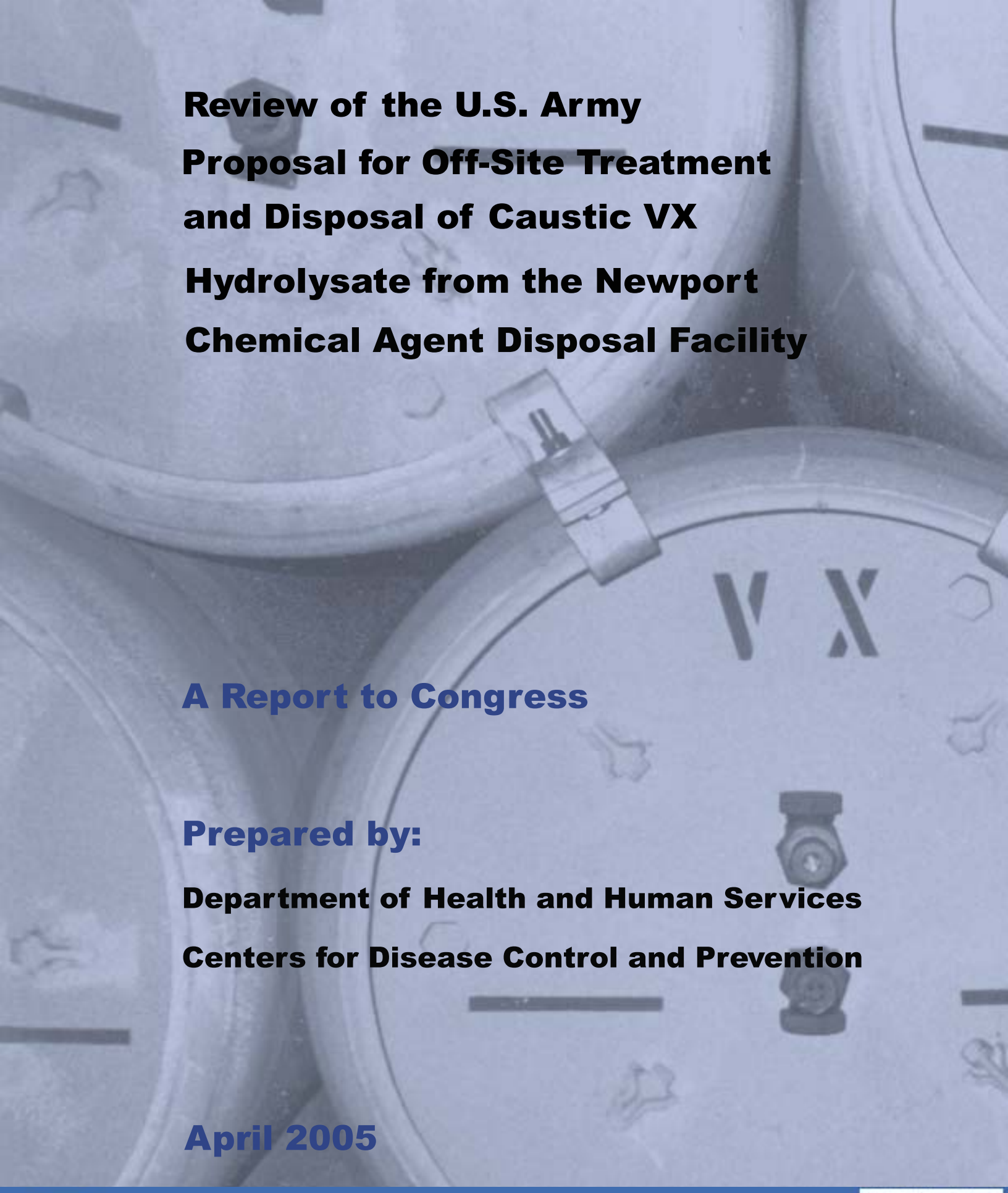

Review of the U.S. Army Proposal for Off-Site Treatment and Disposal of Caustic VX Hydrolysate from the Newport Chemical Agent Disposal Facility

A Report to Congress

Prepared by:

Department of Health and Human Services

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DEPARTMENT OF HEALTH AND HUMAN SERVICES
Centers for Disease Control and Prevention

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SUMMARY

The U.S. Army proposal for caustic VX hydrolysate (CVXH) transportation, treatment, and discharge into the Delaware River has raised concerns and questions about potential impacts on public health and the environment. This report describes the findings from the Centers for Disease Control and Prevention (CDC) evaluation of this proposal. CVXH is the waste product of the hydrolysis reaction of nerve agent VX, water, and sodium hydroxide that will be generated at the Newport Chemical Agent Disposal Facility (NECDF) in Newport, Indiana. The proposal is to transport CVXH from NECDF to the DuPont Secure Environmental Treatment (SET) Chambers Works facility in Deepwater, New Jersey, for secondary treatment and subsequent discharge in the Delaware River. Please note that the term *CVXH* is referred to in some reports as *Newport caustic hydrolysate* or *NCH*.

CDC's review of the CVXH disposal plan examined several critical issues, including (1) potential health hazards associated with the waste produced at NECDF, (2) potential risks associated with transportation of the material from Indiana to New Jersey, (3) ability of the DuPont facility to adequately treat the CVXH in addition to the ability of NECDF to produce caustic VX hydrolysate meeting clearance criteria, and (4) potential ecologic impact associated with discharge of the DuPont-treated material into the Delaware River. Because CDC did not have the expertise to review DuPont's ecologic report, CDC requested assistance from the U.S. Environmental Protection Agency (EPA), Region II. A summary of the results of CDC's evaluation are described below:

- CDC found that the potential human health hazards of the untreated CVXH are associated predominantly with its corrosive and caustic properties and not nerve agent effects, although trace levels of VX and EA 2192 (a degradation product with nerve agent properties) may be present. The toxicity of CVXH does not preclude handling and transportation provided that proper precautions are in place.

- The transportation plan meets Department of Transportation regulations, and precautions in the plan are adequate to protect the public, personnel, and environment.

Major Findings:

- The potential human health hazards of caustic hydrolysate are associated predominately with its corrosive and caustic properties.
- The precautions in the transportation plan are adequate to protect the public.
- The DuPont process should be capable of treating the major components of the waste with noted exceptions.
- More information is needed to evaluate the ecological risk of discharge of this waste into the Delaware River.

- CDC's technical review of the DuPont SET indicated it is a viable process and should be capable of treating the major components of CVXH (see subsequent discussion on phosphonic acids). However, the NECDF VX stockpile utilizes two chemicals (referred to as stabilizers), diisopropylcarbodiimide (DIC) and dicyclohexylcarbodiimide (DCC), added to prevent VX degradation during storage. The data indicate that CVXH produced from DIC-stabilized VX at the 8% agent loading level should meet the Army's clearance criteria for VX and EA 2192 during storage and can be treated at DuPont. The term "loading" refers to the total percentage of VX added to the NECDF process for reaction. Loadings greater than 8% of DIC-stabilized VX or any treatment of VX stabilized with DCC is not recommended until the treatment effectiveness is demonstrated and confirmed. Consequently, only a portion of the Newport VX stockpile currently can be processed to meet clearance criteria.

- The Environmental Protection Agency's (EPA's) analysis indicates that the DuPont risk assessment does not contain adequate information to determine that the aquatic ecologic risk from the discharge of treated CVXH to the Delaware River is acceptable. Further, the EPA expressed concerns that the 20 ppb clearance criterion for VX in CVXH is based "solely on the protection of humans from a drinking water source and may not be protective of aquatic organisms through ingestion or dermal exposure."

CDC does not recommend proceeding with the treatment and disposal at DuPont until EPA's noted deficiencies in the ecologic risk assessment are addressed.

In conclusion, while the CDC found that the Army/Dupont proposal was sufficient to address critical issues in the areas of potential human toxicity, transportation, and treatment of CVXH (generated from recommended VX loading and stabilizer), EPA concluded that the information regarding the ecologic risk of treated CVXH discharge into the Delaware River was inadequate.

Consequently, CDC cannot recommend proceeding with the treatment and disposal at the DuPont SET facility until EPA's noted deficiencies are addressed.

INTRODUCTION

The U.S. Army proposal for CVXH waste transportation, treatment, and discharge of treated material into the Delaware River has raised concerns and questions about potential impacts on public health and the environment. In a March 29, 2004, letter to the CDC, the four U.S. Senators from New Jersey and Delaware, along with four members of Congress (two from each State) requested that CDC formally review the proposal for off-site treatment of CVXH to determine "if there are public health risks involved with the Army's proposal." Additionally, the Governors and environmental protection officials of the affected States (Delaware and New Jersey) have publicly expressed concerns about the proposal.

Public Laws 99-145 (1986), and 91-121 (1970), as amended by 91-441 (1971) (50 U.S.C. 1521 and 1512) require the Department of Defense to obtain public health review and oversight by the Department of Health and Human Services of plans for the testing, transportation, and disposal of lethal chemical weapons. This function was delegated to CDC from the Office of the Surgeon General in 1981. CDC's public health oversight role usually ends when the lethal chemical warfare materials are destroyed, generally meaning that they have been reduced to hazardous waste that potentially contain only trace levels of chemical warfare agent. At that time the oversight responsibility falls under existing transportation and environmental disposal regulations. With respect to this specific proposal, however, CDC evaluated the off-site disposal plan pursuant to the congressional request, despite initial Army process information suggesting the waste would no longer contain detectable VX. This decision to conduct the evaluation was documented in a CDC letter to Congress dated April 16, 2004. CDC's review of NECDF process safety is not within the scope of this report; however, process safety at NECDF is reviewed by CDC as part of its routine oversight of chemical warfare agent disposal activities.

This evaluation was conducted in response to a request from several senators and members of Congress.

BACKGROUND

The Chemical Stockpile

The stockpile at Newport Chemical Depot, Newport, Indiana, consists of the chemical nerve agent O-ethyl S-[2- (diisopropylamino) ethyl] methyl phosphonothioate (VX) stored in bulk quantities (1,269 tons in 1,690 containers). VX contains phosphorus, oxygen, carbon, hydrogen, nitrogen and sulfur and is referred to as an organophosphate. VX is stabilized with several percent of either DIC or DCC or both to protect against decomposition. Forty-six percent of the stockpile at Newport consists of VX stabilized with DIC (potentially with small amounts of DCC stabilizer as a contaminant), 16% stabilized with DCC, and 38% stabilized with both DIC and DCC.

The Newport Chemical Agent Disposal Facility

NECDF was designed, and is to be operated, as a pilot-plant facility to destroy VX using caustic hydrolysis in a hot (194°F) aqueous solution of sodium hydroxide. This process forms CVXH, referred to in some reports as Newport caustic hydrolysate or NCH. The original plan was to further treat the resulting CVXH on-site by supercritical water oxidation (SCWO) to destroy organic components and then to ship the final SCWO effluent (brine) to a treatment, storage, and disposal facility. Because of mechanical problems encountered in the SCWO engineering scale test, conducted in Corpus Christi, Texas, in 2000, the Army initiated studies to directly ship NECDF CVXH off-site for disposal as an alternative to on-site SCWO treatment. The terrorist attacks of September 11, 2001, and continuing questions about the feasibility of implementing SCWO on-site within a reasonable timeframe supported the Army's decision to adopt "Project Speedy Neutralization." This approach involves shipping the CVXH to an existing treatment, storage, and disposal facility.

Issues Related to Destroying VX

Detailed testing of the caustic hydrolysis, as a process to destroy VX, began in the 1990s as part of the Army's Alternative Technologies and Approaches program. Various "recipes" for the destruction of the VX chemical agent stored at NECDF using sodium hydroxide were tested. Initially, an agent loading of 33% by weight was chosen for the program.

Confirmation of the completeness of destruction of VX depends on the analytical methods available to measure residual VX and EA 2192 (a degradation product) levels in the CVXH. During the past ten years, improvements in analytical techniques and instrumentation, coupled with increased personnel experience with these analyses, have lowered the detectable concentration of VX to the low parts per billion (ppb) levels and the detectable concentration of EA 2192 to the low tenths of parts per million (ppm) levels. However, the complexity and variability of the 33% VX loading caustic hydrolysate continued to complicate the VX analysis.

In October 2003, the Project Manager for Alternative Technologies and Approaches began to investigate the use of reduced VX agent loading in the hydrolysis reaction as a means of resolving analytical problems related to characterization of 33% agent loading CVXH. The Army currently plans to begin operation destroying DIC-stabilized VX at the 8% agent loading level and then, through a carefully monitored ramping-up process, move to 16% agent loading of DIC-stabilized VX.

The CVXH that will result from the caustic hydrolysis of VX at NECDF will consist of an organic phase and an aqueous phase. The organic phase exists both as an upper layer, floating on top of the aqueous phase, and as a suspension of droplets distributed throughout the aqueous phase (also known as an "emulsion"). The extent of organic layer forming above the aqueous layer depends on the amount of VX agent loaded into the batch to be treated. For instance, at 8% VX loading, only a thin sheen of organic layer reportedly is formed. However, at 33% VX agent loading, the organic layer comprises 3–5% of the mixture.

The Army's Proposal

The Army is investigating shipping the untreated caustic VX hydrolysate to the DuPont Secure Environmental Treatment (SET) facility in Deepwater, New Jersey for final treatment and disposal. The stated SET process objectives are to treat 3,000 to 7,000 gallons per day of CVXH. Process objectives will be (1) control of wastewater and sludge odors, (2) control of SET wastewater treatment plant operations (*e.g.*, effective dissolved organic carbon [DOC] removal, manageable foaming, pH control, solids management), and (3) meeting permit compliance limits for effluent biochemical oxygen demand (BOD5), whole effluent toxicity, total suspended solids, and ammonia.

The pH adjustment of the CVXH is the first step of the pretreatment process prior to introducing the waste to the biologic treatment system. Peroxide treatment, to destroy odorous substances, follows CVXH pH adjustment. The final step in the treatment train utilizes a two-stage powder activated carbon treatment system® (PACT®); testing of the process was conducted under conditions emulating the actual plant flow rate and hydraulic retention time. The solids in the effluent will be settled, dewatered, and buried in a permitted hazardous waste landfill on site at DuPont. The remaining effluent, which includes other plant waste, then will be disposed in the Delaware River. A proposal to remove phosphonates from the effluent has been developed by DuPont, and this report was provided to CDC on March 2, 2005. This new process will be evaluated separately in a subsequent CDC report.

APPROACH

This comprehensive evaluation of the CVXH disposal plan included examination of several critical aspects, including (1) potential health hazards associated with the waste produced at NECDF, (2) potential risks associated with transportation of the material from Indiana to New Jersey, (3) ability of the DuPont facility to adequately treat the CVXH in addition to the ability of NECDF to produce caustic VX hydrolysate meeting Army-defined clearance criteria while also meeting DuPont acceptance requirements, and (4) potential ecologic impact associated with discharge of the DuPont-treated material into the Delaware River. Each aspect of the shipment, treatment, and disposal were evaluated as described below.

- DuPont's report, *Health Hazard Considerations for Safe Management of Newport Caustic Hydrolysate,* along with original referenced studies and supplemental material provided by DuPont and the U.S. Army, were reviewed and evaluated in a collaboration between CDC and the Division of Toxicology of the Agency for Toxic Substances and Disease Registry (ATSDR). Because the primary scientific studies cited in support of DuPont's report were not peer-reviewed, ATSDR/CDC had these studies independently peer-reviewed before examination. The final ATSDR evaluation was peer reviewed external to the government in addition to the usual approval process for CDC/ATSDR documents.

- DuPont's transportation report, *Transportation Safety Assessment and Risk Management Plan*, was reviewed and evaluated by CDC in collaboration with the Department of Transportation (DOT). This evaluation comprised two aspects. The first aspect was to determine whether the plan is consistent with DOT regulations for shipping hazardous materials. Representatives from DOT assisted CDC in making this determination. The second aspect involved examination of the transportation plan with respect to the specific hazards associated with caustic VX hydrolysate. CDC conducted this evaluation directly. The entire CDC evaluation of the transportation plan was reviewed by DOT, peer-reviewed external to the government, and subjected to the normal approval process for CDC documents.

In conducting this evaluation CDC partnered with several organizations, including the Agency for Toxic Substances and Disease Registry, the Environmental Protection Agency and Carmagen Engineering, Inc.

This report was peer-reviewed by subject matter experts in toxicology, ecology and engineering.

- DuPont's treatability report, *Treatability of Newport Caustic Hydrolysate*, and DuPont's subsequent *Basic Data Report* were reviewed and evaluated in close collaboration between CDC and a contractor, Carmagen Engineering, Inc., of Rockaway, New Jersey. Carmagen assembled a group of experts knowledgeable in the requisite disciplines to assist CDC in this review and assessment. The group consisted of a former chairman of the National Research Council Stockpile Committee, a retired assistant director for the CDC Division of Laboratory Sciences, a retired Program Manager for Chemical Demilitarization, a professor at Stevens Institute of Technology, a retired regional laboratory director for EPA, and a former environmental health and safety manager/process design manager for ARCO Chemical. Because the reliability of the DuPont process partly depends on the ability of NECDF to produce CVXH in a consistent manner that meets DuPont acceptance criteria, Carmagen also evaluated the NECDF process to produce CVXH. The Carmagen report was peer-reviewed external to the government in addition to the normal clearance process for CDC documents.

- Because CDC did not have the expertise to review DuPont's ecologic report, *Screening Level Ecological Risk Assessment for Discharge of Effluent from the Treatment of Newport Caustic Hydrolysate*, CDC requested assistance from the U.S. Environmental Protection Agency (EPA), Region II. EPA agreed to independently evaluate the ecologic risk associated with discharge of SET-treated CVXH in the Delaware River. EPA internally peer-reviewed their evaluation, and CDC had the EPA assessment peer-reviewed external to the government.

Each of the evaluations is attached in its entirety (attachments 2-5), along with a list of abbreviations (attachment 1). The external peer-review comments are available upon request. Because of data gaps, the complexity of issues examined, and interrelations between the different aspects of the proposal, several lengthy rounds of formal questions and requests for information were submitted to DuPont, the U.S. Army, and Army contractors. The findings from this evaluation are based primarily on data requested by and provided to CDC. Each evaluation itemizes the pertinent materials reviewed. CDC cannot guarantee the completeness or accuracy of all information used to complete this evaluation. Therefore, significant new information that may become available after publication of this report could change CDC's findings and conclusions.

Finally, in the interest of ensuring technical accuracy, the Department of Health and Human Services provided officials at the Department of Defense (DoD) with a draft copy of this report in December 2004. Comments were received from DoD officials in January 2005 and were addressed by CDC and EPA. A final external peer-review of the entire report, plus EPA's findings and the responses to comments from DoD officials was conducted, and the results of each of these efforts are available upon request. Once the report was completed, the DoD requested to provide official comments.

FINDINGS

The major findings for each aspect of the evaluation are presented below.

Health Hazard Considerations for Safe Management of Newport Caustic Hydrolysate [Caustic VX Hydrolysate]

- The untreated CVXH is highly corrosive (pH > 13). The major potential human exposure pathway for the material is dermal contact that could result in severe, possibly irreversible, burns to the skin or eyes. Overall, the risk from an accidental spill appears to be comparable to that expected for any highly corrosive material with high pH.

- Although the individual DuPont and U.S. Army toxicity studies are limited in scope and applicability, the studies—considered in their totality—do not preclude the handling and transportation of untreated CVXH if appropriate engineering and administrative controls and personal protective equipment are used.

- Regarding ethyl methylphosphonic acid (EMPA) and methylphosphonic acid (MPA), two degradation products contained in CVXH, if an accident occurs during handling and transportation, groundwater or surface water contamination and subsequent human ingestion is unlikely but possible. Limited data are available to determine the risks from exposure to nonlethal ingestion of EMPA and MPA. However, oral lethality studies indicate the two substances have a Hodge and Sterner toxicity rating of 4 (slightly toxic).

- Although the health effects demonstrated in animal toxicity studies of exposure to CVXH were not due to residual VX or EA 2192 (another degradation product, potentially present in CVXH, with nerve agent properties), the data in one of the cited studies were inconclusive due to the lack of appropriate study controls.

- The clearance criteria for VX and EA 2192 are suitable for the risk management approaches proposed by the Army. According to these criteria, the CVXH will be certified to be non-detected for VX and EA 2192 using analytical methods with an EPA method detection limit of #20 ppb for VX and #1 ppm for EA 2192. The 20 ppb criterion for VX is the same as that used for the U.S. Army emergency drinking water standard for soldiers.

Transportation Safety Assessment and Risk Management Plan

- The DuPont transportation plan appropriately addresses key risk management considerations, as well as DOT's regulations for transporting hazardous materials.

- Precautions used to manage the corrosivity hazard characteristic in the event of a spill are adequate to protect response personnel from the caustic nature of the CVXH, low-level residual agent VX, or residual EA 2192 at levels estimated for maximum credible event analysis.

- Transportation of CVXH produced when processing VX with the DIC stabilizer at 8% loading is feasible. However, transportation of CVXH produced with VX stabilized with DCC or at agent loadings greater than 8% is not recommended at this time because of uncertainties in the amount of organic layer and potential residual VX exceeding 20 ppb and/or EA 2192 exceeding 1 ppm.

Treatability of Newport Caustic Hydrolysate [Caustic VX Hydrolysate]

Production of Caustic VX Hydrolysate at NECDF

- The data demonstrate the effectiveness of neutralizing DIC-stabilized VX using sodium hydroxide at the 8% VX agent loading rate. Scale-up of the process from laboratory/bench-scale to pilot-scale should be feasible. However, because NECDF will be a pilot facility, process changes must be anticipated, along with resultant variations in hydrolysate composition sent for off-site treatment.

- The VX agent loading recipe and the specific stabilizer (DIC, DCC) employed significantly impacts the destruction process, hydrolysate composition, analytical methods validation, and possibly solids formation. Scale-up of the process from 8% to 16% VX agent loading and processing of DCC-stabilized VX are of particular concern because of the potentially significant VX concentration in the resulting organic layer, and possible problems in the analysis of CVXH. The process and analytical data for VX stabilized with DCC or mixtures of DIC and DCC have not been provided to CDC. [1]

[1] On March 2, 2005, CDC received the U.S. Army Technical Data Report 81-05, VX-Sodium Hydroxide Hydrolysate Manufacture (CAMDS 100 gallon reactor) dated August 26, 2003. CDC will include a review of this report in a subsequent report.

- The impact of potential solids formation during the hydrolysis process on operations (e.g. possible blockage of the in-line static mixer, control valves, and sampling system), VX analytical methods, and off-site hydrolysate treatment is unknown. The transition from 8% to 16% VX agent loading, as well as variation in the VX stabilizer characteristics, is of concern and requires additional detailed studies.

Analytical Methods for VX and EA 2192 in Caustic VX Hydrolysate

- The current analytical methods for the analysis of VX agent and EA 2192 in 8% VX loaded, DIC-stabilized CVXH are adequate to detect and quantify at the established clearance levels for VX (#20 ppb) and EA 2192 (#1 ppm).

- The Army's proposed use of EPA's method detection limit (MDL) concept in the clearance of off-site shipment does not preclude analytical instrument detection of low-levels of VX and EA 2192 (generally below 20 ppb for VX and 1 ppm for EA 2192) in the DIC-stabilized, 8% agent loading CVXH. The perception that the clearance criteria (defined as "non-detected" with a MDL of #20 ppb VX or #1 ppm EA 2192) indicate absence of analytically detectable VX and/or EA 2192 could be misleading. While CDC believes that utilizing the MDL approach would not result in public health concerns, the Army needs to address potential public misperceptions regarding the detection or non-detection of VX in CVXH. A simpler reporting scheme (i.e., non-detected, detected at <20 ppb, or detected at >20 ppb) should be considered.

- The overall quality assurance/quality control (QA/QC) plan and procedures for the NECDF laboratory are well designed and documented. However, NECDF laboratory personnel must continue to implement the QA/QC plan by developing day-to-day operational data to demonstrate that all analytical systems are operational and under control before plant startup.

Treatment of Caustic VX Hydrolysate at DuPont

- The DuPont facility should be able to effectively treat the CVXH generated from an 8% VX agent loading with DIC stabilizer (i.e., pH adjustment, thiolamine destruction, conversion of EMPA to MPA), with the exception of MPA, for which only minimal reduction has been demonstrated. DuPont has recent developed a process to remove phosphonates, including MPA. CDC will evaluate this process in a separate report.

- The performance of the DuPont facility should be unaffected when treatment of material is alternated between Aberdeen sulfur mustard hydrolysate and Newport CVXH.

- The DuPont treatability studies have not yet demonstrated the effective treatment of CVXH produced from 16% agent VX loading, nor has effective treatment been shown for CVXH produced from 8% agent VX loading, where the VX was originally stabilized with DCC or a mixture of DIC and DCC stabilizers.

Screening Level Ecological Risk Assessment for Discharge of Effluent from the Treatment of Newport Caustic Hydrolysate [Caustic VX Hydrolysate] - Summary of EPA Findings

- DuPont's Screening Level Ecological Risk Assessment (SLERA) does not contain information adequate to conclude that there is no unacceptable risk from the discharge of treated CVXH to the Delaware River. Also, a number of constituents of the discharged waste were omitted from the analysis.

- Several issues need to be addressed before treatment and discharge of this treated CVXH to the Delaware River can occur, including whole effluent toxicity testing procedures, potential for the presence of VX nerve agent and other toxic breakdown products in the CVXH, addition of phosphorus to the estuary, and the National Pollutant Discharge Elimination System permit.

- The EPA expressed concerns that the 20 ppb clearance criteria for VX is based "solely on the protection of humans from a drinking water source and may not be protective of aquatic organisms through ingestion or dermal exposure."

- EPA believes that the conclusions of the SLERA for discharge of treated CVXH in the Delaware River are not valid.

As additional ecologic assessment information is made available, EPA and CDC will conduct further evaluation of this proposal.

CONCLUSIONS

The potential human toxicity of the untreated CVXH predominantly is associated with its corrosive and caustic properties and not nerve agent effects, although low levels of VX and EA 2192 may be present in CVXH. The transportation plan meets DOT regulations, and precautions in the plan are adequate to protect the public and personnel. The database supports the position that CVXH produced with DIC-stabilized VX at the 8% VX agent loading level should meet the Army's clearance criteria for VX and EA 2192. Loadings greater than 8% of DIC stabilized VX or any treatment of VX stabilized with DCC is not recommended until the treatment effectiveness is demonstrated and confirmed. Therefore, based on information provided for this review, only a portion of the Newport VX stockpile can be processed to meet clearance criteria. The technical review of the DuPont SET indicated it is a viable process and should be capable of treating the CVXH. EPA's ecologic analysis indicates the DuPont assessment does not contain information adequate to determine that the ecologic risk from the discharge of treated CVXH to the Delaware River is acceptable. Consequently, CDC cannot recommend proceeding with the treatment and disposal at the DuPont SET facility until EPA's noted deficiencies are addressed.

Attachment #1

LIST OF ABBREVIATIONS

ALD	approximate lethal dose
ATSDR	Agency for Toxic Substances and Disease Registry
BOD5	five day biological oxygen demand
ºC	degrees Celsius
cal/g	calories per gram
CAMDS	Chemical Agent Munitions Disposal System
Carmagen	Carmagen Engineering, Inc.
CAS	Chemical Abstract Services
CDC	Centers for Disease Control and Prevention
CFR	Code of Federal Regulations
CHPPM	U.S. Army Center for Health Promotion and Preventive Medicine
CVXH	Caustic VX Hydrolysate (equivalent to VX hydrolysate or Newport caustic hydrolysate)
CWA	chemical warfare agent
DA	U.S. Department of the Army
DCC	dicyclohexyldicarbodiimide
DIC	diisopropylcarbodiimide
DIP	dissolved inorganic phosphorus
DOC	effective dissolved organic carbon
DOT	U.S. Department of Transportation
EA 2192	S-[2-diisopropylaminoethyl] methylphosphonothioic acid
EMPA	ethyl methylphosphonic acid
EPA	U.S. Environmental Protection Agency
ºF	degrees Fahrenheit
FMEA	Failure Mode and Effects Analysis
g	grams
g/L	grams per liter
GC/IT/MS/MS	gas chromatography coupled with ion-trap mass spectrometry
GC-ITMS	gas chromatography-–ion -trap mass spectrometry
gpd	gallons per day
H_2O_2	hydrogen peroxide
H_2SO_4	sulfuric acid
HD	sulfur mustard
HI	Hazard Index
IERP	Integrated Emergency Response Plan
IMPA	isopropyl methylphosphonic acid
ISO tanks	transportable tote containers
LC/IT/MS/MS	liquid chromatography coupled with ion–trap mass spectrometry
LD_{50}	classical lethal dose in 50% of animal population
LLVX	Low Level VX
m/z	mass-to-charge ratio
MDL	[U.S. EPA defined] method detection limit
mg/kg	milligrams per kilogram

mg/kg/d	milligrams per kilogram per day
Min	minutes
MPA	methyl phosphonic acid
MSDS	Material Safety Data Sheet
N	nitrogen
N	not determined
NaOH	sodium hydroxide
NCEH	National Center for Environmental Health
NCH	Newport (Indiana) Caustic Hydrolysate (equivalent to caustic VX hydrolysate)
NECDF	Newport Chemical Agent Disposal Facility
NJDEP	New Jersey Department of Environmental Protection
NJPDES	New Jersey Pollution Discharge Elimination System
NPDES	National Pollutant Discharge Elimination System
NRC	National Research Council
OECD	Organization for Economic Cooperation and Development
P	phosphorus
PACT®	Powdered Activated Carbon Treatment System
PAM	pamphlet
pH	negative log of hydrogen ion concentration
PI	Performance Indicator
PMATA	Project Manager for Alternative Technologies and Approaches
ppb	parts per billion
ppm	parts per million
PRG	preliminary remediation goal
Q	acceptable [with] qualifications
QA/QC	quality assurance/quality control
QC	quality control
RCWA	recovered chemical warfare materials
RfD	reference dose
S/N	signal-to-noise
SAIC	Science Applications International Corporation
SAR	structure activity relationships
SCWO	Supercritical Water Oxidation
SET	[DuPont] Secure Environmental Treatment [Chamber Works]
SLERA	Screening Level Ecological Risk Assessment
SPE	solid-phase extraction
TB MED	Army's Medical Technical Bulletin
Team	Carmagen Team
TSDF	Treatment, Storage, and Disposal Facility
U	unacceptable
µg/mL	microgram per milliliter
USEPA	U.S. Environmental Protection Agency
VX	O-ethyl S-([2-(diisopropylamino) ethyl)] methyl phosphonothioate
wt. %	weight percent

Attachment #2

Review of the Toxicology and Health Hazard Considerations for Safe Management of Newport (Indiana) Caustic VX Hydrolysate

By

Agency for Toxic Substances and Disease Registry
in collaboration with the
Centers for Disease Control and Prevention
Atlanta, Georgia

November 3, 2004

SUMMARY

The Centers for Disease Control and Prevention (CDC) requested that the Agency for Toxic Substances and Disease Registry (ATSDR) assess DuPont Report 14523, *Toxicology Assessment of Health Hazard Considerations for Safe Management of Newport Caustic Hydrolysate,* dated March 3, 2004, and its supporting documentation as part of a larger evaluation of the proposed transportation and disposal of caustic VX hydrolysate (CVXH), waste material produced by the reaction of the nerve agent VX with sodium hydroxide. In response to this request, ATSDR conducted the following assessment in collaboration with CDC. Please note that in this report, the more technically accurate term *CVXH* generally is used in place of *Newport caustic hydrolysate* or *NCH*.

It should be noted that the CVXH toxicity testing discussed in ATSDR's assessment was conducted on 33 weight percent loading material. The current treatment plan by the Army is to process at an 8 weight percent loading. Because of the lower loading in the current plan, the toxicity testing that was conducted at the higher loading percentages should be considered "worst case" in terms of the potential toxicity of the CVXH.

The major findings and conclusions of the ATSDR assessment are as follows:

- The untreated CVXH is highly corrosive. The major human exposure pathway for the material is dermal contact, which could result in severe, possibly irreversible, burns to the skin or eyes. Overall, the health risk from exposure resulting from an accidental spill appears comparable with that expected for any highly corrosive material with high pH.
- Although the individual toxicity studies are limited in scope and applicability, the studies—considered in their totality—do not preclude the handling and transportation of untreated CVXH if appropriate engineering and administrative controls and personal protective equipment are used.
- The supporting studies do not provide adequate data on the nature of the toxicity of ethyl methylphosphonic acid (EMPA) and methyl phosphonic acid (MPA) (constituents of CVXH). EMPA and MPA are highly water soluble; therefore, if an accident occurs during handling and transportation, groundwater or surface water contamination and subsequent human ingestion are unlikely, but possible, outcomes. Limited data are available to determine the risks from exposure to nonlethal ingestion of EMPA and MPA. However, oral lethality studies indicate the two substances have a Hodge and Sterner toxicity rating of 4 (slightly toxic).
- While the effects in animals following administration of CVXH are not likely due to residual VX or EA 2192 (a degradation product of VX with nerve agent properties potentially present in CVXH), the data in one of the cited studies are not conclusive due to lack of appropriate controls.
- Clearance criteria for VX and EA 2192 are suitable for the risk management approaches presented.

INTRODUCTION

ATSDR was provided copies of the toxicity studies examined by DuPont, as well as other studies commissioned by the Army or its contractors. The studies examined major components of the CVXH. Because neither the studies cited by DuPont nor the other toxicity studies provided were peer-reviewed, ATSDR first had the studies peer-reviewed. An ATSDR contractor identified nongovernmental independent professionals for the peer review. After receiving the peer-reviewer comments, ATSDR reviewed DuPont's report and referenced studies to generate the following comments.

DuPont stated that its assessment of potential health risks of CVXH was conducted to support decisions related to the transportation and treatment of CVXH at the DuPont Secure Environmental Treatment (SET) facility. DuPont and the Army proposed that the CVXH be transported from the Newport Chemical Agent Disposal Facility in Newport, Indiana, to the DuPont SET Facility in Deepwater, New Jersey, for final treatment and discharged into the Delaware River.

The DuPont assessment states that the composition of the CVXH is 80% water with minor amounts of sodium hydroxide (Chemical Abstract Services [CAS]# 1310-73-2), diisopropylamino ethylthiolate (thiolamine, CAS# 5842-07-9), ethyl methylphosphonic acid (EMPA, CAS# 1832-53-7), and methylphosphonic acid (MPA, CAS# 993-13-5). Approximately 1% is composed of "other compounds," including ethanol (CAS# 64-17-5), diisopropylamino ethyl disulfide (CAS# 65332-44-7), and diisopropylamine (CAS# 108-18-9).

ANALYSIS AND DISCUSSION

DuPont's assessment concludes CVXH is not a Department of Transportation (DOT) poison or toxic material and has no nerve agent characteristics. DuPont indicates that CVXH is corrosive and capable of damaging the eye and skin after contact exposure. Gastrointestinal injury can result from ingestion. In support of these conclusions, the DuPont assessment of CVXH cited the following studies:

- Finlay, C. Ethyl Methylphosphonate: Oral Approximate Lethal Dose (ALD) in Rats. Haskell Laboratories, February 26, 2004.
- Finlay, C. Methylphosphonic Acid: Oral Approximate Lethal Dose (ALD) in Rats. Haskell Laboratories, February 26, 2004.
- Manthei J, Way R, Gaviola B, Burnett D, Bona D, Durst H, Thompson S. Toxicological Evaluation of VX Decontamination Wastestreams According to DOT Test Procedures, February 1999.
- Kemper, R. Ethyl Methylphosphonate: Computational Toxicology Analysis. Haskell Laboratories, March 1, 2004.
- Kemper, R. Methylphosphonic Acid: Computational Toxicology Analysis. Haskell Laboratories, March 1, 2004.

The Army subsequently provided additional studies:

- Manthei J, Way R, Gaviola B, Bona D, Burnett D. Alternative Technology Program: Intravenous Toxicological Evaluation of Four VX Wastestreams in Mice." U.S. Army ERDEC, ECBC-TR-173, August 2001.
- Janus, E.R. Analysis of EA2192 Monitoring and Sampling Issues at Newport Chemical Agent Disposal Facility. Environmental Health Risk Assessment Program. U.S. Army Center for Health Promotion and Preventive Medicine, November 2001.
- McDonald, J., and Campen M., Revised Final Report, Acute Inhalation Toxicity Testing of 2-(diisopropylamino)Ethyl Mercaptan. Lovelace Respiratory Research Institute, April 2, 2004.

Analysis of the Finlay (2004) studies

The studies conducted by Finlay (2004) determined a lethal dose of 2300 milligram per kilogram (mg/kg) and 3400 mg/kg for MPA and EMPA, respectively. The chemicals were administered as a single oral (intragastric intubation) dose to one rat per dose level; body weights and clinical signs of toxicity were observed for 14 days postexposure. These studies provide useful information about lethality. The Finlay (2004) studies were "approximate lethal dose" studies that use fewer animals but have been shown to closely predict the results of classical lethal dose in 50% of animal population (LD_{50}) studies. However, the studies presented no information to assess the nature of the acute toxicity—that is, this study generated no information about the type of toxic effects (i.e., organ system affected). Therefore, DuPont's statement in its toxicology assessment—"…MPA and EMPA have relatively low acute oral toxicity…"—provides limited perspective on the toxicity of these components of CVXH. In reality, the Findlay studies were lethality studies, not acute exposure studies; the "acutely toxic effects" observed at 2300 mg/kg MPA and 3400 mg/kg EMPA were death. With respect to handling and transportation of CVXH, however, the likelihood of ingestion of CVXH (including MPA and EMPA) is low. The Hodge and Sterner toxicity rating for MPA and EMPA is 4 (slightly toxic). Therefore, although cited studies were limited in scope, when considered in conjunction with the toxicity rating and potential exposure scenarios, MPA and EMPA components do not introduce excess risk in handling and transportation activities.

Analysis of the Manthei et al. (1999) study

The Manthei et al. (1999) study, performed by the Army, provided toxicity data to establish shipping and packaging criteria (for CVXH) according to 49 Code of Federal Regulations (CFR). In this study, severe dermal injuries occurred when the CVXH homogenate was applied to rabbit skin at 1000 mg/kg; and gastrointestinal injury and death (two of 12 rats) occurred in rats dosed orally at 500 mg/kg. The study concluded that this compound was less than a Level III toxic according to 49 CFR. If, as is our understanding, the Level III requirement is for an LD_{50} of <500 mg/kg, then the CVXH would appear to meet this requirement. For caustic compounds, 40 CFR outlines

corrosivity characterization needs. Under some circumstances, DOT recommends further toxicity tests for more complete characterization (49 CFR 173.137 and 1992 Organization for Economic Cooperation and Development Guideline No. 404).

Additionally, toxicity testing of the top organic layer of test material killed 12 of 12 dermally treated rabbits (500 mg/kg) and 12 of 12 orally treated rats (1000 mg/kg). The animals died from agent (VX)-associated effects. Subsequent testing revealed that the organic layer contained 2000 ppm VX. The Manthei et al. (1999) abstract states that a follow-up study would be conducted, but as of this writing, no follow-up study has been provided. However, it is clear that the samples were contaminated with VX as a result of laboratory error, rendering the results of this study questionable. Furthermore, this high-level VX contamination was not consistent with other work by the same laboratory. In summary, the results of this particular part of the Manthei et al. (1999) study must be discounted as not representative of the toxicity of CVXH.

DuPont's assessment states that the CVXH contains no VX (later clarified to "no detectable VX) with a MDL (method detection limit) of twenty parts per billion (ppb) or less" (DuPont Position on the Question of VX in Hydrolysate, July 24, 2004). The ATSDR review assumes this to be the case because the CVXH will be analyzed for VX and must meet the 20 ppb criteria before shipment.

Analysis of the Manthei (2001) Study

In another study by Manthei (2001), adult, male ICR mice were dosed intravenously with CVXH. LD_{50} values were calculated to be 349.5 mg/kg, 39.0 mg/kg, and 279.3 mg/kg for the bottom, top, and homogenate samples, respectively. Chemical analysis indicated no VX at or above the detection limit of 20 ppb in the bottom layer or the homogenate. The top layer was not analyzed for VX. Effects observed included convulsions, exophthalmus, straub tail, collapse, and prostration. Although the toxic signs in the mice probably resulted from by-product salts, the investigators did not use controls needed to determine whether the effects were due strictly to the by-product salts and not to residual VX or EA 2192. The conclusion was based on the absence of observed tremors and salivation. The use of controls or acetylcholinesterase activity would have provided more definitive results. ATSDR concludes that the upper organic layer material on CVXH is more toxic than the aqueous lower layer, and the effects in the animals probably resulted from by-product salts and high pH (caustic nature).

Analysis of the McDonald and Campen (2004) Study

The McDonald and Campen (2004) study was designed as an acute toxicity screen for diisopropylamino ethylthiolate (thiolamine), which typically is used as a basis for establishing a dose regimen in subchronic and other studies. Decreased body weight gain and nasal porphyrin accumulation was observed in the high dose groups (316 mg/m^3). Because no sham or age-matched control animals were used in this study, it is not possible to draw definitive conclusions about these effects. McDonald and Campen (2004) noted the pathology analysis was a crude indicator of a lack of toxicity of this

component of CVXH. The usefulness of this study in assessing inhalation toxicity of thiolamine for use in the CVXH assessment is limited.

Analysis of the Kemper (2004) studies

As stated in the DuPont assessment, the computational toxicology analyses of MPA and EMPA (Kemper 2004) did not provide useful predictions of the acute toxicity of these chemicals. The positive predictions of toxicity for developmental effects for both MPA and EMPA (by the Toxicity Prediction by Computer-Assisted Technology [TOPKAT] model), and bacterial mutagenicity for EMPA (by the Deductive Estimation of Risk from Existing Knowledge [DEREK] model), and the negative prediction for skin sensitization (by TOPKAT) are not reliable because the query structures are poorly represented in the TOPKAT or DEREK models' datasets. The report also provides a nonuseful large predictive oral LD_{50} range (which appears to be the predicted 95% confidence limits), instead of the single predicted LD_{50} value it should have provided. Thus, ATSDR agrees with DuPont that the Structure Activity Relationships analyses performed did not provide useful predictions of the toxicity of these chemicals.

The results of the DEREK analysis (by Kemper 2004) suggested that EMPA could cause mutagenic effects in bacteria. The DuPont document states that mutagenicity is unlikely on the basis of negative test results for isopropyl methylphosphonate (IMPA), a close structural analogue of EMPA. However, because of its chemical structure, IMPA would not be expected to react similarly in the body as EMPA. Thus, whether IMPA should be used as a surrogate to make conclusions about the mutagenicity of EMPA is not clear.

Analysis of the Janus (2001) Study

The purpose of the Janus (2001) paper was to calculate a Performance Indicator (PI) value for EA 2192. The document states that PIs are "developed to monitor and evaluate discrete subsystem requirements that must be demonstrated to achieve the design and technical performance goals of the Newport Pilot Plant." The document briefly discusses the relative potency of VX and EA 2192, stating that EA 2192 toxicity is generally within the same order of magnitude as VX, therefore, it is appropriate to use the interim VX reference dose (RfD) to calculate the PI for EA 2192. The document uses an algorithm to calculate the PI that is based on U.S. Environmental Protection Agency (EPA) Region IX's Preliminary Remediation Goal (PRG) approach. In this algorithm, the interim oral RfD for VX (of 6E-07 mg/kg/day) is used to develop a dermal PI value of 1.128 ppm for EA 2192. The PI methodology appears appropriate; however, the EPA PRG User's Guide/Technical Background Document states, "For many chemicals, a scientifically defensible data base does not exist for making an adjustment to the oral slope factor/RfD to estimate a dermal toxicity value." Whether the permeability coefficient, as used in the PI algorithm, is appropriate is unclear because the caustic nature of the CVXH will compromise the ability of the stratum corneum to serve as a protective barrier, thereby allowing more direct entry. Nonetheless, Manthei et al. (1999) did not observe VX or EA 2192 effects after dermal application of caustic VX hydrolysate to rabbits (1000 mg/kg

for 24 hours). Therefore, ATSDR believes that the PI appears to be suitable for worker protection when appropriate personal protective equipment is used to handle CVXH.

FINDINGS

- Although the individual toxicity studies were limited in scope and applicability, the studies considered in their totality do not preclude the handling and transportation of CVXH, assuming appropriate engineering, administrative, and personal protection policies are in place.

- Although the studies on MPA and EMPA do not provide data on the nature of the toxicity, the oral lethality studies indicate that the two compounds have a Hodge and Sterner toxicity rating of 4 (slightly toxic). Furthermore, oral ingestion of MPA and EMPA during handling and transportation of CVXH is unlikely.

- MPA and EMPA are highly water-soluble; therefore, if an accident occurs during handling and transportation, groundwater or surface water contamination and subsequent human ingestion is an unlikely, but possible outcome. Data are insufficient to determine the risks from exposure to nonlethal ingestion of MPA and EMPA.

- Information about thiolamine is limited. Mercaptans in general are well-known noxious volatile odorants and skin irritants.

- Although the effects noted in the intravenous studies (Manthei et al. 2001) probably do not result from residual VX or EA 2192 in the CVXH, the data are not conclusive because of a lack of appropriate controls to distinguish between agent effects and by-product salts or high pH (caustic) at the 33% VX loading. In another study (Manthei et al. 1999), lack of nerve agent effects were observed after CVXH exposure in dermally exposed rabbits and orally exposed rats.

- The PI of 1 ppm for EA 2192 appears to be adequate given the Manthei et al. (1999) data, which did not note any VX or EA 2192 effects in rabbits after dermal exposure to CVXH. Although no chemical analysis for EA 2192 was conducted, this CVXH fraction obtained from a 33% VX loading is assumed to have contained at least representative quantities of EA 2192. For the 8 weight percent loading CVXH planned for disposal, the concentration of EA 2192 probably would be lower than that found in these experiments.

- As the DuPont assessment indicates, CVXH is highly corrosive. This is supported by the Manthei et al. (1999) study and the chemical property information. The major human exposure pathway is dermal contact, which will result in severe, possibly irreversible damage. Eye injury is also possible, and inhalation of aerosolized CVXH potentially could damage the respiratory tract.

CONCLUSION

ATSDR believes that, in the event of an exposure after an acute release, the greatest concern would be the caustic nature of the CVXH, which potentially could cause severe burns upon contact. Overall, the risk from an accidental spill appears to be comparable with what would be expected for any highly corrosive material with a high pH.

Attachment #3

Review of the Transportation and Risk Management Provisions for Caustic VX Hydrolysate

By

Centers for Disease Control and Prevention
in collaboration with the
Department of Transportation

November 3, 2004

INTRODUCTION

CDC prepared this report to analyze DuPont's *Transportation Safety Assessment and Risk Management Plan* Safety, dated March 3, 2004. CDC considered this component of the response from two perspectives, described as follows:

First, CDC determined whether the transportation plan is consistent with Department of Transportation (DOT) requirements for shipping hazardous materials from the point of generation—Newport, Indiana—to the point of final treatment and disposal—Deepwater, New Jersey. This determination differs from typical CDC reviews because of the different hazard characteristics and larger volumes involved; therefore, CDC requested and received assistance from DOT in conducting this part of the review.

Second, CDC determined whether the safeguards, emergency planning, and other risk management considerations that will be applied to this proposed project are comparable to transportation of other potentially hazardous substances, such as recovered chemical weapons material (RCWM). Some of the criteria considered by CDC included route selection considerations, shipping containment provisions, emergency planning, and notification activities. CDC is conducting this analysis directly. Considerable overlap exists in the safety considerations required by DOT and the safety provisions considered by CDC in reviews of RCWM transportation plans.

BACKGROUND

The Newport Chemical Agent Disposal Facility proposes to treat agent VX with sodium hydroxide to produce caustic VX hydrolysate (CVXH) with no agent detected ≤20 parts per billion (ppb). This clearance criteria is equivalent to the Army's drinking water standard for nerve agents for field use by soldiers, and CDC considers it appropriately conservative for use as a clearance criteria for shipment of waste.

The CVXH can be characterized as being predominantly caustic and aqueous with a smaller organic fraction, the extent of which depends on the VX loading rate used in the batch process. Batch VX loadings of 8%, 16%, and 33% have been examined for the Newport facility. The current plan calls for plant startup using an 8% loading of VX stabilized with diisopropylcarbodiimide (DIC), and this is the only VX loading rate fully evaluated in this review. Please note that in this report, the more technically accurate term *CVXH* generally is used in place of *Newport caustic hydrolysate* or *NCH*.

Other major by-products of interest in the caustic VX hydrolysate are ethyl methyl phosphonic acid (EMPA), methyl phosphonic acid (MPA), thiolamine, and EA 2192. EMPA and MPA are of interest because of their potential for persistence in the environment, and thiolamine is of interest because of its strong and disagreeable characteristic odor. As a general matter, EA 2192 exhibits nerve agent properties similar to VX. However, EA 2192 will be limited to ≤1 part per million (ppm) for a cleared batch of CVXH, a concentration deemed by CDC to be suitable for the risk management

practices contained in this proposal. Toxicity considerations of these by-products are discussed in the full CDC report.

DISCUSSION

CDC considers four broad functional areas applicable to the proposed Newport CVXH transportation plan.

- Packaging and Containment—The DuPont transportation plan discusses several options for the containment, including dedicated tank trucks and transportable tote containers ("ISO tanks"). The materials of construction and strength of the container design were considered, as were placement of valves, remote operability characteristics designed to minimize personnel potential exposure to tank contents, and vulnerability of the valves to bump hazards. DOT, in correspondence to CDC, noted that the plan "proposes to use equipment and procedures that go beyond what the regulations require for materials with the specific hazard and risk involved."[1]
- Personnel Qualifications—The transportation plan proposes use of two hazardous materials shippers that have "excellent safety records" as evidenced by "very low DOT recordable accident rates" and "very favorable DOT safety ratings." Each of the two shippers reportedly maintains high qualification standards by employing experienced personnel who have passed rigorous background checks. Extensive training, including hazardous materials spill response, will be required of the drivers for this project. A team of two prequalified drivers will be used for each trip.
- Route Planning—DuPont analyzed potential risk associated with four identified highway routes and one combined rail and highway route for transporting the CVXH from Newport, Indiana, to Deepwater, New Jersey. Factors considered included number, length, and duration of each trip; accident potential based on historic truck accident rates for each route; general population exposure potential for each route; potential environmental impact from accidental CVXH release for each route; and emergency response capability for each route. A commercially available risk analysis algorithm was used to quantitatively estimate total potential impact potential for each route option analyzed.
- Emergency Preparedness—DuPont describes its Integrated Emergency Response Plan (IERP) used to support ongoing transportation incidents. A detailed specific emergency response plan would be developed for this proposed CVXH shipping plan and shared with appropriate state and local responders along the selected transportation route. DuPont also has IERP teams in place in Belle, West Virginia, and Deepwater, New Jersey, to serve as regional service centers to support incident responses if needed. In accordance with the IERP, these teams consult with and advise on-scene DuPont personnel and local emergency response personnel. As needed, additional on-scene advisors or response resources may be deployed.

[1] E-mail correspondence from Reeves (DOT) to Decker (CDC), May 19, 2004, re: Transportation Plan for Chemical Weapons Waste

DuPont's transportation analysis is predicated on the assumption that the CVXH poses a corrosivity hazard with no attendant nerve agent properties. Most transportation plans reviewed by CDC involve limited amounts of chemical warfare agents moved in one or a very limited number of moves. This plan differs both in the volumes of and predominant characterization of the material to be moved.

CDC asked DOT personnel to review the DuPont transportation plan for overall consistency with DOT requirements for hauling hazardous materials. DOT determined the plan generally met or exceeded DOT requirements. However, DOT recommended that the shipping designation for the CVXH be reconsidered to reflect that it is a corrosive liquid, basic, inorganic, not otherwise specified, rather than the organic corrosive designation described in the plan. DOT's review reflected DuPont's characterization of the CVXH.

In evaluating RCWM transportation plans, CDC also typically reviews agent air monitoring. Air monitoring for chemical agent before and after a move of RCWM is usually an integral part of a plan to detect any breech in containment so corrective action can be taken. For the CVXH, the Army and DuPont have stated that VX agent is required to be destroyed to ≤20 ppb to qualify for shipment.[2] Because this clearance level would produce minimal safety hazard when compared with the corrosive nature of the CVXH, agent air monitoring for VX would not be useful and consequently was not included in the DuPont proposal.

Batch processing studies indicate that, if VX survives, it would partition into the organic fraction of the caustic VX hydrolysate. The Army has stated that, at an 8%–16% VX loading, the organic fraction should be limited to approximately <1%–3% of VX hydrolysate. In the absence of mixing or agitation, the organic fraction separates, and layers on top of the aqueous component of the CVXH. At an 8% VX (DIC-stabilized) batch loading, the organic layer remains nearly indistinguishable from the much larger inorganic, aqueous fraction. The CVXH will be reprocessed if VX is detected above the MDL. However, the current sampling and analytical method used for process batch clearance does not attempt to evaluate potential VX in the organic layer of CVXH but instead evaluates the organic and aqueous components as a mixture.

Examination of the impact of potential agent VX survival in the organic fraction of the CVXH requires estimation of an upper-bound level for the VX concentration within this fraction. On the basis of existing batch studies, CDC believes a reasonable upper-bound estimate is approximately 1–10 ppm of residual VX. This assumes a maximum of ≤20 ppb VX for the CVXH mixture and a VX loading of 8%. CDC noted, however, that one study showed a VX residual of approximately 2100 ppm in the organic layer (at a VX feed rate of 33%) of VX/sodium hydroxide (NaOH) batch hydrolysate,[3] despite analysis

[2] Presentation to CDC by Parsons and U.S. Army Chemical Materials Agency, May 24, 2004, re: Response to CDC questions regarding proposed operations at the Newport Chemical Agent Disposal Facility.
[3] Manthei JH, Way RA, Gaviola BI, et al. Toxicological Evaluation of VX Decontamination Wastestreams According to Department of Transportation (DOT) Test Procedures, U.S. Army ERDEC, 1999 February.

showing that the hydrolysate mixture had ≤20 ppb VX. CDC contacted the lead author on this study to ask whether follow-up work was conducted to resolve and clarify this finding. Although recommended, the study was not repeated. The author believed, however, that this VX finding in the organic layer resulted from a sample mishandling in the laboratory and is not consistent with his laboratory's other studies of VX/NaOH hydrolysate.

A maximum credible event could involve a 5000-gallon tank truck or tote in an in-transit accident that ruptures the containment. If the above study result is the outlier it appears to be, then human exposure to VX at an estimated maximum of 1–10 ppm could occur with direct, unprotected contact with the organic fraction of the spilled material. The nerve agent effects of this level of VX and possible concurrent EA 2192 at the 1-ppm level are difficult to assess. However, to reach this maximum exposure to VX, the organic fraction (estimated at <0.5% by volume of the total contents for the 8% loading level CVXH) would need to remain undiluted from any mixing from the spill, which CDC believes is highly unlikely. Mixture and dilution of the organic fraction with the much larger aqueous fraction, to the extent that the corrosivity of the spilled material would present the most significant hazard, would be more likely.

Inhalation exposure to VX vapor in a spill is believed to be negligible given its low initial assumed concentration in the CVXH and the relatively low volatility of VX. Because of the corrosivity of the bulk of the CVXH, emergency responders are required to take appropriate precautions to avoid contact with the spilled material; consequently, prevention of exposure to low residual VX, even if the organic fraction remains intact, should not require extraordinary measures. As with any release of hazardous liquid materials, untrained observers and the public should be kept away from the active response zone.[4]

To be thorough, CDC sought to evaluate the likelihood and potential impact of a shipment of off-specification CVXH that could contain residual VX above the clearance level (≥20 ppb VX). At CDC's request, the Army's contractor evaluated the probability of human or system error resulting in shipping of off-specification CVXH.[5]

The review of off-specification scenarios identified a potential cross-contamination link (a three-way valve that controls flow of both hydrolysate and agent) that could result in agent VX reaching the CVXH holding tank after batch reactor sampling. This potential link, without mitigation, reportedly would result in a calculated annual event frequency of shipping off-specification CVXH of approximately 1 per 20,000. Processing estimates for NECDF range from a low of less than 200 shipments per year up to a maximum of about 900 shipments per year if the entire stockpile is processed in one year. For cross-contamination to risk health or safety of transportation personnel would require

[4] The risk concerns of residual VX discussed herein also would apply to the low level residual EA 2192 that could reside in the hydrolysate.

[5] "Quantitative Subsystem Hazard Analysis of Potential for Off Site Transfer of Hydrolysate Containing Above the 20 ppb Method Detection Limit", Mary Kay O'Connor Process Safety Center, Texas A&M University System (TAMUS), August 2004.

coincidence of the event with a shipping accident large enough to release the VX hydrolysate and to splash the drivers or other people who might be in the area of the accident. The DuPont transportation review estimates the maximum likelihood of an accident involving a release of CVXH at 1 in 13,000. This estimate is based on actual observed transportation accident statistics in the United States. Combining the probabilities of two independent events—an off-specification shipment of CVXH involved in an accident severe enough to release its contents—yields an event likelihood of well under 1 in 1,000,000, which risk management specialists consider insignificant. Add to this the probability of a responder or other person being splashed during the event, and the total risk would be further reduced. Nonetheless, Dupont should consider deferring CVXH shipment during severe weather, such as heavy prolonged rains, icing, and snowstorms, to reduce accident risk.

CDC believes the potential agent-related risk to human health and safety from a transportation accident involving off-specification CVXH is negligible. Nonetheless, the Material Safety Data Sheet (MSDS) for CVXH should recommend as a precaution that medical response personnel evaluate anyone having direct skin contact with released CVXH for possible nerve agent effects so appropriate medical intervention can be taken if needed. However, nerve agent effects are extremely unlikely, and the corrosiveness of caustic VX hydrolysate is likely to be the major concern.

Finally, the highly odorous nature of normal-process CVXH should be noted. Although the cause of the odors would not be expected to result in adverse health impacts directly, knowledge that the spilled material originated from a facility processing agent VX could result in considerable confusion and possible panic during the event. This characteristic of CVXH should be described clearly to avoid potential misunderstandings. The MSDS for CVXH should alert responders to its disagreeable odor characteristics to help inform both responders and the public and to minimize possible confusion or concern over exposure to airborne VX.

CONCLUSIONS

This transportation analysis was based on information about CVXH produced with VX at the 8% loading level and stabilized with DIC. The remainder of the stockpiled VX, which is stabilized with DCC or with a mixture of DIC and DCC, is not addressed in this review because of inadequate characterization of the organic layer.

The DuPont plan appropriately addresses CDC's key risk management considerations, as well as DOT's requirements for transporting hazardous materials. The predominant potential hazard during transportation of CVXH is its corrosivity. Precautions used to manage this hazard in a spill are adequate to protect response personnel from the low-level residual agent VX or residual EA 2192 at levels estimated for maximum credible event analysis.

MATERIALS REVIEWED

1. E-mail correspondence from Reeves (DOT) to Decker (CDC), May 19, 2004, re: Transportation Plan for Chemical Weapons Waste

2. Presentation to CDC by Parsons and U.S. Army Chemical Materials Agency, May 24, 2004, re: Response to CDC questions regarding proposed operations at the Newport Chemical Agent Disposal Facility.

3. Manthei J, Way R, Gaviola B, Burnett D, Bona D, Durst H, Thompson S. Toxicological Evaluation of VX Decontamination Wastestreams According to DOT Test Procedures, February 1999.

4. Manthei J, Way R, Gaviola B, Bona D, Burnett D. "Alternative Technology Program: Intravenous Toxicological Evaluation of Four VX Wastestreams in Mice." U.S. Army ERDEC, ECBC-TR-173, August 2001.

5. "Quantitative Subsystem Hazard Analysis of Potential for Off Site Transfer of Hydrolysate Containing Above the 20 ppb Method Detection Limit", Mary Kay O'Connor Process Safety Center, Texas A&M University System (TAMUS), August 2004.

6. DuPont Technical Assessment on U.S. Army Newport (Indiana) Project, Executive Summary, E.I. du Pont de Nemours and Company, March 2004.

7. Burke C. Transportation Safety Assessment and Risk Management Plan – Shipments of Newport (Indiana) Caustic Hydrolysate (NCH) Newport IN to Deepwater NJ, DuPont Safety, Health and Environment Excellence Center, March 2004.

8. Zimmerman G, Ensminger J, Saulsbury J. Transportation Analysis for the Off-Site Shipment of Liquid Process Effluent from the Newport Chemical Agent Disposal Facility at the Newport Chemical Depot, Indiana, Oak Ridge National Laboratory for the U.S. Army Chemical Materials Agency, December 2003.

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Attachment #4

Assessment of the Treatability of Caustic VX Hydrolysate at the DuPont Secure Environmental Treatment Facility

By

Carmagen Engineering, Inc.
in consultation with the
Centers for Disease Control and Prevention

November 3, 2004

SUMMARY

To completely ascertain the capability and effectiveness of the DuPont Secure Environmental Treatment (SET) facility to treat caustic VX hydrolysate (CVXH), the Centers for Disease Control and Prevention (CDC) and Carmagen Engineering, Inc. (Carmagen), recognized that, in addition to reviewing the DuPont treatability test results, the Newport Chemical Agent Disposal Facility (NECDF) destruction process and the analytical methodologies for CVXH clearance also had to be assessed to ensure that the hydrolysate being shipped to the SET facility will be adequately characterized and that VX and EA 2192 levels in the CVXH will meet Army clearance specifications. Please note that in this report, the more technically accurate term *CVXH* generally is used in place of *Newport caustic hydrolysate* or *NCH*. These assessments were considered essential elements to ensure safe SET facility operations. Therefore, the Carmagen Team (Team) focused its review in three areas consisting of (1) process issues at NECDF, (2) analytical methods, and (3) CVXH treatment at DuPont. The review comprised several meetings with people from the Army, Chemical Materials Agency, Parsons, and DuPont at which presentations were made, followed by in-depth discussions. These meetings were followed up by written questions and requests for additional documentation. Documentation received in response to the Team's questions and requests for additional information was substantial.

The major findings from the three areas examined by the Team are shown below. *These findings are valid only for an 8% diisopropylcarbodiimide (DIC)-stabilized VX hydrolysate. The current database is insufficient to allow extrapolation to other VX loadings or stabilizers.*

Process Issues (Chapter 2)

Only laboratory/bench-scale runs have been completed for the process, and scale-up to the integrated full-size facility is based on anticipated processing conditions. Recently, several safety studies were completed that recommended changes in the design and operation of the NECDF. The impact of the responses to these recommendations and possible facility changes on the final process is unknown.

Finding 2.1. The database supports the efficacy of neutralizing DIC-stabilized VX using sodium hydroxide at the 8% VX-loading rate. Scale-up of the process from laboratory/bench scale to pilot scale should be operationally feasible. However, because the NECDF will be a pilot facility, changes must be anticipated in operating mode and hydrolysate composition sent for off-site treatment.

Finding 2.2. VX loading (weight percent) and the specific stabilizer (DIC; dicyclohexyldicarbodiimide [DCC]) employed significantly impact the process, hydrolysate composition, analytical methods validation, and possibly solids formation. Scale-up of the process from 8% to 16% VX loading is of particular concern (because of the similarity of the organic-phase volumes from 16% to 33% VX-loading batches), the potentially high VX concentration in the resulting organic layer, and the analytical problems identified with 33% VX loading.

Finding 2.3. The impact is unknown of solids formation during hydrolysis on operations (potential for blockage of the in-line static mixer, control valves, and sampling system), VX analytic methods, and off-site hydrolysate treatment. The transition from 8% to 16% VX loading, as well as stabilizer change, is of concern and requires additional detailed studies.

Analytical Methods (Chapter 3)

The purpose of the review and evaluation of the analytical methods was to define the adequacy of the proposed NECDF analytical methods to meet current programmatic requirements for detecting and quantifying VX and EA 2192 in the CVXH.

Finding 3.1. The methods for analyzing VX and EA 2192 in 8% VX-loaded, DIC-stabilized CVXH are adequate to detect and quantify at the established clearance levels for VX and EA 2192 (non-detected with a U.S. Environmental Protection Agency (EPA) method detection limit (MDL) of ≤20 parts per billion [ppb] for VX and ≤1 part per million [ppm] for EA 2192).

Finding 3.2. The use of the EPA's method detection limit (MDL) for clearance levels does not preclude analytical instrument detection of low levels of VX and EA 2192 (generally <20 ppb VX and <1 ppm EA 2192) in the CVXH. The perception that the MDL clearance criteria indicate absence of analytically detectable VX and EA 2192 could be misleading. While CDC believes that utilizing the MDL approach would not result in public health concerns, the Army needs to address potential public misperceptions regarding the detection or non-detection of VX in CVXH. A simpler reporting scheme (i.e., non-detected, detected at <20 ppb, or detected at >20 ppb) should be considered.

Finding 3.3. The overall quality assurance (QA) and quality control (QC) plan and procedures for the NECDF laboratory are well designed and documented. However, NECDF laboratory personnel must continue to implement the QA/QC plan by developing day-to-day operational QC data to demonstrate that all analytical systems are operational and under control before plant startup.

Caustic VX Hydrolysate Treatment (Chapter 4)

Once transported to the SET facility, CVXH will be further treated to adjust the pH and remove the organic by-products by a series of physicochemical and biologic processes. The DuPont treatability studies were designed and executed to obtain scale-up parameters for engineering design and regulatory compliance, rather than (except for a few specific species) to assess fate, transport, and biodegradability of environmental contaminates. The treatability studies also investigated the capability of the SET facility to treat alternating hydrolysate feeds from Aberdeen (sulfur mustard [HD]) and Newport (VX).

Finding 4.1 The SET facility effectively treats the CVXH generated from an 8% VX loading with DIC stabilizer (i.e., pH adjustment, thiolamine destruction, conversion of ethyl methylphosphonic acid to methyl phosphonic acid [MPA]), except for MPA, for which only minimal reduction is demonstrated.

Finding 4.2. The SET facility treatment performance should be unaffected when treatment of hydrolysate feeds from Aberdeen (HD) and Newport (VX) is alternated.

Finding 4.3. The DuPont treatability studies have not yet demonstrated the effective treatment of 16% VX-loaded CVXH, nor of 8% VX-loaded CVXH with DCC or a mixture of DIC and DCC stabilizers.

Table of Contents

1. Introduction

1.1 Background

The Newport Chemical Depot, Newport, Indiana, stockpile comprises the chemical nerve agent O-ethyl S-[2- (diisopropylamino) ethyl] methyl phosphonothiolate (VX) stored in bulk quantities (1269 tons in 1690 containers). VX contains phosphorus double-bonded to an oxygen atom and single-bonded to a carbon atom. VX is stabilized with several percent of either diisopropylcarbodiimide (DIC) or dicyclohexyldicarbodiimide (DCC) to protect against decomposition. Forty-six percent of the stockpile at Newport consists of VX stabilized with DIC (potentially with small amounts of DCC stabilizer as a contaminant), 16% stabilized with DCC, and 38% stabilized with both DIC and DCC. VX is highly toxic and lethal in both liquid and vapor forms. Because munitions containing agent and energetics are not present at Newport, the process requirements for disposing of only ton containers of agent are less demanding than the processing requirements for the more complex stockpiles at most sites.

The Newport Chemical Agent Disposal Facility (NECDF) was designed and is to be operated as a pilot-plant facility because the process has been demonstrated only at a laboratory/bench scale. Production operation will begin only after pilot-scale operations have been completed, the data reviewed and assessed, and approval granted by the State of Indiana and the federal government. Because pilot-plant operations generally uncover unknown elements, the probability is high of process modifications and change—including possible changes in the analytical methods and procedures used to support plant operations and hydrolysate clearance—during this piloting period.

The NECDF was designed to destroy VX using caustic hydrolysis in a hot (194 degrees Fahrenheit [°F]) solution of sodium hydroxide. Initially the plan was to further treat the resulting hydrolysate on-site by Supercritical Water Oxidation (SCWO) and to ship the final SCWO effluent (brine) to a Treatment, Storage, and Disposal Facility (TSDF). Mechanical problems encountered in the SCWO engineering-scale test, conducted in Corpus Christi, Texas, in 2000, led to initiation of studies to directly ship the NECDF hydrolysate to an off-site treatment facility as an alternative to on-site SCWO treatment. The terrorist attacks of September 11, 2001, and continuing questions about the feasibility of implementing SCWO on-site in any reasonable timeframe supported the decision to adopt “Project Speedy Neutralization.” This involves shipment of the neutralized product (i.e., caustic hydrolysate) off-site for further treatment.

Detailed testing of the caustic hydrolysis process began with the Alternative Technologies and Approaches program in the 1990s. The “recipe” for NECDF agent destruction using sodium hydroxide was tested on a laboratory scale, and an agent loading of 33% was chosen for the program.

Confirmation of the efficiency of destruction of VX depends on the analytical methods available to monitor for residual VX and EA 2192 levels in the resultant hydrolysate. During the past ten years changes in analytical techniques and instrumentation, coupled

with increased personnel experience with these analyses, have lowered the detectable concentration of VX to the low parts per billion (ppb) levels and the detectable concentration of EA 2192 to the low tenths of parts per million (ppm) levels for 8% VX loading hydrolysate. However, the complexity and variability of the 33% VX loading hydrolysate continued to complicate the VX analysis.

By October 2003, the Project Manager for Alternative Technologies and Approaches had begun to investigate the use of reduced VX loading to preserve resources and obviate the need to resolve differences in data and data interpretation for the 33% VX-loading hydrolysate. The program plans to begin operations at 8% VX loading of DIC-stabilized agent and then, through a carefully monitored ramping-up process, move to 16% VX-loading, DIC-stabilized agent.

1.2 Nature of the Caustic VX Hydrolysate

The hydrolysate that will result from the caustic hydrolysis of VX at the NECDF comprises an aqueous phase and an organic phase. The organic phase exists both as an emulsion with droplets distributed throughout the continuous aqueous phase and as a visible organic layer that floats on top of the continuous aqueous phase. The extent to which a separate organic phase floats on the lower aqueous layer depends on the VX loading. As the VX loading increases, the quantity of organic phase available to form an organic layer (above that which forms a stable [or metastable] emulsion) increases.

At 33% agent loading (weight percent), the organic layer was significant (3%–5% by volume). The VX concentration in this organic layer was approximately 20 times the concentration in the bulk hydrolysate (>20 ppb), although disagreement exists within the program about the validity of the measurements (Wojciechowski, 2003). For 16% agent loading, the organic layer was 2–3 volume percent; for 8% agent loading, the separate "organic layer" was only a sheen at the surface of the hydrolysate. The "organic layer" has not been analyzed at 8% and 16% agent loadings; only mixed (homogenized) samples were analyzed. Obtaining samples of this organic layer for 8% agent loading poses significant technical difficulties. Centrifugation of a 550-milliliter (mL) sample of 8% CVXH showed that the maximum organic layer that could be "separated" was 0.45%–0.5%. These differences demonstrate the significant impact of agent loading on hydrolysate characteristics.

1.3 Clearance

Since its inception, a key tenet of the Army Chemical Demilitarization program has been safety of the workers and public. Department of the Army (DA) Pamphlet (PAM) 385-61, entitled "Toxic Chemical Agent Safety Standards," defines the approach for verifying the thoroughness of the neutralization process as using laboratory analyses to ensure that the chemical agent is ≤20 ppb. This concentration is measurable and is a quantifiable upper limit concentration in drinking water (20 ppb criterion is for soldiers). However, the procedure and methodology to verify the 20 ppb criterion in CVXH have been a

challenge (see Section 3). As stated in the Low Level VX (LLVX) panel report (Science Applications International Corporation [SAIC], 2003):

> The panel is not aware of any document that clearly states the exact criteria for offsite shipment of VX hydrolysate from NECDF or any document that codifies the Army's commitment to the public for offsite shipment.

The report, *Generation and Clearance of Hydrolysate for Treatability Studies in Support of Newport Operations*, states:

> To clear the hydrolysate, the analytical results must be non-detect for VX with a method detection limit (MDL) of less than or equal to 20 parts per billion (ppb). Non-detect is defined as the absence of a signal in the VX retention time window for ion 128, or a signal with a signal-to-noise (S/N) ratio of less than or equal to 3, or a concentration below the calculated MDL.

These criteria are incompatible in that an analytical response for VX could be classified as "analytically detected" by implementation of the "analyte retention time/signal-to-noise (S/N) ratio equal to or greater than 3" detection criteria, but reported as "non-detect" by the "less than the established MDL" criterion (see Section 3).

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1.4 Analytical Methods

Significant resources were expended for almost a decade to develop an analytical method that could reliably and accurately measure VX concentration in CVXH at lower and lower levels for a 33% VX agent loading without success. The newer analytical methods demonstrated the presence of detectable levels of VX in 33% DIC-stabilized CVXH and the inability to demonstrate an MDL of ≤20 ppb. This unexpected result led to an aggressive investigation of the causes and possible solutions for addressing the issue to bring the plant into operation.

An independent assessment panel was convened in October 2003 to evaluate the significance of the observation of "persistent" LLVX in caustic hydrolysate at the 33% agent loading level and to determine whether data were sufficient to confirm whether VX forms in CVXH (SAIC, 2003). Two conclusions of the panel were:

> There are significant uncertainties in the Solid Phase Extraction (SPE)/gas chromatography-ion trap mass spectrometry (GC-ITMS) method that make it difficult or impossible to quantify LLVX.
>
> It is not possible to determine the origin of the "persistent" LLVX in VX hydrolysate from the currently available data. The panel could not rule out formation of VX in VX hydrolysate or the hypothesis that has been advanced that there is a quasi steady state concentration of VX in VX hydrolysate due to a competition between agent destruction and formation. The current data from the analytical method did not enable the panel to determine if detectable VX was

originating from VX hydrolysate (that is, either residual untreated VX or formation within the VX hydrolysate matrix) or was formed during the analytical procedure.

Consequently, efforts during the past year have been devoted to evaluating the effect of reduced VX loading on

- VX caustic hydrolysis destruction,
- VX reformation during long-term storage, and
- VX formation after a reduction in pH accompanied by a concomitant formation of an organic layer.

This evaluation has paralleled the development, evaluation, and validation of analytical methodologies for measuring VX and EA 2192 in the 8% DIC-stabilized CVXH. At the time of this writing, methods for analyzing VX and EA 2192 in 8% DIC-stabilized CVXH and VX in 16% DIC-stabilized CVXH had been established in the NECDF laboratory, and the performance of these methods had been validated through various precision and accuracy studies. Implementation and validation of methods for ethyl methylphosphonic acid (EMPA), methyl phosphonic acid (MPA), and thiolamine in 8% DIC-stabilized hydrolysate are expected to be completed shortly. Similar work on other methods required for 16% DIC-stabilized hydrolysate and 8% DCC-stabilized hydrolysate were scheduled for completion later in 2004. Validated methods for anticipated processing conditions are essential to ensure that hydrolysate shipped off-site to a TSDF meets Army criteria.

1.5 Carmagen Engineering, Inc.

The Centers for Disease Control and Prevention (CDC) engaged Carmagen Engineering, Inc. (Carmagen) to assemble a group of knowledgeable experts (Team) to help evaluate the DuPont Technical Assessment on U.S. Army Newport (Indiana) Project (March 2004). The Team consisted of a former chairman of the National Research Council Stockpile Committee, a retired assistant director for the CDC/NCEH Division of Laboratory Sciences, a retired Program Manager for Chemical Demilitarization, a professor at Stevens Institute of Technology, a retired regional laboratory director for EPA, and a former environmental health and safety manager/process design manager for ARCO Chemical. Specifically, Carmagen was asked to evaluate the "Treatability of Newport (Indiana) Caustic Hydrolysate" portion of the DuPont report.

To ascertain the capability and effectiveness of the DuPont Secure Environmental Treatment (SET) facility at Chambers Works (Deepwater, New Jersey) to treat CVXH, the Team recognized that an assessment of the NECDF destruction process and an examination of the analytical methodologies to be used for CVXH clearance were required to ensure that the hydrolysate being shipped to the SET facility will be adequately characterized and that VX and EA 2192 levels in the CVXH will meet Army clearance specifications. These assessments were considered essential elements to ensure safe SET facility operations. Therefore the Carmagen Team focused on three areas:

- Process Issues (NECDF),
- Analytical Methods, and
- Caustic VX Hydrolysate Treatment (DuPont).

The review comprised several meetings with people from the Army, Chemical Materials Agency, Parsons, and DuPont at which presentations were made and discussed in depth. These meetings were followed up by written questions and requests for additional documentation. Documentation received in response to the Team's questions and requests for additional information was substantial.

1.6 Report Outline

The report contains five chapters.

- Introduction—Discusses the historical evolution of the NECDF project and the charge to and approach taken by the Carmagen Team.
- Process Issues—Discusses the impact of VX loading on the process, i.e., nature and extent of the two-phase CVXH, VX partitioning to the organic layer, clearance quality assurance (QA) and quality control (QC), scale-up, and storage.
- Analytical Methods—Reviews and evaluates the use and data quality objectives of VX and EA 2192 measurements, sampling procedures, validation of methods, and QC of the analytical processes.
- Caustic VX Hydrolysate Treatment—Describes pH adjustment, oxidative pretreatment, PACT® biotreatment, and VX and EA 2192 destruction.
- Major Findings—Presents major findings.

2. Process Issues

2.1 Introduction

Although the primary purpose of this report is to examine issues associated with the treatability of the hydrolysate produced by the Newport facility, as noted in the Introduction, a discussion of processing issues is important. The composition of hydrolysate sent for treatment depends on the nature of the VX being hydrolyzed (i.e., agent loading, stabilizer), neutralization process, process operating conditions, process effectiveness, and consistent process operation. Confirmation of the composition of the hydrolysate (efficacy of treatment) is related to the accuracy of the analytical methodologies (see Chapter 3) and whether the sample(s) used for the analysis represent the batch being processed. The satisfactory treatment of each batch is determined on the basis of analysis of the hydrolysate samples.

Only laboratory/bench-scale runs have been completed for the process, and scale-up to the integrated full-size facility is based on the anticipated processing conditions. At startup, NECDF intends to operate the reactor at a VX loading of 8%, rather than the 33%

originally planned. This has process and operational consequences that are discussed later in this chapter. The Army proposes that VX loading will be increased to 16% as experience is gained with the process and equipment, and when analytical methodologies and successful off-site treatment capability demonstrated at the higher loading are validated. The change from the proposed 33% VX loading to 8% VX loading will increase substantially the total quantity of hydrolysate to be treated and the length of time the Newport facility will operate.

2.2 Process Description

The process for VX neutralization at Newport uses batch processing (Figure 2-1). Each batch consists of the following sequential steps:

1. The reactor is charged with caustic.
2. The reactor is heated to approximately 194ºF.
3. The reactor circulation loop is activated, and the agitator in the reactor is started.
4. Agent is added to the reactor using a feed line in the recirculation piping. The amount of agent added is determined by the VX loading target for a given batch. Two phases are present in the reaction mixture—an aqueous phase and an organic phase. The relative volumes of the two phases are determined by the VX loading.
5. VX and caustic are mixed by the agitator in the reactor and by the static mixer in the recirculation piping. The static mixer is designed to achieve an organic droplet size of approximately 10–30 microns (μm).
6. After the reaction has been circulated at temperature (194ºF) for a period of time sufficient to complete the hydrolysis reaction, the mixture is cooled and a sample taken from the recirculation line. If the sample meets the criteria for VX and EA 2192 destruction, the resulting mixture (the hydrolysate) is pumped from the reactor to storage. If the VX and EA 2192 destruction criteria are not met, then the mixture is reheated, and processing continues. This is repeated until the batch is successfully processed.
7. After the batch is processed, it will be transferred to intermediate storage, and then shipped off-site for final treatment.

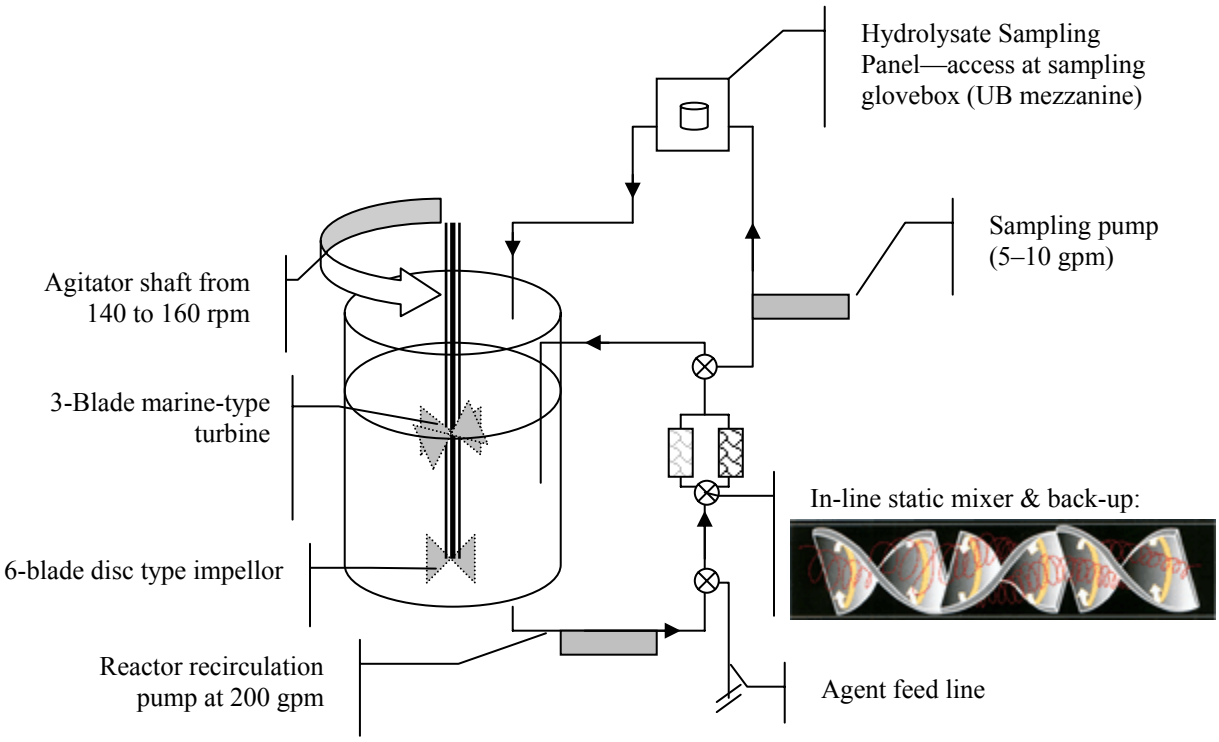


Figure 2-1. Hydrolysate reactor

Texas A&M performed a safety study of the Newport facility using fault-tree techniques. One scenario examined was "Offsite Transfer of Hydrolysate Containing Excess VX Concentration."

The Executive Summary of this report stated:

> *Fault tree analysis techniques were applied to the VX project speedy neutralization (PSN) process and related process support systems in order to estimate the frequency that the cited hazard scenario can be expected to occur.*
>
> *The study results indicate that the best estimate for an annual frequency of this undesired event is 5 x 10^{-5}.*

The annual frequency is estimated at 1 in 20,000 chance for CVXH being outside of specification for VX (>20 ppb). The existing design does not detect contamination of acceptable hydrolysate after the batch sampling procedures have been completed. The amount of potential contamination is minor and not thought to present a public health risk. This issue could be corrected by good engineering practices such as physical isolation using piping blinds, spool pieces or a double block and bleed valve configuration or by development of a sampling method at the storage tank. CDC has alerted Army representatives regarding this design issue as part of the normal oversight activity. Any potential design changes to the facility and schedule impacts need to be balanced by the national security risk associated with extended storage of the VX.

At the time of this report, the recommendations in Safety Study Reports by Texas A&M and other safety studies relating to the design and operation of the Newport facility were still being evaluated for implementation.

2.3 Process Chemistry

The process chemistry involved with VX neutralization is complex when an extremely high destruction of VX is required. At the time this report was written, investigations into the process chemistry are still under way, and not all of the details of the main and side reactions involved (e.g. solids formation) were fully understood. The major variables that affect the chemistry include the agent loading (i.e., the relative amount of agent per unit volume of caustic in the reactor at the start of the batch) and the type of stabilizer present in the agent being processed. (The stabilizers used to minimize the decomposition of the VX during storage were DIC or DCC or DIC + DCC).

The main reaction by which VX is neutralized by caustic is well understood and is pseudo-first order with respect to VX concentration. However, the presence of two phases (organic and aqueous), the presence of VX in the organic phase, the creation of EA 2192, and the presence of stabilizers complicate the physical and chemical process. If all other system parameters and the composition of initial caustic solution remain constant, then the size, composition, and partitioning of the reaction products between the aqueous and organic layers depend on the VX loading. Mass transfer limitations become more pronounced as the droplet size increases and the organic layer is formed. This will affect the rate, as well as the pathways of the reactions, and may produce different final products. In addition, some of the ton containers are now known to contain gelled/solid material. How much of this material will be removed with the VX and how much will remain in the ton container is uncertain. The effect of any gelled/solid material on the chemistry or operation of the neutralization reactor mixing process and sampling system also is unknown.

The purpose of the agitator and the static mixer are to mix the phases and to transform the organic phase into tiny droplets. The smaller the droplet size, the faster the diffusion processes in leaching and neutralizing the VX in the organic droplets. Therefore, VX is rapidly destroyed at the start of the batch operation; then a slower, diffusion-limited process follows as the VX in the organic phase droplets is neutralized. Moreover, the size

and chemical compositions of the dispersed droplets and the organic layer will differ for the various VX loadings and stabilizer types.

In a response to questions from CDC, the Army and its contractor (Parsons) summarized these issues:

> *Because of the highly reactive nature of hot caustic, less than 0.1% of the VX added to the reactor during the FILL period accumulates in the reactor with virtually all of this residual VX removed during the first minute of REACT. Additional REACT time is needed to destroy residual VX that partitions into the organic phase during FILL, and to ensure that EA2192 is non-detect. ……. It is expected that the NECDF's full-scale pilot reactor will provide the necessary mixing and droplet size to produce non-detectable levels of both VX and EA2192. This conclusion is based on laboratory-scale results and full-scale pilot plant calculation results provided herein. The actual reaction time required to obtain non-detectable levels of both VX and EA2192 will be determined during Controlled Start-up testing of the full-scale NECDF pilot plant. If the reaction time required to obtain non-detectable levels of both VX and EA2192 determined during Controlled Start-up differs from that which was predicted during laboratory-scale testing, the types and configuration of the elements within the static mixer and the volumetric flow rate through the recirculation line can be changed, as needed.*

This response accurately describes the process, neglecting the effect of any gelled/solid materials in the feed to the reactor or generated within the reactor.

As previously noted, the reaction originally was designed to have used a 33% agent loading in each batch. However, studies demonstrated that, at 33% agent loading, a significant organic phase (3%–5% by volume) formed during the reaction, and this organic layer separated from the aqueous phase during storage and floated on top. Remaining (un-neutralized) VX partitioned into this organic phase, and the VX concentration in this organic phase was approximately 20 times the VX concentration in the bulk hydrolysate (nominally <20 ppb). Therefore, operation with 33% agent loading could have resulted in a "significant" volume of organic phase with a "high" VX concentration in storage tanks and during transportation. This was considered unacceptable, and modifications to the process were proposed and implemented.

Additional investigation showed that operation at 16% agent loading reduced the organic layer to approximately 2–3 volume percent. At 8% agent loading, the organic layer was only a sheen on the surface of the hydrolysate (approximately 0.5% by volume determined by centrifuging the sample). The VX concentrations in the organic phase for 8% and 16% agent loadings had not been determined at the time this report was written.

Significant changes in organic liquid loading occur between 8% VX loading and 16% VX loading (approximately a 1:5 volume ratio at a minimum) and between the 16% and 33% VX loading (approximately 1:1.5 ratio). The physical and/or chemical processes involved and the reason(s) for such a significant increase in organic loading between 8% and 16% VX loading have been the subject of some investigation, but no conclusion has been reached.

Laboratory studies have demonstrated that the reaction times required to complete neutralization vary with agent loading and stabilizer. With DIC-stabilized agent (approximately 46% of the Newport stockpile), the reaction times are 2.5–4 hours for 8% loading and 4–6 hours for 16% loading. With DCC-stabilized agent, the reaction time is 10–14 hours for 8% loading. The reason(s) for the apparent additional processing time required by DCC-stabilized agent is (are) not fully understood. The amount of stabilizer in each ton container also can vary significantly. Therefore, what is valid for 8% VX loading stabilized with DIC may not be valid for 16% VX loading case and other stabilizers. The data do not warrant generalizations that apply to all VX loadings and stabilizers.

In addition, laboratory studies have determined that solids are generated during the neutralization process. These solids have been variously described as a sticky gel and as a more coherent material. The amount of solids, their composition, and the amount of VX, (if any) these solids contain have not been determined.

The presence of solids in the hydrolysate within the reactor may be problematic in the full-scale unit and impact plant operations. Concern has been expressed that the solids may precipitate onto the surfaces of the agitator in the reactor and result in an imbalance that could cause mechanical failure of this item. A more likely source of concern may be the potential blockage of the in-line static mixer or deterioration of the performance of control valves, particularly the three-port valve that controls the introduction of chemical agent to the reactor and the transfer of the hydrolysate to the storage tanks. The in-line mixer is constructed deliberately with small flow paths (10–30 μm) to break up the organic phase into small droplets. Any solids formation could result in blockage, with the potential for reduced production rates and the need to remove the in-line mixer for cleaning. Solids also can also be deposited on the surfaces of the internal parts of the three-port valve, impacting valve closure and enabling leakage of agent, thereby contaminating previously sampled and acceptable hydrolysate batches as they are transferred from the reactor to the storage tanks. Another possibility is that modification of the process equipment to incorporate an upstream filter may be required. Furthermore, the solids may negatively impact the sampling system and the analytic measurements and treatment of the hydrolysate.

Appendix K of the documentation, provided in response to CDC Question 1, discusses solids formation. The “Conclusions” section of this document states

a. Formation of solids in 8 weight % hydrolysate have (SIC) the potential to impact process throughput due to reactor hardware

plugging in the pumps or static mixer. Preventative maintenance needs to be scheduled as experience determines.

b. Difficulties have been encountered clearing the hydrolysate with gelatinous material. When hydrolysate fails to clear, more processing is required. Detailed analysis of the gelatinous material may lead to procedures that could expedite clearance.
c. Further testing is underway to characterize the observed solids and identify whether stabilizer type (DCC vs. DIC) or VX loading causes changes in solid volume or content.
d. At [the Chemical Agent Munitions Disposal System (CAMDS)], twenty five batches of DCC hydrolysate and one batch containing DIC hydrolysate were processed without process failure due to these solids. (Note—Whether a static mixer with very small passages [such as at Newport] was installed at CAMDS) is not known)

In the subsystem hazard analysis of the process, the following finding (Failure Mode and Effects Analysis [FMEA] Item 01-04-134) was noted:

> *Over-or Under-Reaction Creates Gelatinous Matrix in Neutralization Reactor Containing VX*
>
> *Several mis-operations and reaction inconsistencies can result in the creation of a gelatinous matrix in the neutralization reactor (1- and 2-L401). It might not be possible to completely prevent this occurrence. A study is being performed to identify ways to dissolve or solubilize any gelatinous matrix that might form. Additional information or data from the study could determine methods to prevent the polymer formation and ways to mitigate such a formation if it occurs. This evaluation addresses FMEA Item 01-04-134.*

Whether this finding in the safety studies documenting issues associated with solid/gel formation in the reaction system has been addressed at the time this report was completed is not known.

Except for solids formation and its possible effects, the scale-up of the reactor from laboratory to full-scale operation should succeed. Adequate heating and cooling have been provided for the reactor system, the equipment is simple in design and the batch will be run until the analytic methods demonstrate that VX and EA 2192 have been adequately destroyed. However, the effect of gelled/solid material in the ton containers passed into the reactor does not appear to have been examined in detail. Therefore, no conclusion can be reached about the effects of such material on the neutralization reaction, the destruction efficiency, and the operation of the reaction system.

2.4 Findings

1. Scale-up of the process for 8% VX loading from laboratory-scale data should be operationally feasible. The database supports the efficacy of neutralizing 8% VX (stabilized with DIC) using sodium hydroxide. However, the Newport facility will be a pilot operation when it starts operation, and changes must be anticipated in operating mode and hydrolysate composition sent for off-site treatment.

2. VX loading and the specific stabilizer employed significantly impacts the process, hydrolysate composition, analytical methodology, and possibly solids formation. Scale-up of the process from 8% to 16% VX loading is of particular concern (because of the similarity of the organic-phase volumes between 16% and 33% VX loading batches) and the analytical problems identified with 33% VX loading.

3. The effects of solids formed during the hydrolysis reaction in the process on the hydrolysate and on the efficacy of treatment at a TSDF are unknown. The solids may contain VX. The impact of solids formation on the operation of the reaction system and, in particular, the potential for blockage of the in-line static mixer and other components (including the sampling system) is unknown. In addition, the presence of solids may impact the VX analytics, as well as the off-site hydrolysate treatment process.

4. At the time this report was written, all the findings from safety studies had not been fully addressed. In particular, findings relating to possible solids formation in the reactor and the required process modifications to provide additional assurance that no off-specification CVXH is shipped from the Newport facility may affect the CVXH composition shipped off-site.

3. Analytical Methods

3.1 Introduction

The purpose of this review and evaluation is to define the adequacy of the proposed methods for the analysis of VX and EA 2192 in the CVXH to meet the programmatic requirements of the NECDF. The scope of this review is limited to laboratory analyses of hydrolysate from the neutralization of DIC-stabilized VX at the 8% VX-loading level. Adequate analytical data were not available to evaluate analyses of hydrolysate related to other VX-loading levels or stabilizers.

3.2 Sampling Representativeness

We recognize that the validity of the clearance process depends on the sample taken and delivered to the laboratory for analysis; the sample must truly represent the total hydrolysate process batch. To evaluate the sample procurement process, all available documents describing the design and operation of the equipment and the sampling procedures were reviewed. We also had detailed discussions with NECDF personnel.

NECDF personnel believe the sampling will be highly representative on the basis of the mixing capability of the reactor, the design and operation of the sampling equipment, and the detailed protocols that have been established. On the basis of our understanding of reviewed information, we agree—as long as solids formation does not block the sampling points. The planned sampling program should provide representative samples for CVXH batches to the laboratory for analyses.

QA/QC procedures are in place to ensure and document adequate training of personnel, performance of sampling equipment, availability and quality of supplies, proper and complete recordkeeping, establishment and maintenance of chain of custody, and the safety of plant and laboratory personnel.

Maintaining representativeness of the analytical sample during transfer of the 5-mL analytical portion from the plant batch sample will be challenging because of the potential for separation of an organic layer. The laboratory method for VX analysis in CVXH calls for the analyst to "verify hydrolysate is as homogeneous as possible" during the subsampling process. This process can be highly subject to analyst technique error and will require careful QC.

3.3 Analysis of VX in Caustic VX Hydrolysate

3.3.1 Data Evaluation/Interpretation Criteria

Instrument or qualitative detection as defined in Laboratory Field Instruction (LAFI)-A-30-053:

> Consider VX present in the sample if the following criteria are met:
>
> 1. Retention time of analyte peak within +/- 0.1 minute of average standard VX retention time.
> 2. The m/z 128 ion, the m/z 139 ion, and the m/z 167 ion maximize within 0.05 minute of each other.
> 3. The m/z 139 and 167 ions may not be present at concentrations <1 microgram per milliliter (μg/mL) in the sample.
> 4. The m/z 128 ion response must be at least three times the background noise level, i.e., S/N ratio 3 or greater.
>
> Quantitative criterion as defined by the Army is as follows:
>
> MDL, calculated according to U.S. Environmental Protection Agency (EPA) procedure published in the Code of Federal Regulations (40 CFR, Part 136, Appendix B) $\leq$20 ppb.

3.3.2 Method Description and Documentation

LAFI-A-30-053 provides a comprehensive, step-by-step description of the method for analyzing VX in CVXH. The method is based on multiple hexane extractions of the hydrolysate, followed with solid-phase extraction techniques for initial fractionation of the extract, then final separation and detection of the VX using gas chromatography (GC) coupled with ion-trap (IT) mass-spectrometry/mass-spectrometry (MS/MS) techniques. The use of high-resolution capillary GC coupled with the dual-phased MS/MS IT techniques gives this method extremely high selectivity and sensitivity for VX in the hydrolysate. Stated in layman's terms, the method can detect and quantify VX in the highly complex CVXH mixture at $\leq$20 ppb with a high level of confidence against both false positives and false negatives.

The laboratory QC procedures defined in LAFI-A-30-053 and in Section 11.2 of the NECDF Laboratory Quality Control Plan, Revision 2, are consistent with procedures and requirements published in EPA SW-846. Implementation of these procedures should provide the QC data needed to define the overall validity of the analytical results.

Evaluation of MDL data for 8%VX-loaded, DIC-stabilized hydrolysate shows that, with this type of hydrolysate, the NECDF laboratory can consistently generate MDL values below the 20-ppb criterion. In a study to characterize batch-to-batch variation, the NECDF laboratory generated three MDL values for each of two batches of hydrolysate. The six MDL values ranged from 6 to 17 ppb, with a mean of 11 ppb, with no appreciable differences between the two hydrolysates.

In summary, the current method for analyzing VX in CVXH is adequate to detect and quantify VX well below the established clearance level of 20 ppb. The GC/IT/MS/MS technique provide a method with extremely high analyte selectivity and sensitivity. The method consistently shows an instrument detection limit below the 5–10 ppb range.

3.4 Analysis of EA 2192 in Caustic VX Hydrolysate

3.4.1 Data Evaluation/Interpretation Criteria

Instrument or qualitative detection as defined in LAFI-A-30-030:

Consider EA 2192 present in the sample if the following criteria are met:

1. Retention time of analyte peak is within +/- 1.0 minute of the average retention time of the standard EA 2192 during instrument calibration.
2. The m/z 162 ion is present with a 128/162 ion ratio of 0.3.
3. At EA 2192 concentrations <1 mg/mL the 128/162 ion ratio may not equal 0.3, but m/z 162 ion must be present.
4. The m/z 128 ion response must have a minimum S/N ratio of 3.

Quantitative criterion as defined by the Army:

MDL, calculated according to EPA procedure published in 40 CRF, Part 136, Appendix B, ≤1 ppm.

3.4.2 Method Description and Documentation

LAFI-A-30-030 provides a comprehensive, step-by-step description of the method for analyzing EA 2192 in CVXH. The method consists of a simple 1:25 dilution of the CVXH sample, followed by analyte separation using liquid chromatography (LC) techniques, with final detection and quantification using dual-phase IT/MS/MS. The use of LC/IT/MS/MS techniques results in a highly sensitive, extremely selective analysis of EA 2192 in the CVXH.

Laboratory QA/QC procedures defined in LAFI-A-30-030 and the NECDF Laboratory Quality Control Plan are consistent with those published in EPA SW-846. Analytical data characterizing the performance of this method are limited. MDL data show values of 0.23 ppm and 0.09 ppm; both well below the clearance level of 1 ppm. Precision and accuracy data show overall very good precision of the method with analyte recoveries ranging from 82% to 95%.

In summary, the current method for analyzing EA 2192 in CVXH is adequate to detect and quantify EA 2192 in laboratory-generated hydrolysate well below the established clearance level of 1 ppm. Data also indicate that the qualitative (analytical presence) instrument detection limit of the method is consistently <0.1 ppm.

3.5 Use of Analytical Data for Clearance

The Army has stated its intended use of VX and EA 2192 analytical data in the clearance of CVXH for off-site shipment, as follows:

> Since its inception, a key tenet of the Army Chemical Militarization program has been the safety of the workers and the public. Department of the Army (DA) Pamphlet (PAM) 385-61, entitled "Toxic Chemical Agent Safety Standards," defines the approach for verifying the thoroughness of the neutralization process as using laboratory analysis to assure that the chemical agent is at a level less than or equal to 20 ppb. This level has been deemed protective of soldiers and Department of Defense personnel. The Project Manager for Alternative Technologies and Approaches (PMATA) elected to use the standard EPA method detection limit (MDL) as the means for determining whether the detection limit specified in the DA PAM has been met. Thus, the requirement for successful neutralization of VX is that the hydrolysate must be non-detect for VX with an MDL of 20 ppb or less.

The Army also has stated that EA 2192 must be "non-detect with an MDL of 1 ppm or less."

As discussed in Sections 3.3 and 3.4, we believe that NECDF methods LAFI-A-30-053 for VX in CVXH and LAFI-A-30-030 for EA 2192 in CVXH can provide valid qualitative and quantitative data for detecting and quantifying VX and EA 2192, respectively, in the concentration ranges needed for programmatic clearance of the hydrolysate material for off-site shipment. NECDF's intended practice for measuring and reporting "non-detects" is potentially misleading. Specifically, we are concerned with the Army's plan to classify and report analytical results above the instrument detection level, but below the established MDL, as "non-detects." While CDC believes that utilizing the MDL approach would not result in public health concerns, the Army needs to address potential public misperceptions regarding the detection or non-detection of VX in CVXH. A simpler reporting scheme (i.e., non-detected, detected at <20 ppb, or detected at >20 ppb) should be considered.

The Army's clearance criteria of "non-detect with an MDL less than an established concentration level" combines two related, but different, analytical chemistry concepts. First, "instrument or analytical detection" is a qualitative-based "yes or no" criterion. Second, MDL is a statistically calculated, quantitative criterion.

The first criterion, "detection," addresses two questions: (a) Was an instrument response observed at the expected retention time of the analyte? and (b) If so, was the level of that response greater than three times the background noise (S/N ratio $\geq$3)? If the answers to both of these questions are "yes," then according to instructions in LAFI-A-30-053 and LAFI-A-30-030, the analyte (either VX or EA 2192) is considered "present" or "detected." If the answer to either question is "no," then the result of the analysis is a "non-detect."

The second criterion, MDL, addresses the level of confidence in the quantitative value calculated from the observed instrument response using an established calibration curve for the instrument. EPA's definition of an MDL, calculated according to the published procedures in 40 CFR, Part 136, Appendix B, is the minimum concentration of a substance that can be measured and reported with 99% confidence that the analyte concentration is greater than zero. This is a highly conservative criterion designed to all but completely eliminate false-positive results. Failure to meet the quantitative-based MDL criterion does not negate the analytical "presence" established by the "detection" criterion.

Our issue is that the Army, through its current use of the EPA MDL concept, could improperly classify analytical data as "non-detects" when, in fact, the data have been determined analytically as "detects." Although EPA-prescribed uses of the MDL concept may be appropriate for many applications in regulatory monitoring, in this public health-driven application, it is open to criticism when low-level instrument detects are discarded.

We are not suggesting that using the MDL concept and reporting "analytical detects" as "non-detects" will compromise the process of clearing the CVXH concentration at 20 ppb for VX and 1 ppm for EA 2192. Rather the issue is improper classification of analytical

results. Usually no issue would involve MDL, if the MDL was used only to help determine a quantitation level at which a reliable number can be provided to help make an action decision. In this case, the Army used "detection," not a quantitative level, as its primary clearance criterion. We stated in sections 3.3 and 3.4 that the current NECDF methods can support a clearance process on the basis of quantifiable measurements. The Army could report analytical results as "less then," rather than as "detects" and "non-detects," which would more accurately represent the analytical data.

3.6 Quality Assurance and Quality Control Procedures

The Laboratory Quality Control Plan clearly defines the comprehensive laboratory QA/QC procedures and techniques. This document defines the procedures for: preparation and verification of analytical standards; the certification, maintenance, and calibration of analytical instruments; the certification of methods and personnel; and the QC procedures, techniques, and samples used to define the operational status of the analytical processes and the basic validity of the analytical data. The overall QA/QC plan and procedures are well designed and documented.

3.7 Findings

1. The planned sampling program should provide representative samples for CVXH batches.

2. The current method for analyzing VX in CVXH (LAFI-A-30-053) is adequate to detect and quantify VX in laboratory-generated, 8% VX-loaded, DIC-stabilized hydrolysate well below the established clearance level of 20 ppb.

3. The current method for analyzing EA 2192 in CVXH (LAFI-A-30-030) is adequate to detect and quantify EA 2192 in laboratory-generated, 8% VX-loaded, DIC-stabilized hydrolysate well below the established clearance level of 1 ppm.

4. The use of EPA's MDL for clearance levels does not preclude analytical instrument detection of low levels of VX and EA 2192 (generally <20 ppb VX and <1 ppm EA 2192) in the CVXH. The perception that the clearance criteria (defined as "non-detected" with a MDL of ≤20 ppb VX or ≤1 ppm EA 2192) indicate absence of analytically detectable VX and/or EA 2192 could be misleading. While CDC believes that utilizing the MDL approach would not result in public health concerns, the Army needs to address potential public misperceptions regarding the detection or non-detection of VX in CVXH. A simpler reporting scheme (i.e., non-detected, detected at <20 ppb, or detected at >20 ppb) should be considered.

5. The overall QA/QC plan and procedures are well designed, and documented. NECDF laboratory personnel must generate day-to-day operational QC data to demonstrate that all analytical systems are operational and under control before plant startup according to written plans and procedures.

4. Caustic VX Hydrolysate Treatment

4.1 Introduction

The CVXH is the liquor obtained from the alkaline hydrolysis of the chemical agent VX at elevated temperatures. The details of the processes that generate the CVXH at the Newport facility are described earlier in this report. Once transported to the DuPont SET facility, CVXH will be further treated to remove the organic by-products by a series of physicochemical and biologic processes. The exact composition and phase characteristics of the CVXH received at the SET plant will depend on the stabilizer type and VX loading used in the NECDF process batch. The major parameters and characteristics of 8% VX–loaded, DIC-stabilized hydrolysate (which is the main focus of this report), as received by DuPont, are given in the Table 4.1 for two separate CVXH samples.

pH	TOC, mg/L	COD mg/L	TN mg/L	EMPA mg/L	MPA mg/L	Thiolamine mg/L
>13	33,852	61,000	6,739	39,135	2,789	11,200
13.1	44,147		4,334	35,937	2,826	42,900

total organic carbon (TOC), total nitrogen (TN), milligrams per liter (mg/L)

Table 4.1 Characteristics of caustic VX hydrolysate generated from 8% VX loading with DIC stabilizer

The DuPont treatability studies were designed and executed to obtain scale-up parameters for engineering design and regulatory compliance. Because of their relatively high concentrations in the CVXH, only thiolamine, EMPA, and MPA were analyzed or monitored within the treatment train or in the process effluent. Trace contaminates, such as VX and EA 2192, were not monitored during the studies. (Note: Because of the high 1500- to 2000-fold dilution factor in the DuPont SET process, monitoring of these compounds may not be analytically possible.)

The pH adjustment and neutralization of the CVXH is the first step of the pretreatment process before introduction of the waste to the biologic treatment system. CVXH neutralization is followed by peroxide treatment to destroy odorous substances. The most recent biotreatability studies, the final step in the treatment train, use two-stage PACT®-activated sludge systems that are operated under conditions emulating the actual plant flow rate and hydraulic retention time. In addition to CVXH, the reactors received mustard (HD) hydrolysate from the Aberdeen operations because an alternating treatment scheme may be implemented at the DuPont SET facility.

The studies described in the two DuPont treatability reports (March 3, 2004, and July 19, 2004) were performed with different types of hydrolysates. The inconsistencies in the samples used to conduct the treatability studies make evaluation of the entire treatment process on the same basis and extrapolation of the treatability studies to pilot-plant performance challenging. For example, the pH adjustment and neutralization experiments reported in the Basic Data Summary Report (July 19, 2004) were conducted using 16% VX–loaded, DIC-stabilized CVXH (actual), but the biotreatability studies were

performed with 8% VX-loaded, DIC-stabilized CVXH (actual). Although 20% sulfuric acid was used in the pH-treatment experiments, DuPont proposes to use 5% acid in the full-scale process. The heat of reaction for acidification was measured for 8% and 16% VX-loaded CVXH (reformulated)[1] with DCC stabilizer, not DIC, which is the focus of our investigation. In summary, the studies reported in the Technical Assessment and the Basic Data Summary Report suffer from inconsistencies with respect to the type of CVXH used in each test. The experimental findings do not support the assumption that the CVXH has identical physical and chemical properties regardless of the VX loading and stabilizer type. The volume of the organic layer formed, which differs for 16% VX-loaded CVXH and 8% VX-loaded CVXH, clearly indicates that the system chemistry differs depending on how much VX is added to the caustic solution. Moreover, the volume of the organic layer formed during hydrolysis is not directly proportional to the VX loading. Therefore, linear extrapolations of the experimental results obtained in the preliminary treatment studies should not be used to predict performance at higher agent loadings, and equating the 8% VX-loaded 7000-gallons per day (gpd) CVXH with 16% VX-loaded 3500-gpd CVXH (Table 5, Basic Data Summary Report) for design and modeling purposes should be avoided.

Because the Army's stated objective is to begin operations with 8% VX-loaded, DIC-stabilized CVXH, the assessment of the DuPont treatability studies focused mainly on treatment of the CVXH at this condition. Occasionally, however, other data and material reported by Parsons on the VX alkaline hydrolysis treatment are cited to support the main findings of this assessment. Data are insufficient to assess treatment of CVXH at other VX loadings and for other stabilizers. In the following sections, the hydrolysate acidification process, the peroxide oxidation, and the biologic treatment studies are evaluated and the major findings presented.

4.2 Extent of Treatment

4.2.1 pH Adjustment

The CVXH acidification experiments were conducted with actual CVXH (16% VX-loaded, DIC-stabilized) titrated with 20% sulfuric acid to a final pH of 4–6. The titration curve obtained from the actual CVXH was compared with the aqueous layer from a centrifuged sample after separation of the organic layer. The heat of reaction also was computed, but for 8% and 16% VX-loaded, DCC-stabilized (reformulated) CVXH. The results of these experiments demonstrated that

- The organic layer is destroyed. pH adjustment produces a homogeneous amber yellow clear solution.
- The process generates 3.07 calories per gram (cal/g) during the titration of 8% VX-loaded, DCC-stabilized (reformulated) CVXH, producing a temperature increase of 6.4 ºC. This energy is expected to dissipate through heat losses during plant operation, and cooling and heat exchanger installation will be unnecessary.

[1] Reformulated VX hydrolysate was prepared by diluting 33% VX loaded hydrolysate to achieve the desired VX loading.

- Removal of the organic layer lowers the buffering capacity of the mixture (hydronium ions appear to be consumed during destruction of the organic layers).
- The process increases the volume of the CVXH waste by about 30%. If 5% sulfuric acid is used, as DuPont proposes to avoid cooling the reaction mixture, the volume increase will be close to 100%, further diluting the sample by a factor of 2. The effect of the 5% sulfuric acid on the organic treatment is unknown; the available reports did not present data using 5% sulfuric acid.

In response to the May 25, 2004, clarification questions (Responses to CDC Clarification Questions, Final, 17 June, 2004), Parsons indicates that pH adjustment does not destroy the organic layer. DuPont's 3 March 2004 report, "Treatability of Newport (Indiana) Caustic Hydrolysate" (Reich et al), confirmed that the adjustment of pH without additional treatment measures aggravates the odor of hydrolysate. Furthermore, the uncharged form of thiolamine is poorly-soluble and results in the formation of a large organic layer, on the order of 10% by volume. This organic layer is presumed to have a low flashpoint, which would add risk to the shipping process.

However, DuPont and its treatability study as presented in the Basic Data Summary Report, states

> *The sample was observed to change from a yellowish cloudy color to a slightly amber clear color once a single phase was formed which occurred around pH 6.0. Once a single phase formed, there was no longer any organic material coating the glass.*

Addition of a strong acid to the CVXH profoundly affects the physical and chemical stability of the organic droplets dispersed in the hydrolysis liquor and the dissipation of the organic layer. Attachment 1, "Characterization of Droplets Resulting from NECDF Static Mixers," of the Parsons report (July 22, 2004) states that the average size of the colloidal droplets ranges from 5 to 10 μm, with specific gravity of about 0.87 and strong negative charges. This charge most likely keeps the droplets suspended, preventing efficient collisions and subsequent aggregation. The electrophoresis experiments to determine the particle surface charge were performed with 16% VX- loaded, DIC-stabilized CVXH (actual). No experimental data are presented in the Parsons white paper on the properties of the droplets formed in the hydrolysate from the 8% VX-loaded, DIC-stabilized CVXH. The Parsons reports documented, and experimental observations by DuPont verified, that the volume of the organic layer and the size distribution and dispersion of the droplets in the final CVXH depends on the VX loading. The higher the loading rate the larger the resulting organic layer volume. However a direct proportional relation does not appear to exist (i.e., doubling the VX loading does not increase the volume of the organic layer by a factor of two). Visual observations by Parsons personnel of the formation of the organic layer estimated that the layer thickness remains unchanged for up to 4 months. However, no kinetic information is provided about the rate of formation of the organic layer.

Given that the organic droplets carry an overall negative charge, addition of hydronium ions should compress the electrical double layer that typically exists in the boundary of the organic-aqueous interface and allow the attraction forces to take over. Because this is not observed, i.e., addition of sulfuric acid does not appear to enhance flocculation or layer formation and separation, we can conclude that either the solubility of the organic phase is higher or its components become chemically unstable and decompose at lower pH or both. The disappearance of the organic phase during pH adjustment supports this.

The exact composition of the organic layer is not known, but the response of the whole (as received) CVXH to the addition of sulfuric acid suggests that it imparts alkalinity to the sample, probably because of weak organophosphorous acids and carbonates in the process water. More sulfuric acid (about 30 grams [g]) is required to reduce the pH of the whole CVXH sample than the aqueous layer to a pH of 8 (Figure 1 of the Basic Data Summary Report). However, the two titration curves intersect at a pH of 7 indicating that the same amount of acid is needed to bring the solutions to this endpoint. From that point, further addition of small amounts of acid brings about a steep pH drop in the aqueous layer but has little effect on the whole CVXH (as received), until about 380 g acid (x-axis of Figure 4-1), where pH drops substantially. This behavior is consistent with a chemically reactive solution. The organics exert a hydronium ion demand in excess of the amount required to neutralize the base. The organic layer appears to react with the hydronium ions participating in a chemical reaction rather than to be simple acid-base equilibrium chemistry. Moreover, the observation that this step modifies the odorous intensity of the mixture provides additional evidence that the organic components undergo significant chemical changes during pH adjustment.

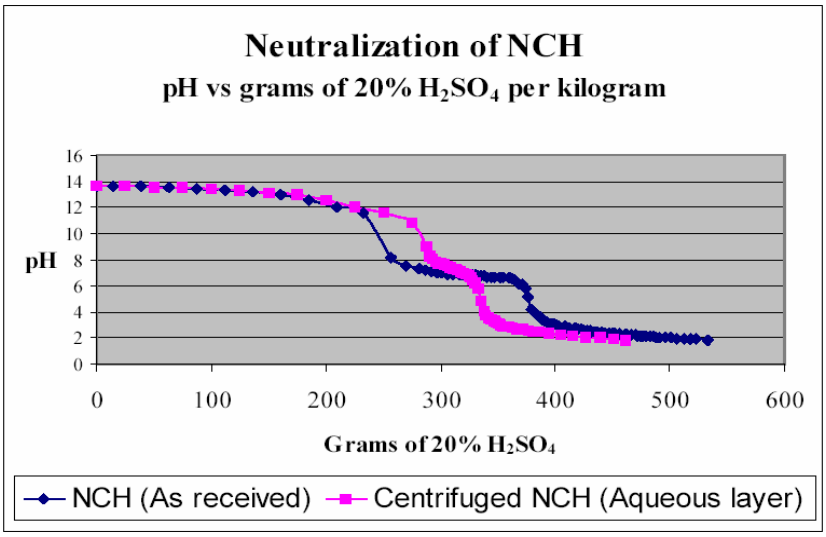


Figure 4-1 Caustic CVXH titration curves provided by DuPont in the Basic Data Summary Report.

4.2.2 Hydrogen Peroxide Oxidation

Once the pH of the hydrolysate is adjusted to a pH of 4–6, the mixture is treated with 10% peroxide to control objectionable odors emanating from the CVXH caused mainly by the volatilization of thiolamine. Peroxide and the free radicals formed by its addition to the reaction mixture attack the organics present in the hydrolysis liquor and initiate thiolamine destruction. Again, these studies were conducted with 16% VX- loaded, DCC-stabilized CVXH (actual or reformulated). Thiolamine is destroyed quickly by the peroxide, with most of the compound depleted within the first minute of reaction (Figure 4-2). After 20 minutes, the concentration drops below the detection limit of 5 ppm. The degradation products of thiolamine are presented in the Technical Assessment Report (March 3, 2004). Four compounds were identified as possible thiolamine degradation products: acetic acid, diisopropyl amine, urea, and 2-diisopropylaminoethyl ethyl disulfide. Acetic acid and urea are readily biodegradable compounds and are expected to break down in the two-stage PACT® bioreactors. However, the biodegradability of isopropyl amine and the 2-diisopropylaminoethyl ethyl disulfide is not documented in the Technical Assessment Report or the Basic Data Summary Report; only qualitative references (page 49 of the Technical Assessment Report) state that samples analyzed from the effluent of one of the bioreactors had no detectable amounts of thiolamine or any of its oxidation products. No other information is provided that confirms the biodegradation of these two by-products. EMPA and MPA remain unaffected by the peroxide process.

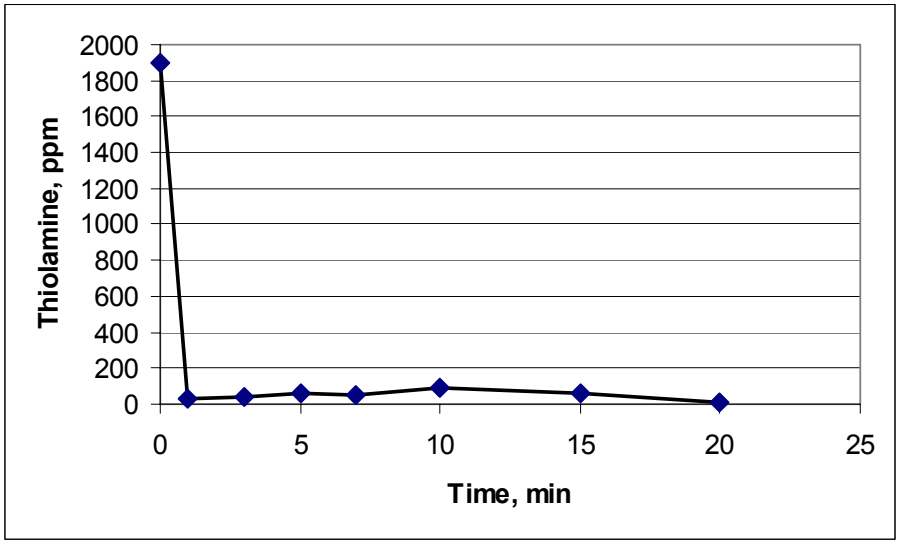


Figure 4-2 Destruction of thiolamine by hydrogen peroxide oxidation.

The oxidation step is an exothermic process releasing approximately 14 cal/g of heat. This value was obtained from a reformulated 16% VX–loaded, DCC-stabilized, CVXH that was first treated with 20% sulfuric acid to a pH of 6.4, then subjected to 20% weight equivalent of 10% hydrogen peroxide solution. Gas-generation measurements conducted in 2-liter flasks showed that the amount of gas generated during the peroxide oxidation is

negligible. The lack of gas evolution suggests that the degradation of thiolamine is incomplete; in other words, the compound is not mineralized to the simple innocuous carbon dioxide and water.

4.2.3 PACT® Biotreatment

Two sets of biodegradation experiments were conducted using one- and two-stage PACT® bioreactors. The first treatability study was performed with CVXH; in the second, both CVXH and HD hydrolysate from Aberdeen were tested to determine the effect of alternating the bioreactor feeds on the performance of the biologic system. Co-processing will be necessary when both types of hydrolysates will be sent for treatment to DuPont's SET facility. The objectives and the criteria of both studies were stated in the Basic Data Summary Report:

1. To confirm that the anticipated rates of CVXH can be processed successfully through the SET [wastewater treatment plant (WWTP)], enhancing the database provided by the original treatability study;
2. To assure that the CVXH can be processed at appropriate rates while HD hydrolysate from Aberdeen is being managed at the WWTP using a plan to either alternately campaign each hydrolysate or process the pretreated hydrolysates simultaneously;
3. To ascertain the degree of improvement in treatment that can be anticipated with a two stage PACT® system.

As for the earlier Treatability Study there were three general criteria for judging the treatment of CVXH to be successful:

1. Ability to maintain satisfactory control of wastewater and sludge odors.
2. Ability to maintain control of SET WWTP operations (e.g., effective dissolved organic carbon [DOC] removal, manageable foaming, pH control, solids management, etc.)
3. Ability to assure permit compliance (e.g., effluent BOD5 [5-day biochemical oxygen demand], BOD5 percent removal, effluent TSS, effluent NH3-N and WET). In addition the fate of EMPA, MPA and thiolamine were monitored.

As mentioned before, the studies were designed to provide information about system performance in terms of regulatory compliance and to obtain design parameters for scale-up.

To ensure adequate treatment, two PACT® bioreactors were operated in series. This biologic system, in addition to the microbial degradation, was dosed with activated carbon, which in general enhances the treatment capacity by removing recalcitrant compounds that are resistant to biodegradation. Six reactors were set up to evaluate various treatment scenarios using 8% VX-loaded, DIC-stabilized CVXH and the HD hydrolysate. The flow rate and retention time in the bioreactors were set to simulate actual plant conditions treating 7000-gpd CVXH and 15,000- and 25,000-gpd HD

hydrolysate. A large dilution of the hydrolysate, to the order of approximately 2000 times, occurred at introduction of the pretreated CVXH to the biologic PACT® system. Appropriate controls were used throughout the study, and all pertinent system parameters were monitored to assess system performance. However, the fate of individual compounds as they pass through the bioreactors is not as well documented. Only EMPA and MPA were monitored in the pilot-plant effluent.

The data presented in figures 7, 8, 9, and 10 and tables 8 and 9 of the Basic Data Summary Report indicate that, after a short acclimation period, the removal efficiency, as measured by DOC and BOD reduction, stabilizes to an average of about 85%–90% in all reactors. Even during the acclimation period, the removal does not drop below 75%. This high-removal efficiency also is observed in the alternating Aberdeen/DIC CVXH influents, indicating that the biologic system is not affected by these input changes. The 7000–gpd, 8% VX-loaded CVXH is equated to 3500–gpd, 16% VX-loaded CVXH (Table 5). However no evidence suggests that this is a valid approach. See Section 4.3 for a discussion of the potential differences on the composition and general chemistry of the 8% and 16% VX-loaded CVXH.

The Technical Assessment and Basic Data Summary reports clearly document the conversion of EMPA to MPA. Both compounds remain unaffected by the pH reduction, and conversion during peroxide treatment appears to be limited. Biologic treatment by the two-stage PACT® process converts essentially all of the EMPA to MPA but appears not to affect the MPA decomposition. Data are sufficient to support this conclusion. The slight decrease in MPA effluent concentration most likely results from partitioning in the organic sludge.

DuPont's Technical Assessment and Basic Data Summary reports contain no information about the fate of VX or EA 2192 during treatment of the CVXH in the DuPont SET facility. The presence of these two compounds in the plant effluent in trace amounts cannot be excluded.

4.3 Environmental Persistence and Agent Loading Effects

The major hydrolysis products of VX are well characterized, and the reaction rate and pathways depend strongly on solution pH and temperature (Figures 4-3 and 4-4). With solubility of approximately 30 grams per liter (g/L), VX is considered to be highly mobile in the environment and can persist for days or even weeks in slightly acidic waters. Other VX hydrolysis products in the CVXH include EMPA, which has a half life in soils of about 8 days, with MPA being the major transformation product.

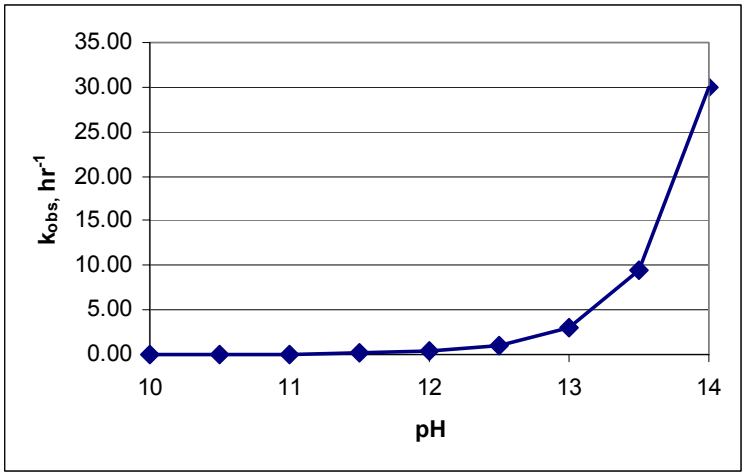


Figure 4-3 pH dependence of apparent rate constant for VX hydrolysis

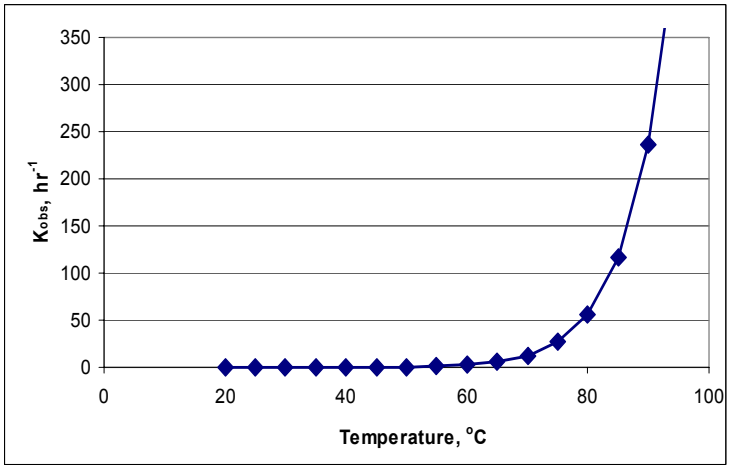


Figure 4-4 Temperature dependence of apparent rate constant for VX hydrolysis at a pH of 7.7.

As discussed in Section 4.2.3, the treatability studies with the 8% VX-loaded CVXH demonstrates conversion of EMPA to MPA in the activated sludge bioreactors. MPA is stable in the environment because it is resistant to hydrolysis, photolysis, and thermal decomposition. It is also soluble in water and has a low coefficient for sorption onto soil particles. Therefore, it can migrate easily in the soil and groundwater (Munro et al., 1999). Another major by-product of the hydrolysis of VX at neutral and high pH values, is EA 2192 (S-(2-diisopropylaminoethyl)methyl phosphonothioic acid), an environmentally persistent highly toxic compound with infinite water solubility.

Some of the hydrolysis products, namely EA 2192, EMPA and MPA, are stable at neutral pH; whether these, or other byproducts that are not identified or exist at low concentrations, can react and form stable VX molecules is questionable. This is a concern because the CVXH is adjusted to a pH below 6 in preparation for the oxidation and

biologic treatment. Parsons attempted to partially address this concern by studying the CVXH over a 5-hour period at a pH of 10 or 71 days at a pH of 14. These conditions, however, do not represent the low (<6) pH range in the system after pH adjustment. Neutral pH is a worst-case scenario because of the stability of the by-products at those conditions and the possibility of recombining to reform VX. Thermodynamic analyses also should have been performed to assess the tendency of the pH-adjusted CVXH to move toward VX reformation. Because experimental data are not presented, the questions regarding possible VX reformation remain unanswered.

4.4 Findings

1. The 8% VX-loaded, DIC-stabilized CVXH is treated by pH adjustment to a pH <6 to eliminate the two-phase mixture, followed by hydrogen peroxide oxidation to destroy the odor-causing thiolamine, and finally biologic treatment to convert most of the EMPA to MPA.
2. The DuPont SET facility effectively treats the CVXH generated from an 8% VX loading with DIC stabilizer, except for MPA, for which only minimal reduction is demonstrated.
3. Alternating feeds from Aberdeen HD hydrolysate and CVXH did not affect the performance of the DuPont bench-scale reactor.
4. The effects of the SET facility on the destruction of any trace quantities of VX and EA 2192 in the CVXH are unknown. In addition, the fate of diisopropyl amine and 2-diisopropylaminoethyl ethyl disulfide through the SET plant is not well documented.
5. The possibility of VX reformulation at acidic (<6) pH conditions (after pH adjustment) in the Dupont SET treatment process has not been adequately investigated and remains unresolved.
6. Effective treatment of 16% VX-loaded CVXH and 8% VX-loaded CVXH with DCC or DIC/DCC stabilizers were not demonstrated in the DuPont studies.

5. Major Findings

NECDF was designed to destroy VX using caustic hydrolysis in a hot solution of sodium hydroxide. Initially the plan was to further treat the resulting waste on-site by SCWO and to ship the SCWO effluent to a TSDF. After the terrorist attacks of September 11, 2001, the plan was modified to eliminate on-site SCWO treatment and ship the resulting hydrolysate directly off-site for treatment at a TSDF. Critical to this modified plan was the development and validation of analytical methods to clear the hydrolysate for shipment. The stringent Army clearance levels for VX and EA 2192 proved challenging to the analysts. The original plan to operate at 33% VX loading was abandoned, and the program plans to begin operations at 8% VX loading and move to 16% VX loading.

This programmatic change has necessitated an intensive effort to develop the analytical methods needed to assess process performance and suitability of the hydrolysate for off-

site shipping, process modification to ensure adequate mixing and VX droplet size, and search for a TSDF capable of treating the hydrolysate. The current plans are for NECDF to ship the CVXH to the DuPont SET facility in Deepwater, New Jersey.

CDC engaged Carmagen Engineering, Inc., to assemble a team of experts (Team) to assist in the evaluation of the DuPont SET facility's treatment of the CVXH. The Team recognized that an assessment of the NECDF destruction process and an examination of the analytical methods to be used for CVXH clearance were required to ensure that the hydrolysate being shipped to SET will be adequately characterized and that VX and EA 2192 levels in the CVXH meets Army specifications.

The Team addresses its findings in chapters 2–4 of the report. The reader is encouraged to review all of the findings, as well as the supporting documentation in each chapter. The major findings follow.

Process Issues (Chapter 2)

Finding 2.1. The database supports the efficacy of neutralizing DIC-stabilized VX using sodium hydroxide at the 8% VX-loading rate. Scale-up of the process from laboratory/bench scale to pilot scale should be operationally feasible. However, because the NECDF will be a pilot facility, changes must be anticipated in operating mode and hydrolysate composition sent for off-site treatment.

Finding 2.2. VX loading (weight percent) and the specific stabilizer (DIC, DCC) employed significantly impact the process, hydrolysate composition, analytical methods validation, and possibly solids formation. Scale-up of the process from 8% to 16% VX loading is of particular concern (because of the similarity of the organic-phase volumes from 16% to 33% VX-loading batches), the potentially high VX concentration in the resulting organic layer, and the analytical problems identified with 33% VX loading.

Finding 2.3. The impact is unknown of solids formation during the hydrolysis process on operations (potential for blockage of the in-line static mixer, control valves, and sampling system), VX analytic methods, and off-site hydrolysate treatment. The transition from 8% to 16% VX loading, as well as stabilizer change, is of concern and requires additional detailed studies.

Analytical Methods (Chapter 3)

Finding 3.1. The methods for analyzing VX and EA 2192 in 8% VX-loaded, DIC-stabilized CVXH are adequate to detect and quantify at the established clearance levels for VX (20 ppb) and EA 2192 (1 ppm).

Finding 3.2. The use of EPA's MDL for clearance levels does not preclude analytical instrument detection of low-level VX and EA 2192 (generally <20 ppb VX and <1 ppm EA 2192) in the CVXH. The perception that the MDL clearance criteria indicate absence of analytically detectable VX and EA 2192 could be misleading. While CDC believes

that utilizing the MDL approach would not result in public health concerns, the Army needs to address potential public misperceptions regarding the detection or non-detection of VX in CVXH. A simpler reporting scheme (i.e., non-detected, detected at <20 ppb, or detected at >20 ppb) should be considered.

Finding 3.2. The overall QA/QC plan and procedures for the NECDF laboratory are well designed and documented. However, NECDF laboratory personnel should continue implementing the QA/QC plan by developing day-to-day operational QC data to demonstrate that all analytical systems are operational and under control before plant startup.

Caustic VX Hydrolysate Treatment (Chapter 4)

Finding 4.1. The SET facility effectively treats the CVXH generated from an 8% VX loading with DIC stabilizer (i.e., pH adjustment, thiolamine destruction, conversion of EMPA to MPA), except for MPA, for which only minimal reduction is demonstrated.

Finding 4.2. The SET facility treatment performance should be unaffected when treatment of hydrolysate feeds from Aberdeen (HD) and Newport (VX) are alternated.

Finding 4.3. The DuPont treatability studies have not yet demonstrated the effective treatment of 16% VX-loaded CVXH, nor of 8% VX-loaded CVXH with DCC or DIC + DCC stabilizers.

6. References

DuPont. DuPont Technical Assessment on U.S. Army Newport (Indiana) Project. 3 March, 2004.

DuPont. Basic Data Summary Report for Newport Caustic Hydrolysate. 19 July, 2004.

Munro, N.B., Talmage, S.S., Griffin, G.D., Waters, L.C., Watson, A.P., King, J.F., and Hauschild, V. The sources, fate, and toxicity of chemical warfare agent degradation products. Environ Health Perspect. 1999;107(12):933–974.

Parsons. CVXH Analytical Testing Results (Response to CDC Request for Information: Item No. 1). 15 May 2004.

Parsons. Sampling Protocols (Response to CDC Request for Information: Item No. 2). 14 May 2004.

Parsons. Analytical Methods for VX in Hydrolysate (Response to CDC Request for Information: Item No. 4). 14 May 2004.

Parsons. Newport, Indiana Process Variability Impact on Secondary Treatment (Response to CDC Request for Information: Item No. 6). 14 May 2004.

Parsons. Responses to EPA Questions to DuPont [16 questions]. 14 June 2004.

Parsons. Responses to Additional CDC and EPA Questions [9 EPA questions, 19 CDC questions]. 17 June 2004.

Parsons. Responses to CDC 29 June, 2004 Questions [11 requests and 5 questions]. 22 July 2004.

SAIC. Assessment of Low-Level VX in CVXH LLVX Independent Assessment Panel. October 2003.

Texas A&M University System. Quantitative Subsystem Hazard Analysis of Potential for Off-Site Transfer of Hydrolysate Containing VX Above the 20 ppb Method Detection Limit. Draft Report. August 2004.

Wojciechowski P, Mokos J. Analysis for VX in Hydrolysate at NECDF. Presentation to CDC, 27 March 2003.

Attachment #5

Assessment of the Screening Level Ecological Risk Assessment for Discharge of Effluent from the Treatment of Newport (Indiana) Caustic Hydrolysate (NCH)

By

United States Environmental Protection Agency, Region 2
at the request of the
Centers for Disease Control and Prevention

October 5, 2004

UNITED STATES ENVIRONMENTAL PROTECTION AGENCY
REGION 2
290 BROADWAY
NEW YORK, NY 10007-1866

OCT - 5 2004

Tom Sinks, Ph.D
Acting Deputy Director for Programs
National Center for Environmental Health
Agency for Toxic Substances and Disease Registry
Centers for Disease Control and Prevention
1825 Century Blvd., Mail Stop E-28
Atlanta, GA 30345

Dear Dr. Sinks:

In response to a request from several New Jersey and Delaware Senators and Congressmen for a formal review of the Army's proposal for off-site treatment of the VX hydrolysate at the DuPont wastewater treatment facility and discharge to the Delaware River, the Centers for Disease Control and Prevention (CDC) agreed "to conduct a review of the off-site disposal plan within our areas of expertise." In turn, CDC requested that the United States Environmental Protection Agency's (EPA) Region 2 office review and comment on the Screening Level Ecological Risk Assessment for Discharge of Effluent From The Treatment of Newport (Indiana) Caustic Hydrolysate (NCH) prepared by DuPont dated March 3, 2004. This letter outlines EPA's comments on this document.

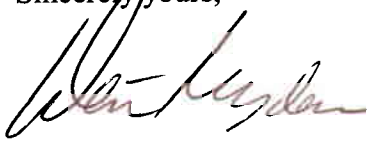
The basic question that EPA Region 2 was asked to respond to was "From an ecological standpoint, is the disposal of material as presented in the DuPont Chambers ecological risk assessment acceptable?" Based on our review of the information provided and the amount of outstanding issues that need to be addressed, EPA's position is that DuPont has not demonstrated that the disposal of material as presented in the ecological risk assessment is acceptable.

Enclosed is a detailed discussion of EPA's findings. In summary, the Screening Level Ecological Risk Assessment (SLERA) does not contain adequate information to conclude that there is no unacceptable risk from the discharge of treated VX hydrolysate to the Delaware River, and a number of constituents were left out of the analysis completely. In addition, there are several additional issues that need to be addressed before treatment and discharge of this treated hydrolysate to the Delaware River can occur including: whole effluent toxicity tests procedures, the potential for the presence of VX nerve agent and other toxic breakdown products in the hydrolysate, the addition of phosphorus to the estuary, and the NPDES permit with New Jersey.

Therefore, EPA believes that the conclusions of the SLERA are not valid and that the ecological risk process on the Army's proposal to discharge treated VX hydrolysate to the Delaware River must continue.

If you have any questions regarding this letter, please contact me at (212) 637-3725 or have your staff contact Grace Musumeci, Acting Chief of the Strategic Planning and Multi-Media Programs Branch at (212) 637-3504.

Sincerely yours,



Walter Mugdan, Director
Division of Environmental Planning and Protection

Enclosure

cc: (w/ enclosure)
Linda Anderson, Centers for Disease Control and Prevention
John A. Decker, Centers for Disease Control and Prevention
Artie Block, Agency for Toxic Substances and Disease Registry

ENCLOSURE A

General Comments

The Screening Level Ecological Risk Assessment (SLERA) lacks conservatism. SLERAs are meant to be "conservative assessments in that they provide a high level of confidence in determining a low probability of adverse risk, and they incorporate uncertainty in a precautionary manner" (USEPA, 2001). The goal of a screening assessment is to minimize the likelihood of underestimating potential or current risk to ecological receptors through the use of conservative assumptions ensuring that the results will most likely overestimate actual risk.

DuPont's lack of conservatism in the SLERA is illustrated by the following:

- The SLERA does not include and evaluate all detected constituents found in the VX hydrolysate. DuPont focused the assessment only on the "principal constituents"of ethyl methylphosphonic acid (EMPA) and methylphosphonic acid (MPA). The Waste Characterization Profile Sheet located in Appendix B of the March 2004 Treatability Study indicates that several metals including arsenic, chromium, and lead were found in low ppm concentrations in the hydrolysate. Metals were also found in the hydrolysate as indicated in a July 2002 Oak Ridge National Laboratory report prepared for the Army (Oak Ridge National Laboratory, 2002). EA2192 or (S-[2-diisopropylaminoethyl] methylphosphonothioic acid), another breakdown product of VX nerve agent, is not included in the SLERA (more on this constituent below).

- Because some compounds in the hydrolysate mixture are unidentified, a conservative screening assessment of the mixture toxicity should be performed by assuming that unidentified chemicals are as toxic as the most toxic identified chemical in the mixture and by applying a concentration addition model to all constituents. The results would not constitute a risk estimate but could be used to determine whether the issue of mixture toxicity can be eliminated or requires more study.

- Maximum concentrations of all detected hydrolysate constituents, not just the "principal components," must be used in the screening level risk quotients. Concentrations for both EMPA and MPA are estimated in the SLERA.

- Dilution factors should not be used for estimating the in-stream concentrations of MPA and EMPA or any other detected constituents. In order to be conservative, the maximum hydrolysate concentrations for all detected constituents must be used in the risk calculations without a dilution factor.

- The Risk Characterization section of the SLERA should contain a Hazard Index (HI) calculation for constituents that have the same ecological effect endpoint and/or the same mechanism of toxic effect. EMPA and MPA were assumed to have similar toxic mechanisms in the SLERA and their hazard quotients should have been added together to

calculate a hazard index. All detected nerve agent breakdown products found in the hydrolysate with similar toxic mechanisms as EMPA and MPA should be included in the Hazard Index calculations.

In order to have a high degree of confidence in the predictive value of the hazard quotient method, there must be great certainty in the constituent concentrations and NOAELs used in the SLERA. Based on the non-conservative assumptions used in this SLERA, USEPA has little certainty in both the concentrations and NOAELs used in the hazard quotient calculations and therefore, does not believe that a statement of "no unacceptable risk" can be made for hazard quotients less than 1. The use of more conservative assumptions in the SLERA as listed above will certainly increase the risk quotients and risk indices. These increases will ultimately produce higher risk quotients that may approach or exceed 1 indicating a potential for adverse ecological effects and that a more thorough risk assessment is warranted

Toxicity Test Issues

A full Summary of Findings and Technical Recommendations (Enclosure B) follows this and provides an overview of the toxicity tests, a data review, and recommendations. Only the recommendations are presented here as follows:

- The data from the Treatability Study and the pure chemical testing are acceptable as screening evaluations.

- The results from the data study are not acceptable due to the limited effluent concentrations used in testing. The acute toxicity testing done for the data study must be re-run with the following concentrations of effluent after treatment through the second bio-reactor: 12.5%, 25%, 50%, 75% and 100%. Testing must be conducted with the following three species that are currently listed in the NJPDES permit: *Pimephales promelas* (fathead minnow), *Cyprinodon variegatus* (sheepshead minnow) and *Ceriodaphnia dubia*. The sheepshead minnow is included because any tests conducted on effluent from the treatment of NCH through the first and second phase PACT must consider all scenarios under the current NJPDES permit. This includes a discharge into the Delaware estuary when the receiving water salinity is greater than 3.5 ppt. When salinity is greater than 3.5 ppt the NJPDES permit states that testing must be conducted with the sheepshead minnow, *C. variegatus*.

- In addition, because the NJPDES permit is under review it is likely that chronic endpoints (which were to be reviewed for inclusion in the current permit) will be required. Therefore, chronic testing should be conducted on the final NCH effluent using species to be determined by the NJDEP in the new NJPDES permit. At a minimum, chronic testing with the same three species used for acute testing, ie *P. promelas, C. variegatus* and *C. dubia,* should be conducted to provide more sensitive endpoints to the data study than acute testing alone.

- All testing must be conducted following all quality control procedures as outlined in the EPA acute and chronic testing manuals (EPA 2002, 2002a & 2002b) in order for the data to be acceptable.

Some of these required QA/QC procedures include:

- test with both freshwater and marine species
- use controls on all tests
- conduct/pass reference toxicant tests with organisms cultured in-house or supplied from an outside source
- use organisms of the same age at start of the test and ensure ages are within the proper age range
- use required number of replicates and number of organisms per replicate for all tests
- ensure sample holding times are less than 36 hours
- use concentrations of 12.5%, 25%, 50%, 75%, and 100% effluent.

VX nerve agent and other toxic breakdown products could be present in the hydrolysate.

The VX nerve agent method detection limit in the hydrolysate is 20 ppb. According to a May 15, 2004 US Army document prepared by Parsons titled VX hydrolysate analytical testing results Response to CEC Request for Information: Item No. 1, this limit evolved from a Department of the Army pamphlet that states "The thoroughness of the neutralization process will be verified by laboratory analyses to assure that an agent concentration above the emergency drinking water standards in TB Med 577 does not exist . . . " The drinking water standard for nerve agents is listed as 0.02mg/l (20 ppb) in the Army's Medical Technical Bulletin Sanitary Control and Surveillance of Field Water Supplies (TB Med 577). This detection limit is based solely on the protection of humans from a drinking water source and may not be protective of aquatic organisms through ingestion or dermal exposure.

Acute exposure studies of the VX nerve agent have been performed demonstrating that 7 out of 10 juvenile striped bass were killed after 14 to 20 hours of exposure to 20 ppb (method detection limit) of VX nerve agent. All of the white perch (10 of 10) exposed to 25 ppb (slightly above the detection limit) of VX nerve agent in aqueous medium died in approximately 9 hours (Weimer, et.al, 1970). This report stated that "the effects of chronic exposures to lower levels of VX have not been studied." These chronic exposure studies, using aquatic species included in the NPDES permit, should be performed prior to discharge of the hydrolysate effluent to the river. Discharge of even small amounts of VX nerve agent remaining in the hydrolysate effluent to the Delaware River could have potentially adverse effects on aquatic organisms since this effluent is planned to be discharged about two times per day for approximately two years.

EA2192 is another toxic breakdown product generated during the destruction of VX nerve agent. According to a November 2001 US Army Center for Health Promotion and Preventive Medicine report, "based on its persistence and toxicity it has been suggested in several reports that EA2192 be viewed as a serious consideration wherever VX is being destroyed." The report also states that EA2192 may "pose a greater potential for chronic toxicity" than VX and once in solution, it is extremely persistent in the environment. This constituent was not included or evaluated in the SLERA nor were any data on this constituent's toxicity presented in the document.

There is no information demonstrating that the SET is capable of treating VX nerve agent or EA2192 that may be present in the hydrolysate so that if they were present in the effluent, they

would go untreated and be directly discharged into the Delaware River. Important aquatic species that could be adversely affected by the presence of VX nerve agent, EA2192, and any other toxic breakdown products in the river include striped bass, shad, white perch as well as invertebrates such as crabs, clams, and lobsters.

The addition of phosphorus to the Delaware River could be detrimental.

Based upon the data presented in the risk assessment, we cannot accurately predict the availability of phosphorus in the receiving waters based on breakdown of the phosphonic acid compounds, which are proposed to be discharged. If they are easily broken down to biologically available phosphorus which is generally considered to be total phosphorus (portions of both the inorganic and organic phases of total phosphorus have been found to be biologically available), they will have more of an impact than if they do not break down easily in the environment.

As discussed in Chapter 2 of EPA's October 2001, "Nutrient Criteria Technical Guidance Manual: Estuarine and Coastal Waters," often both nitrogen (N) and phosphorus (P) "elicit greater phytoplankton biomass stimulation than the sum of both N and P added separately. There are reported cases where both N and P are required to elicit phytoplankton biomass production response in estuaries, suggesting that N and P supply rates are equally limiting." This Guidance goes on to state that, "a number of temperate estuaries exhibit seasonal shifts in nutrient limitation with winter-spring P limitation and summer-fall N limitation."

In addition, according to the Draft National Coastal Condition Report II (USEPA, 2004), the tributaries of the Delaware River near the outfall of the SET already have poor grades for water quality, dissolved inorganic phosphorus (DIP), and benthic index. Although the current conditions in the Delaware Estuary do not demonstrate that eutrophication is occurring, it is unclear of the effect of the addition of MPA and other phosphorus-containing compounds from the discharge of the VX hydrolysate effluent into the Delaware River. The concern is that the addition of these compounds could increase the amounts of DIP in the estuary to such a point that the system would create unwanted algal blooms. Given the fact that the proposed discharge is located in Zone 5 of the Delaware River, which is characterized as the transition zone, an increase in the concentration of P to the system may result in phytoplankton biomass production, as outlined above.

EPA recommends that hydrodynamic modeling considering the addition of MPA and other phosphorus-containing compounds from the discharge of the VX hydrolysate effluent into the Delaware River be conducted to demonstrate that the addition of these compounds will not have any adverse effects on the estuary and its tributaries.

NPDES Permit Issues

DuPont Chambers Work discharges wastewater into the Delaware River under the terms, conditions and provisions of a National Pollutant Discharge Elimination System (NPDES) permit that is administered by NJDEP. The NJDEP has been delegated as the permitting authority for the State of New Jersey. EPA's role in the NPDES program involves oversight of New Jersey

State's NPDES permitting program.

The current permit (NJ0005100) was issued by NJDEP on December 31, 1998 and expired on January 31, 2004. Although the permit has expired, the conditions of the permit are considered to be administratively extended and still in effect, and enforceable. Effluent limitations were included in the permit to address Chamber Work facility's discharge of process wastewater, stormwater, cooling water, groundwater remediation wastewater, leachate, and wastewater delivered from offsite facilities.

The following represent issues that USEPA has concerning the treatment and discharge of the VX hydrolysate at the DuPont SET facility that need to be addressed before the SET's treatment of VX hydrolysate effluent can be discharged to the Delaware River through the permitted outfall:

- DuPont needs to clarify whether their Chamber Works facility was authorized under the current NJPDES permit (NJ0005100) to treat the Army's Newport Caustic Hydrolysate (NCH).

- The current NJPDES permit issued for this facility (NJ0005100) that expired January 31, 2004 does not include a limit nor a requirement to monitor and report on MPA, thiolamine, and EA2192 if DuPont is allowed to accept the Army's NCH for treatment. USEPA is concerned that the Army's VX hydrolysate sent to DuPont's SET treatment facility for treatment will contain MPA, thiolamine, and EA2192, which are not limited, and will be discharged to the Delaware River and Estuary. In sufficient dosages, these pollutants may present serious hazards to aquatic organisms. Based on DuPont's study, SET WWTP has limited effects on the treatment of MPA. There is a concern about the environmental effects of MPA and other toxic breakdown products that may be associated with the Army's wastewater.

- Since the proposed Army project is expected to take several years to complete, we recommend the Army's application be addressed and evaluated by NJDEP in the upcoming renewal process. Additionally, the Army's proposal would be considered a major alteration per 40 CFR 122.62 (a) (1) since the addition of this wastestream will result in changes in the permittee's practice that are different in the DuPont's NJPDES renewal application.

- The Army and/or DuPont should provide effluent characterization studies so that a decision can be made on whether additional limitations and/or conditions on the identified pollutants are necessary in the renewal permit.

REFERENCES

DuPont, 2004. Treatability of Newport (Indiana) Caustic Hydrolysate.

Oak Ridge National Laboratory, 2002. Accelerated Neutralization of Chemical Agent and Off-Site Shipment of Liquid Process Effluents at the Newport Chemical Agent Disposal Facility.

US Army (Parsons), May 15, 2004. VX hydrolysate analytical testing results Response to CDC Request for Information: Item No. 1.

US Army Center for Health Promotion and Preventive Medicine, November 2001. Analysis of EA2192 Monitoring and Sampling Issues at Newport Chemical Agent Disposal Facility

USEPA, 1997. Ecological Risk Assessment Guidance for Superfund: Process for Designing and Conducting Ecological Risk Assessments, EPA/540/R-97/006, Office of Solid Waste and Emergency Response

USEPA, 2001. The Role of Screening-Level Risk Assessments and Refining Contaminants of Concern in Baseline Ecological Risk Assessments, ECO Update, EPA/540/F-01/014, Office of Solid Waste and Emergency Response

U.S. EPA. 2001. Nutrient Criteria Technical Guidance Manual: Estuarine and Coastal Marine Waters, First Edition. Office of Water, Office of Science and Technology, Washington, D.C. EPA-822-B-01-003.

USEPA, 2004. Draft National Coastal Condition Report II (www.epa.gov/owow/oceans/nccr2)

Weimer, J.T., et al. 1970. Toxicity of VX and GD in Aquatic Animals Indigenous to the Carroll Island Test Area Water, DOA, Edwood Arsenal, MD.

ENCLOSURE B

SUMMARY OF FINDINGS AND TECHNICAL RECOMMENDATIONS - DUPONT TOXICITY EXPOSURE DATA FOR NEWPORT CAUSTIC HYSDROLYSATE

ACRONYMS:

ACH: Aberdeen Caustic Hydrolysate, waste currently being treated by DuPont from the Army Aberdeen Test Center, Aberdeen, MD

SET: DuPont Secure Environmental Treatment Center located at the DuPont Chambers Works site in Deepwater, NJ. Operates under NJPDES #0005100 for DSN662 (formerly DSN661).

EMPA: Ethyl Methylphosphonic acid

NCH: Newport Caustic Hydrolysate, or VX Hydrolysate, is the byproduct of the neutralization of VX nerve agent .

MPA: Methylphosphonic acid

PACT: Powdered Activated Carbon Treatment System (DuPont patented technology); multi-step process of aeration, biodegradation and clarification of wastes.

OVERVIEW

The DuPont Chambers Secure Environmental Treatment facility in Deepwater, NJ is seeking an Army contract to treat 4 million gallons of wastewater, Newport Caustic Hydrolysate (NCH), from the neutralization of a stockpile of VX nerve agent in Newport, IN. The Center for Disease Control is reviewing DuPont's Human Health Toxicity Assessment for the project whiled EPA Region 2 reviewed the Ecological Risk Assessment.

As part of the assessment, DuPont contracted with EA Engineering, Science and Technology, Inc, to conduct toxicity tests for three different phases of the project.

1. Treatability Study: Small scale studies designed to test different NCH treatments in order to remove odor, maintain efficient operation of the DuPont PACT biotreatment system and to meet NJPDES permit limits. Acute. 48 hour toxicity tests were conducted using Fathead Minnows, *Pimephales promelas*, on effluents from 10 potential treatments. This study simulated wastes from treatment through the PACT system.

2. Pure chemical testing: EMPA & MPA are major constituents of NCH. The treatability study demonstrated that only a small amount of EMPA will be converted to MPA during processing. Chronic toxicity tests were conducted on EMPA & MPA using a freshwater species, *Ceriodaphnia dubia* a water flea, and the opossum shrimp, *Americamysis bahia*, which is a marine species.

3. Basic Data Biotreatment Study: Designed to test treatment of NCH as processed along with outside wastes handled by SET on a routine basis. Acute, 96 hour toxicity tests were conducted using the Fathead Minnow, *Pimephales promelas,* a freshwater species. This

study simulated wastes from treatment through both first and second stage PACT systems.

DATA REVIEW

1. Treatability Study

The treatability studies were conducted by DuPont using a single stage Eckenfelder reactor which simulates the first of the two-stage PACT used in processing wastewater. Samples of NCH were treated and processed ten different ways through the Eckenfelder to simulate various feed rates and possible ways the facility could control NCH odors and pH with different stabilizers before safely discharging into the Delaware Estuary. EA Engineering conducted limited scale acute 48 hour toxicity tests using fathead minnows on the resulting wastewater. Tests were repeated approximately a month later on the same samples with a CO_2 headspace to control pH drift. LC50s were calculated for each treatment and both series of tests.

The data from the first series of tests conducted on January 8-12, 2004, are acceptable with qualifications. An LC50 cannot be calculated with certainty because the highest test concentration was only 50% effluent. This was based on the SET NJDPES permit limit of an LC50 of ≥50% effluent for acute fathead minnow testing. The 50% effluent concentration should have been bracketed with not only lower concentrations but at least one dilution higher, preferably two concentrations, i.e., 75% and 100%. The data, however, is acceptable to show trends in the various treatments to assist DuPont in determining the best way to process the NCH.

All data from the second series of tests conducted on February 9-13, 2004 are unacceptable for the following reasons:

- holding times for wastewater far exceeded standard 36 hours
- no controls were tested
- DuPont's NJPDES permit does not indicate the use of CO_2 headspace to control pH drift
- two samples were tested at 25% and 50% dilutions while the remaining eight samples were tested at only 50%
- an LC50 cannot be calculated from only one or two concentrations nor without valid control data
- Fatheads were different ages from those tested in first series
- these results may not be combined with the first test series results to estimate an LC50 for each treatment

2. Pure Chemical Testing

Ethylmethylphosphonic acid (EMPA) and methylphosphonic acid (MPA) are major constituents of NCH. After the treatability studies it appeared that the majority of MPA would be released untreated into the Delaware Estuary and that only a small amount of EMPA would be converted to MPA during biotreatment through the PACT. EA Engineering conducted pure chemical chronic toxicity tests using freshwater and marine species (the water flea, *Ceriodaphnia dubia*, and the opossum shrimp, *Americamysis bahia,* respectively) for both EMPA and MPA. The marine species sheepshead minnow, *Cyprinodon variegatus*, was also tested using MPA.

Data was provided for range finding tests and definitive tests. The toxicity data for the definitive tests only were reviewed with emphasis on control survival, test design, reference toxicant testing, water quality, statistical analysis, organism handling/acclimation and effluent holding/handling (See Table 1). There are four possible determinations for reviewed data:

A - Acceptable Q- Acceptable w/Qualifications U- Unacceptable N- Notdetermined

Table 1. QA/QC Checklist for Pure Chemical Testing

Chemical	EMPA	EMPA	MPA	MPA	MPA
Organism	Daphnid *C. dubia*	Mysid *A. bahia*	Daphnid *C. dubia*	Mysid *A. bahia*	Minnow *C. variegatus*
Control Survival	Q[1]	Q[1]	Q[1]	Q[1]	Q[1]
Reference Toxicant	A	Q[2]	A	Q[2]	A
Test Concentrations	A	A	A	A	A
Test Procedures	A	A	A	A	A
Temperature	A	A	A	A	A
Dissolved Oxygen	A	A	A	A	A
pH	A	A	A	A	A
Salinity	N/A	N/A	A	A	A
Acclimation Procedures	A	A	A	A	A
Sample Holding Time	A	A	A	A	A
Statistical Analyses	A	A	A	A	A
Loading Factors	A	A	A	A	A

1 - A sodium hydroxide control should have been run in conjunction with a normal control to test the effect of adjusting the pH of the test solutions prior to testing with sodium hydroxide

2 - Reference toxicant testing with *A. bahia* using KCl was out of acceptable range for IC25.

Results of the definitive testing with MPA and EMPA are acceptable except for those conducted with *A. bahia* due to the out-of-range reference toxicity testing. The reference toxicity test was conducted by the lab which provided the organisms. The out-of-range result may have been avoided if EA had conducted their lab with *A.abdita* after acclimating to test conditions.

3. Basic Data Biotreatment Study

This study built on the treatability study by testing both the first and second stages of the PACT system. It also mimics real life situations in which NCH pretreated with peroxide and then with one of two possible stabilizers would alternate being processed through the PACT with other wastes such as ACH.

There are inconsistancies between the numbering of the samples in Appendix K-1 of this draft report. The numbers in the first table of the appendix, page K-1, appear to match the sample numbers in Table 14 on page 42 of the report; however, the data sheets in Appendix K do not match up with these numbers.

Due to these inconsistencies, it is impossible to review the data for each individual test. The test results, however, are not acceptable because as in the treatability studies, an LC50 cannot be calculated with certainty because the highest test concentration was only 50% effluent. Even though this was acceptable with qualifications for the range finding tests, it is not acceptable for definitive testing.

RECOMMENDATIONS

- The data from the Treatability Study and the pure chemical testing are acceptable as screening evaluations.

- The results from the data study are not acceptable due to the limited effluent concentrations used in testing. The acute toxicity testing done for the data study must be re-run with the following concentrations of effluent after treatment through the second bio-reactor: 12.5%, 25%, 50%, 75% and 100%. Testing must be conducted with the following three species that are currently listed in the NJPDES permit: *Pimephales promelas* (fathead minnow), *Cyprinodon variegatus* (sheepshead minnow) and *Ceriodaphnia dubia*. The sheepshead minnow is included because any tests conducted on effluent from the treatment of NCH through the first and second phase PACT must consider all scenarios under the current NJPDES permit. This includes a discharge into the Delaware estuary when the receiving water salinity is greater than 3.5 ppt. When salinity is greater than 3.5 ppt the NJPDES permit states that testing must be conducted with the sheepshead minnow, *C. variegatus*.

- In addition, because the NJPDES permit is under review it is likely that chronic endpoints (which were to be reviewed for inclusion in the current permit) will be required. Therefore, chronic testing should be conducted on the final NCH effluent using species to be determined by the NJDEP in the new NJPDES permit. At a minimum, chronic testing with the same three species used for acute testing, ie *P. promelas, C. variegatus* and *C. dubia,* should be conducted to provide more sensitive endpoints to the data study than acute testing alone.

- All testing must be conducted following all quality control procedures as outlined in the EPA acute and chronic testing manuals (EPA 2002, 2002a & 2002b) in order for the data to be acceptable.

REFERENCES

DuPont. 2004. Basic Data Summary Report for Newport Caustic Hydrolysate. E. I. DuPont deNemours and Company. Wilmington, DE.

DuPont. 2004. DuPont Technical Assessment on U.S. Army Newport (Indiana) Project, Executive Summary. E. I. DuPont deNemours and Company. Wilmington, DE.

DuPont. 2004. Screening Level Ecological Risk Assessment for Discharge of Effluent from the Treatment of Newport (Indiana) Caustic Hydrolysate (NCH) prepared by DuPont's Haskell Laboratory for Health and Environmental Sciences, E. I. DuPont deNemours and Company. Wilmington, DE.

EA Engineering. 2003. EA Ecotoxicology Laboratory Quality Assurance and Standard Operating Procedures Manual. EA Manual ATS-102. Internal document prepared by EA's Ecotoxicology Laboratory, EA Engineering, Science, and Technolgy, Inc., Sparks, MD.

EA Engineering. 2004. Results of Acute Toxicity Testing with *Pimephales promelas* On Juanuary 2, 2004; Bioreactor Effluent Samples for DuPont Chambers Works Treatability Study. Report Number 4453 prepared by EA Ecotoxicology Laboratory, EA Engineering, Science, and Technology Inc. Sparks, MD.

EA Engineering. 2004. Results of Acute Toxicity Testing with *Pimephales promelas* On 24 June, 2004; Bioreactor Effluent Samples from DuPont Chambers Works Treatability Study. Report Number 4541 prepared by EA Ecotoxicology Laboratory, EA Engineering, Science, and Technology Inc. Sparks, MD.

EA Engineering. 2004. Results of Chronic Toxicity Testing with Ethyl Methylphosphonate to *Ceriodaphnia dubia* and *Americamysis bahia.* Report Number 4483 prepared by EA Ecotoxicology Laboratory, EA Engineering, Science, and Technology Inc. Sparks, MD.

EA Engineering. 2004. Results of Chronic Toxicity Testing with Methylphosphonic Acid to *Ceriodaphnia dubia*, *Americamysis bahia*, and Cyprinodon variegatus. Report Number 4459 prepared by EA Ecotoxicology Laboratory, EA Engineering, Science, and Technology Inc. Sparks, MD.

US EPA. Methods for Measuring the Acute Toxcity of Effluents and Receiving Waters to Freshwater and Marine Organisms. Fifth Edition. EPA-821-R-02-012. U.S. Environmental Protection Agency, Office of Water. Washington, D.C.

US EPA. 2002a. Short-Term Methods for Estimating the Chronic Toxicity of Effluents and Receiving Waters to Freshwater Organisms. Fourth Edition. EPA-821-R-02–13. U.S. Environmental Protection Agency, Office of Water. Washington, D.C.

US EPA. 2002b. Short-Term Methods for Estimating the Chronic Toxicity of Effluents and Receiving Waters to Marine and Estuarine Organisms. Third Edition. EPA-821-R-02–14. U.S. Environmental Protection Agency, Office of Water. Washington, D.C.

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DEPARTMENT OF DEFENSE COMMENTS

The Department of Defense (DOD) has received a copy of the Centers for Disease Control (CDC) report titled "*Review of the U.S. Army Proposal for Off-Site Treatment and Disposal of Caustic VX from the Newport Chemical Agent Disposal Facility*" dated March 2005. The DOD appreciates the opportunity to review and comment upon the report.

We believe that there is a typographical error on the cover and that the report should be titled, "*Review of the U.S. Army Proposal for Off-Site Treatment and Disposal of Caustic VX* ***Hydrolysate*** *from the Newport Chemical Agent Disposal Facility*."

Like the CDC, we believe that safety of the workers, public, and environment is paramount and must be addressed. DOD agrees with a number of the CDC findings and recommendations that support the start of agent destruction operations at Newport and subsequent transport to a commercial treatment, storage, and disposal facility (TSDF). These include:

1) Destruction of the DIC-stabilized agent can proceed forward at an 8% percent loading.

2) The potential hazard of the caustic hydrolysate is predominantly associated with its corrosive and caustic properties and not nerve agent effects.

3) The corrosive and caustic hazards of the hydrolysate do not preclude handling or transportation and the precautions in the transportation plan meet the Department of Transportation regulations to safely protect the public, personnel, and environment.

4) The DuPont Secure Environmental Treatment process is capable of treating the major components in the caustic hydrolysate wastewater.

The DOD recently completed tests on the VX drawn from the stockpile stored at Newport. These tests confirm that the same criteria used to clear 8 % DIC-stabilized VX were met for the entire stockpile and that the issues associated with the DCC stabilized agent or the blended DIC/DCC stabilized agent have been addressed. Additionally, the total quantity of the stockpile that is stabilized with DIC is 60%. The detailed results from these tests are being furnished to CDC to update previously submitted data and address the concerns they have identified in their report.

Early last month the DOD provided a copy of DuPont's phosphonate removal technology report to the CDC for review. The concerns raised by the EPA regarding the contribution of treated caustic hydrolysate to the ecological risk to

the Delaware River are noted, and the DOD will work with the CDC and EPA to address these concerns.

Based on the results of the treatability studies, the DOD is convinced that the pretreatment process developed by DuPont will address potential data gaps raised by the EPA in its findings and address concerns raised over the past year by members of the public.

The DOD appreciates the professionalism and thoroughness of the CDC in completing this study and look forward to working with the CDC scientists to address their concens.