a prototype SCWO unit with a capacity of 1,000 to 1,500 gallons per day. Full *demonstration* of the practical application of this technology to CW agent destruction is therefore estimated by GA to be more than 3 years away.

In discussing the likely success of this application of SCWO, GA tended to be cautious and to emphasize the need for the data that will be developed during the research phase of this work.

GA considers the recent bilateral, as well as current and future multilateral, agreements on CW destruction and nonproliferation to be an ideal opportunity for SCWO technology. For example, the United Nations has announced its intention to destroy the Iraqi CW stockpile, which is considerably smaller than that of the United States. Use of mobile SCWO-based machines for destruction of this type of small stockpile could be an ideal application. Unfortunately, the technology may not be developed in time to be applicable to this particular situation.

STEAM GASIFICATION TECHNOLOGY

A process known as steam gasification (re-forming) treats organic materials with steam at 1,000 to 1,300 °C under reducing conditions to produce carbon monoxide, carbon dioxide, and hydrogen (7). The steam/organic materials stream is recirculated through the high temperature reactor to control destruction efficiency. The carbon monoxide and hydrogen can be reacted over a suitable catalyst to form either methanol or carbon dioxide and

water. Since steam gasification is a reducing process rather than an oxidation process such as incineration PICS will not be formed. This reaction is a temperature-controlled equilibrium process so, in principle, any level of destruction may be achieved by selecting an appropriate temperature.

The current developer is interested in testing its steam gasification system for CW destruction. It has demonstrated the device with CW simulants but not with actual CW agents. The machine is designed to handle bulk objects, including 55-gallon drums filled with waste, and may therefore be suitable for handling properly prepared munitions and CW containers. Drummed wastes are gasified in the drums, one drum at a time, by placing each drum in a chamber operated at 300 to 700 °C. In its current form, halogens are removed from organic materials by pretreatment with alkali, and the remaining dehalogenated organic material is destroyed by steam gasification. Sulfur- and phosphorus-containing materials are converted to salts of their reduced forms hydrogen sulfide and phosphine. In contrast to conventional incineration, steam gasification does not use an airflow so the gas flow output to the environment is minimized.

The developer is offering a “premarket” machine for customer evaluation. The machine is approximately 5 by 6 by 7 feet and costs about \$700,000 when supplied with a drum feeder and flash vaporizer. The company is already working on chemical waste disposal problems for DOE, such as destruction of chlorinated solvents and organic wastes from weapons dismantlement, that do not involve chemical weapons. It has proposed a system that would use one or more mobile steam gasification devices directly in a CW storage igloo or on a truck positioned next to the igloo. In this concept, a modified version of the Army's current M55 rocket shearing system could be coupled to the drum feeder. Passage of hot steam around and through the sheared, drained munition would decontaminate the empty shell. This configuration would have the advantage of avoiding the risk associated with transporting CWs from the igloo to a larger stationary destruction device.

The developer is currently negotiating a contract to destroy napalm bombs located at Camp Pendleton, California, by use of steam gasification. These napalm bombs consist of a 15-foot-long aluminum container filled with napalm and an explosive. The company plans to modify its device to contain an entire bomb during the steam gasification destruction process.

PLASMA ARC TECHNOLOGY

A newly developed Plasma Arc Technology System can process nearly 10 pounds per minute of solid waste or 55 gallons per hour of liquid waste (4). The developer is currently testing plasma arc pyrolysis (PAP) technology,

although it has not specifically tested the system with CW agents. After waste has been atomized in the plasma pyrolysis chamber the resulting elements are cooled in a second portion of the chamber and recombine to form hydrogen, carbon monoxide, and hydrochloric acid. Such plasmas can reach temperatures of 5,000 to 15,000 C. The resulting gases are passed through a wet caustic scrubber for removal of particulate and hydrochloric acid. The remaining gases are combusted with air. The entire system fits on a 45-foot-long transportable tractor-trailer bed.

The most significant limitation of PAP treatment is that only liquids can be treated. Contaminated soil and viscous materials cannot be processed by the system (4). Thus PAP technology in its current form would not be suitable for the treatment of contaminated drained munitions, containers, explosives, or propellants, and the dunnage associated with chemical weapons.

Appendix A References

1. U.S. Department of the Army, "Chemical Agent and Munition Disposal; Summary of the U.S. Army's Experience," Office of the Program Manager for Chemical Demilitarization, Aberdeen Proving Ground, MD, September 1987.
2. Picardi, A., International Environmental Assessment Group, Alexandria, VA, "Alternative Technologies for the Detoxification of Chemical Weapons: An Information Document," prepared for Greenpeace International, Washington, DC, May 1991.
3. U.S. Congress, General Accounting Office, *Stockpile Destruction Delayed at the Army's Prototype Disposal Facility*, GAO/NSIAD-90-222 (Washington, DC: July 1990).
4. U.S. Congress, Office of Technology Assessment, *Dioxin Treatment Technologies-Background Paper, OTA-BP-O-93* (Washington, DC: U.S. Government Printing Office, November 1991).
5. Modell, M., Modell Development Corp., Framingham, MA, personal communication, Nov. 14, 1991.
6. Davison, W., Director, Advanced Processing Systems, General Atomics, San Diego, CA, personal communication, Nov. 19, 1991.
7. Galloway, T., Synthetic Technologies Inc., Richmond, CA, and Sprung, J. L., Sandia National Laboratories, Albuquerque, NM, personal communication, Dec. 20, 1991.