Combining SBR systems for chemical and biological treatment: the destruction of the nerve agent VX

R.L. Irvine***, S.S. Haraburma** and C. Galbis-Reig***

* University of Notre Dame, Notre Dame, IN 46556, USA
** Chemical Demilitarization’s Alternative Technologies and Approaches Project, Newport Chemical Agent Disposal Facility, NECDF Government Office Complex, Newport, IN 47966, USA
*** SBR Technologies, Inc., 200 West Superior, Suite 200, Chicago, IL 60610, USA

Abstract The US Army is pilot testing the neutralization of VX nerve agent stockpiled at Newport, Indiana using caustic hydrolysis in a Sequencing Batch Reactor (SBR). The resulting hydrolysate was tested at the bench-scale for treatment with activated sludge biodegradation in two distinct studies, one in the SBR and another, in the PACT® process. The feed to both biological systems was pretreated to enhance the biodegradability of the hydrolysis products. Both biodegradation studies demonstrated that the hydrolysate could easily meet the Chemical Weapons Convention treaty and US environmental regulations following pretreatment.

Keywords Biological treatment; chemical warfare agent; hydrolysis; nerve agent; periodic process; sequencing batch reactor; VX

Introduction

The United States (US) has stockpiled chemical warfare agents and munitions for more than half a century. In 1985, Public Law 99–145 mandated disposal of M55 rockets containing unitary chemical warfare agents because of their potential for self-ignition. Soon after, the US Army Chemical Stockpile Disposal Program (CSDP) developed a baseline incineration system to eliminate the entire stockpile of chemical weapons. In 1992 the US Congress enacted Public Law 102–484 directing the US Army to dispose of the entire stockpile of chemical warfare agents and munitions by December 31, 2004. The National Research Council’s (NRC) Committee on Review and Evaluation of the Army Chemical Stockpile Disposal Program (Stockpile Committee) began providing technical and scientific advice and counsel to the US Army’s disposal program in 1987. In 1994, the committee endorsed the baseline incineration system as an adequate technology for destroying the stockpile. In response to public concerns about incineration, however, the NRC evaluated alternative disposal technologies.

The National Defense Authorization Act for Fiscal Year 1993 directed the Secretary of the Army to report to Congress on potential alternatives to the Army’s baseline disassembly and incineration process for disposal of lethal chemical agents and munitions (National Research Council, 1993). The legislation required the Army to perform a comparison of the baseline process with alternative technologies recommended for use by the National Academy of Sciences. In a 1994 report (National Research Council, 1994), the NRC recommended research and development of four alternative technology configurations. These included: neutralization followed by on-site or off-site incineration; neutralization followed by wet air oxidation followed by biological treatment; neutralization followed by supercritical water oxidation (SCWO); and neutralization followed by biological treatment.

O-ethyl S-[2-(diisopropylamino) ethyl] methyl phosphonothioate (VX) nerve agent is stockpiled at Newport, Indiana, and Bis (2-chloroethyl) sulfide (HD) mustard agent, at
Aberdeen, Maryland. The US Army selected chemical hydrolysis as the nonincineration technology to neutralize the chemical agent stockpiled in bulk ton containers at both sites. The hydrolysis process was to be followed by on-site biodegradation in the Sequencing Batch Reactor (SBR) (Irvine and Ketchum, 1988) for treatment of mustard hydrolysis products at Aberdeen and on-site SCWO for destruction of VX hydrolysis products at Newport. The caustic hydrolysis of VX reduces its toxicity by more than 10,000 times (Manthei et al., 2001). In order to comply with requirements of the Chemical Weapons Convention (CWC) (international treaty for the destruction of existing chemical weapon stockpiles and the nonproliferation of chemical warfare technology) and with US environmental regulations, extensive laboratory, bench-scale, and pilot-scale testing of individual processing steps was conducted to support engineering designs for the complete integrated processes (Harvey et al., 1994; Harvey et al., 1997; Irvine et al., 1997; DeFrank et al., 1997; US Army Program Manager for Chemical Demilitarization, 1996; McManus et al., 1996; US Army Program Manager for Chemical Demilitarization, 2000).

Following the events of September 11, 2001, the US Department of Defense decided to accelerate the destruction of the chemical agents stockpile at Newport and Aberdeen as safely and quickly as possible. After an extensive period of study it was decided to send the hydrolysates generated at Newport and Aberdeen to off-site treatment, storage and disposal facilities (TSDFs). While a number of disposal technologies were available at the TSDFs evaluated (e.g., incineration, deep well injection, and biological treatment) it was decided to send both hydrolysates to biologically based TSDFs. Because the products of the caustic hydrolysis of VX must be pretreated to enhance biodegradability, pretreatment was investigated in two distinct treatability studies, one employing the SBR for biotreatment, and the other, the PACT® process (patented by DuPont and registered trademark of USFilter/Zimpro Products) (McManus et al., 1996; Perma-Fix of Dayton, 2003). The primary focus of this paper is on the chemical neutralization of VX nerve agent stockpiled at Newport using caustic hydrolysis in the full-scale pilot SBR at the Newport Chemical Agent Disposal Facility (NECDF). The subsequent pretreatment steps that were taken for final biological disposal in an SBR system at a TSDF will be given only brief attention because the sequence of unit operations and processes employed differs little from that conducted at a conventional biological waste treatment at an industrial facility.

Materials and methods
The liquid nerve-agent VX is stored at Newport Chemical Depot (NECD) in carbon steel ton containers (TCs). When filled to capacity each TC holds approximately 0.68 m³ of agent. On January 17, 1997 the Department of the Defense authorized the Program Manager for Chemical Demilitarization’s Alternative Technologies and Approaches Project (PMATA) to pilot test an alternative destruction process to incineration at NECD. The current path forward for destruction of VX agent stockpiled at NECD by the NECDF is caustic hydrolysis at 90°C with 15 min for NaOH fill, 36 min for agent fill, 2.5 hours for REACT, 60 min for hydrolysate cool-down, and 15 min for DRAWD (Parsons, 2004).

System configuration
VX agent will be neutralized in the system depicted in Figure 1. The TCs will be moved from storage and loaded onto the Chemical Agent Transfer System (CHATS) cradle by a forklift and drained. Each CHATS is capable of draining and rinsing two TCs simultaneously. Once in position on the CHATS cradle, an operator (see Figure 2) cranks the TC until the end is fully inserted into the airtight glovebox where agent is then pumped out of the TC into the drained agent storage tank awaiting transfer to the neutralization reactors. The inside of the TC is flushed with a hot caustic solution of sodium hydroxide and water. Hot
caustic solution is pumped from one of the caustic wash tanks, through the TC and back into the originating caustic wash tank where it is held until transferred to the neutralization reactor for processing. Following two caustic washouts, the interior of the container is rinsed with approximately 95 L of hot water. The final step to decontaminate the TC involves circulating hot air (104°C) through the interior of the container for 60 min. The TC is then confirmed externally decontaminated and transported to storage.

Neutralization of VX occurs inside one of the two SBRs, each with a liquid capacity of about 3.8 m$^3$. For a 16.6% VX loading (reaction recipe: 16.6 wt.% VX, 8.8 wt.% NaOH, and 74.6 wt. % water), each SBR will treat agent drained from one TC (i.e., about 0.68 m$^3$) during one cycle. Each cycle begins with the caustic fill phase during which time 3.1 m$^3$ of 11 wt.% NaOH is added to the reactor and heated to 90°C. During the agent fill phase agent is added to the caustic through the static mixer in the recirculation loop at about 19 L/min for 36 min. A control system provides heating and cooling to maintain the temperature until the reaction is completed during a 2.5 hour react phase. Cooling is required to control the

---

**Figure 1** Newport Chemical Agent Disposal Facility system configuration

**Figure 2** Schematic of a CHATS
reactor temperature as the exothermic reaction occurs during fill, and to cool the hydrolysate before transfer to a hydrolysate holding tank. The reactor contents are vigorously agitated with a twin impeller agitator (paddlewheel) operating at 140 revolutions per minute. The upper impeller of the agitator is a three-blade axial flow design, and the lower impeller is a high shear, six-blade turbine design. Further mixing is accomplished by recirculating the VX and caustic through a honeycombed filter called a static mixer. The static mixer reduces the droplet size and increases the contact area between the caustic and the VX.

After the react phase, the reactor contents are cooled to 38°C and sampled. The hydrolysate samples are sent to the on-site laboratory for analysis. The hydrolysate from each cycle is pumped from the SBR to one of the eight hydrolysate holding tanks. The hydrolysate is held in the hydrolysate holding tanks awaiting laboratory confirmation of no detectable VX concentrations (Parsons, 2004).

**Reaction sequence**

VX is neutralized via both a major and minor pathway in the presence of caustic and elevated temperatures. As can be seen from Figure 3, 90% of VX is converted to ethylmethyl phosphonic acid (EMPA) and S-2-(diisopropylamino)-ethanethiol (thiolamine) in the major pathway and 10%, to S-(2-diisopropylaminoethyl) methylphosphonothioic acid (EA2192) and ethanol in the minor pathway. Under caustic conditions, EA2192 decomposes further to methyl phosphonic acid (MPA) and thiolamine. The rate of VX destruction ($r_{VX}$) in dilute solution is first order with respect to both the hydroxide ion concentration ([OH−]) and the VX concentration ([VX]) as shown below:

$$r_{VX} = -k_{VX}[\text{OH}^-][\text{VX}]$$

The rate constant, $k_{VX}$, is equal to 5.2 × 10^{-3} L (mole-s)^{-1} at 22°C and is roughly 117 times greater (i.e., 0.6084 L (mole-s)^{-1}) at 90°C, the temperature selected for hydrolysis at NECDF (Yang et al., 1992; Yang, 1999).

**Analytical methods**

Hydrolysate cannot be shipped off-site until verified to contain nondetectable levels of VX with a method detection limit (MDL) no greater than 20 parts per billion using a solid phase extraction (SPE) gas chromatography (GC) mass spectrometry/mass spectrometry (MS/MS) (ion trap) method. This method relies on the chemical ionization of VX (Z = 267) using a methanol reagent, the capture of the resultant 268+ ion in the ion trap, the release and electron ionization of the 268+ ion to daughter ions. Observed VX levels are quantified using the 128 daughter ion, although the presence of the 139 and 167 ions are used for confirmatory analyses. The determination of an MDL is defined in the US Code of Federal Regulations (CFR) 40 Part 136, Appendix B and involves the evaluation of the variability of the analyte concentration.

Hydrolysate will also be analyzed for schedule 2 compounds, as defined by the Organization for the Prohibition of Chemical Weapons (OPCW) and other waste criteria such as total organic carbon, pH, ignitability, etc. The OPCW, an international organization headquartered in the The Hague, The Netherlands, has responsibility for verifying that signers of the CWC treaty live up to the ban on chemical weapons usage and development. The CWC has two lists of chemicals with which OPCW is primarily concerned. Schedule 1 compounds are the chemical agents (e.g., VX), Schedule 2 compounds are the compounds that theoretically could be used, although not practical in terms of cost and resources needed, as building blocks for the formation of schedule 1 chemical agents. Breakdown
products from the neutralization of schedule 1 compounds are also considered to be schedule 2 compounds.

Results and discussion

Hydrolysis reaction

The Alternative Technology Program (ATP) investigated both stand-alone neutralization and neutralization followed by biodegradation using both sodium hydroxide and water as reagents to detoxify VX. A caustic neutralization process was selected because it was able to hydrolyze the sodium salt of EA2192, a compound that maintains anticholinesterase activity. Following caustic neutralization of VX, the resulting hydrolysate is primarily composed of water, caustic (sodium hydroxide – NaOH) and breakdown products from the hydrolysis of the VX (e.g., the sodium salts of thiolamine, EMPA, and MPA). The sodium salt of EA2192, while produced during the hydrolysis of VX in a minor parallel side-reaction (Figure 3), is simultaneously hydrolyzed to thiolamine and MPA during the reaction period.

Because VX is sparingly soluble at high pH, VX is added to a well-mixed reactor containing hot caustic at a rate that is only slightly greater than its rate of destruction so that accumulation of VX in the reactor is minimized. At a pH of 14, the half-life for VX is between 1 and 2 s. As is shown in Figure 4, the VX accumulates in the fill phase (i.e., 36 min for a VX loading of 16.6%) to a maximum value of about 120 mg/L. At 120 mg/L and a half-life of 2 s, virtually all of this residual VX is removed during the first minute of the react phase. The corresponding overall removal of VX during the fill and react phases is greater than 99.9999% of the initial VX present in a TC.

The hydrolysate has two phases, an aqueous phase in which VX decomposes, and an organic phase, in which VX may accumulate without decomposition. During the fill phase, VX will partition into other separate organic phases. The organic phases are composed of the stabilizer (added to the TCs to preserve VX during storage), the urea of the stabilizer, and a multitude of other organic compounds present in the hydrolysate including thiolamine and ethanol. During the react phase, the rapid hydrolysis reaction reduces VX to extremely low levels in the aqueous phase causing VX that had partitioned into the separate

Figure 3  Primary caustic hydrolysis reactions for VX
organic phases during the fill phase to diffuse into the highly reactive aqueous environment for destruction. The time during the react phase needed to allow the VX to transfer from the organic phase to the reactive aqueous phase depends upon the VX loading. This extra reaction time is critical to the success of the process because hydrolysate cannot be shipped off-site to a TSDF unless VX is shown to be nondetectable when using an analytical procedure that has a MDL of less than or equal to 20 ppb. As a result, the time for the react phase continues for at least 2.5 h after the VX concentration is estimated to be nondetectable (from calculations).

An extended react phase is also needed to ensure that the concentration of EA2192 in hydrolysate shipped to a TSDF is nondetectable with an MDL of less than or equal to 1 ppm. A simple model was utilized to estimate the concentration of EA2192 as a function of time for a VX loading of either 8% (agent from one-half TC per SBR) or 16% (agent from one TC per SBR) for two half-lives: 10.6 min, the expected half-life for EA2192 in caustic at 90°C, and 19.6 min. A half-life of 19.6 min was selected to check the impact of reduced initial hydroxide concentrations on performance. Only the 16% VX loading case is shown in Figure 4. As can be seen from this figure, EA2192 accumulates in the reactor until the end of filling and reduces steadily during the react phase to 1 ppm in less than 2.5 h for the 10.6 min half-life and in over 4 h for the 19.6 min half-life. The actual time needed to ensure that VX is nondetectable (for an MDL of less than or equal to 20 ppb) and EA2192 is nondetectable (for an MDL of less than or equal to 1 ppm) will be evaluated during plant start-up.

Nitrogen will be used to sweep and blanket tanks because of concerns with flammability of compounds such as ethanol. The nitrogen blanket will also minimize the partial oxidation of the thiolamine to its disulfide (i.e., 2, (2-diisopropylamino ethane) disulfide, or RSSR, for “R” as is defined in Figure 3) and consequently the creation of a greater and more varied separate organic phase that could obfuscate VX measurement.

**Pretreatment and biodegradation**

In a 1996 report the NRC concluded that: “The products of hydrolysis do not readily serve as the primary substrate for biological oxidation. Substantial quantities of co-substrate (i.e.,
other waste with high carbon content but low in phosphorus) are required to force the microbial utilization of phosphorus from the methyl phosphonic acid present in hydrolysate. Because of this need for high-carbon cofeed and because only limited success has been achieved in biodegrading Thiol, the hydrolysate is not a good candidate for treatment by on-site biodegradation prior to final disposal.” The NRC report was based on studies that employed extreme dilution (because of the high salt content) and the addition of biodegradable carbon in the form of isopropyl alcohol to achieve removal of EMPA and MPA in a phosphorus limited bench-scale SBR (DeFrank et al., 1997; US Army Program Manager for Chemical Demilitarization, 1996). The microbial consortium selected easily removed the ethyl group from the EMPA to produce MPA and used remaining MPA as a source of phosphorus for growth. While removing the alkyl phosphonates and oxidizing the thiolamine to its corresponding disulfide, this approach generated a relatively large quantity of liquid effluent and biomass and did not mineralize much of the disulfide. Later testing showed that simple pretreatment of VX-hydrolysate by chemical oxidation (i.e., NaOCl, UV/H₂O₂, etc) and, except for MPA, which required Fenton’s reagents for removal, successfully increased the relative biodegradability of the hydrolysate constituents (Honeywell/Parsons, 2002; Perma-Fix of Dayton, 2003).

In 2003, treatability studies were conducted by a biologically based TSDF that used SBRs for biological treatment. Schedule 2 compounds (EMPA, MPA, and thiolamine) were required to be removed or destroyed to less than 0.1% by weight. The system developed by the TSDF met this requirement with a combination of physical and chemical pretreatment steps prior to blending the treated hydrolysate with full-scale plant flow and feeding the combined flow to a two-tank SBR system. The pretreatment steps were oxidation of the thiolamine, pH reduction, addition of a catalyst to facilitate oxidation of phosphonates (MPA and EMPA) to inorganic phosphate, addition of more oxidizing agent, removal of precipitated solids by filtration, and pH adjustment and sparging to remove ammonia. The SBRs had a solids retention time of 50 days; an organic loading of approximately 0.2 kg total organic carbon (TOC) per kg of mixed liquor suspended solids (MLSS) per day and removed more than 90% of the remaining organic 5-day biochemical oxygen demand (BOD₅). The effluent generated from the biological treatment of pretreated hydrolysate in an SBR easily met CWC treaty and US environmental regulations (Perma-Fix of Dayton, 2003).

Conclusions
Neutralization of VX nerve agent stockpiled at Newport, Indiana will use caustic hydrolysis in an SBR. A VX loading of 16.6% (agent from one TC will be processed in one SBR cycle), a 36 min fill phase for agent addition, and a 2.5 h react phase will produce a hydrolysate which is nondetectable for VX for an MDL of less than or equal to 20 ppb and EA2192 for an MDL of less than or equal to 1 ppm. The resulting hydrolysate was pretreated at the bench-scale to enhance the biodegradability of the hydrolysis products and then added to an SBR for biological treatment. The biodegradation study demonstrated that the effluent generated from the biological treatment of pretreated hydrolysate in a SBR met CWC treaty and US environmental regulations.

References


Honeywell/Parsons (April 2002). An Evaluation of Pre-treatment of VX Hydrolysate for Disposition at Non-Incineration Based Treatment, Storage and Disposal Facilities (TSDFs).


US Army Program Manager for Chemical Demilitarization (PMCD; but now known as the Chemical Materials Agency (CMA)) (October 2000). Test and Evaluation Master Plan for the Newport Chemical Agent Disposal Facility.
