The Fate of VX, EMPA, MPA, and Other Constituents in Newport Caustic Hydrolysate

By

DuPont Chemical Solutions Enterprise

October 31, 2005
<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.0 Introduction</td>
<td>3</td>
</tr>
<tr>
<td>2.0 Agent Destruction At Newport</td>
<td>7</td>
</tr>
<tr>
<td>2.1 Fundamental Chemistry</td>
<td>7</td>
</tr>
<tr>
<td>2.2 Mixing</td>
<td>8</td>
</tr>
<tr>
<td>2.3 Rate of Reaction</td>
<td>9</td>
</tr>
<tr>
<td>2.4 NCH Clearance at NECDF</td>
<td>11</td>
</tr>
<tr>
<td>2.5 Storage of NCH at NECDF</td>
<td>11</td>
</tr>
<tr>
<td>3.0 Transportation of NCH</td>
<td>12</td>
</tr>
<tr>
<td>4.0 Newport Caustic Hydrolysate (NCH): Combined Pretreatment and Biotreatment</td>
<td>13</td>
</tr>
<tr>
<td>4.1 Overall Process Description</td>
<td>13</td>
</tr>
<tr>
<td>4.2 Combined Pretreatment Details</td>
<td>16</td>
</tr>
<tr>
<td>4.2.1 8%NCH (DIC) - Removal of Thiolamine, EMPA, and MPA</td>
<td>16</td>
</tr>
<tr>
<td>4.2.2 16% NCH (DIC) – Removal of Thiolamine, EMPA, MPA and Phosphate.</td>
<td>18</td>
</tr>
<tr>
<td>5.0 Newport Caustic Hydrolysate (NCH): Effect of Combined Pretreatment on VX and EA 2192 in Hydrolysate</td>
<td>21</td>
</tr>
<tr>
<td>6.0 Newport Caustic Hydrolysate (NCH): Aquatic Toxicity Testing of Combined Pretreatment and Treatability Reactor Effluents</td>
<td>22</td>
</tr>
<tr>
<td>7.0 Summary</td>
<td>26</td>
</tr>
</tbody>
</table>
The Fate of VX, EMPA, MPA, and Other Constituents in Newport Caustic Hydrolysate

1.0 Introduction

The purpose of this paper is to summarize the scientific studies that have been completed to understand the fate of VX and its breakdown products in the wastewater generated from the VX agent destruction process in Newport, Indiana.

The United States Army requested DuPont to submit a proposal to treat the wastewater from the VX hydrolysis project – termed here as Newport Caustic Hydrolysate (NCH) -- at its Chambers Works Secure Environmental Treatment (SET) wastewater treatment facility in New Jersey. Various government agencies and some of the general public have expressed concerns about the proposal which include:

- potential spills of the NCH during transit from Newport, IN to Chambers Works, NJ,
- potential exposure to workers and contractors at the Chambers Works facility during off-loading and treatment,
- potential harm to aquatic life in the Delaware Estuary from residual VX and other compounds that may remain in the final effluent following treatment, and
- potential stimulation of algal biomass in the Delaware Bay in response to Ethylmethylphosphonic acid (EMPA) and Methylphosphosphonic acid (MPA) loading to the Delaware River.

This paper addresses these concerns by describing and summarizing the work that has been completed on the fundamental chemistry of NCH and its treatment. This paper covers the fate of VX, EMPA, MPA, thiolamine, and EA2192 -- all compounds for which concerns have been raised.

The concern most often raised by elected officials and regulators, with regard to the proposal, is that the NCH may contain residual concentrations of VX that may be harmful to people or the environment. DuPont has stated that it will not accept NCH that contains detectable levels of VX, where the detection limit for VX is defined as 20 parts per billion (20 ug/L) or less. This is the current limit of accurate quantification of VX in samples of NCH. Although this acceptance criterion will be applied throughout the duration of the project, DuPont believes that the actual concentration of VX in the NCH will be far less than 20 ppb, as will be demonstrated in this paper. Further, studies have shown the proposed SET treatment process is effective at eliminating trace levels of VX.
The chemistry of the VX agent destruction reactions being carried out at Newport tell us that the presence of VX should be at a concentration so low that it would be immeasurably small and exhibit no effect on people or the environment. The destruction of VX at the Newport Chemical Agent Disposal Facility (NECDF) is rapid and driven towards completion by the specified reaction conditions of excess caustic, elevated temperature, thorough mixing and extended reaction time. As an additional layer of protection, additional testing has shown the SET treatment process is also effective at destroying trace quantities of VX. Another layer of protection includes oversight and involvement in the analytical work being performed at NECDF. The analytical data set for each batch of hydrolysate will be thoroughly reviewed by DuPont chemists prior to acceptance.

The primary components of NCH are thiolamine, EMPA and MPA. EMPA and MPA are phosphorus-based compounds with low toxicity; however, phosphorus is a plant nutrient, and has been known to stimulate excessive algal growth in aquatic environments. The proposed treatment plan at SET has been shown to be effective in removing these phosphonates by greater than 96%. Thiolamine, an organic compound, is readily destroyed (>99%) in the pretreatment process.

DuPont’s proposed NCH treatment plan involves a combined pretreatment step of aggressive chemical oxidation and precipitation, and two-stage PACT® treatment. PACT® treatment utilizes powdered activated carbon and biotreatment for enhanced wastewater treatment. The chemical oxidation stage destroys organic constituents in the NCH and converts approximately 99% of the EMPA to MPA. The precipitation stage removes more than 95% of the total MPA as well as other breakdown products from the oxidation stage. The effluent from the combined pretreatment step is further treated by the two-stage PACT® biotreatment system.

In order to evaluate the question of whether the pretreatment process would destroy VX or EA2192 a study was performed at NECDF. Samples of hydrolysate were spiked with 200 ppb VX and 1,000 ppb EA2192 and then subject to the oxidative pretreatment step. All samples were non-detect for VX at a nominal detection level of 20ppb and EA2192 at a nominal detection level 200 ppb. These results demonstrate that the oxidation process is capable of destroying trace levels of VX and EA2192. Since this oxidative destruction of VX proceeds through a different mechanism than the treatment at NECDF, it provides another layer of assurance that VX will be thoroughly destroyed and will not impact the Delaware River.
As a final test of treatment effectiveness of the NCH mixture, effluents from the biotreatability reactors were tested for acute\(^1\) and chronic\(^2\) toxicity using the test methodology outlined by the US EPA. The toxicity results from the effluents from the combined pretreatment process and biotreatability reactors indicate that the proposed treatment plan for NCH will not cause any adverse effects to the Delaware River.

A Layers of Protection Approach (LOPA) was adopted to evaluate whether the caustic hydrolysate from NECDF could be handled safely and be protective of the environment. The fundamental chemistry, operational parameters, and analytical verification each provide a layer of protection at NECDF. In addition, the proposed NCH wastewater treatment process in terms of phosphonate (EMPA and MPA) removal efficiency, VX and EA2192 removal demonstration, and the acute and chronic toxicity evaluation provide additional layers of protection. This LOPA analysis shows NCH can be treated safely at the SET facility without adverse affect on the environment.

The following paragraphs evaluate the layers of protection along each step of the process to ensure safe and effective treatment of NCH at DuPont’s SET facility.

The following schematic (Figure 1) shows the treatment steps of the VX Agent at NECDF and subsequent treatment steps to treat the NCH at the DuPont SET facility. A brief description of the process steps is as follows:

A  VX Agent stored in ton cylinders at the Newport (IN) Chemical Disposal Facility (NECDF)

B  Hydrolysate wastewater following destruction of VX Agent at NECDF

C  Effluent from DuPont Chemical Oxidation Pretreatment Step (Oxidation of Thiolamine and EMPA)

D  Effluent from DuPont Chemical Precipitation (Removal of MPA)

E  Effluent from DuPont Wastewater Treatment Plant PACT\(^{\text{®}}\) Process

---


Figure 1

DuPont Hydrolysate Wastewater Treatment Process

A. Stored VX Agent 97%-99% VX Agent

B. Newport Chemical Weapons Disposal Facility, Indiana

C. Receiving Tank

D. Phosphonate Removal Process

E. Effluent discharged to Delaware River per NDEP Permits

Stored VX waste is 85% water and non-detect for VX.

ISO container trucks meet DOT and ASME standards.

Filter

Oxidizer added

Reactor Tank

First Stage PACT® Carbon Bio-treatment

First Stage Clarification Process

Second Stage PACT® Carbon Bio-treatment

Treatment completed

pH Adjustment process

Solids removed to secure onsite landfill.
2.0 Agent Destruction at NECDF

2.1 Fundamental Chemistry

The neutralization process for the disposal of VX involves the sodium hydroxide catalyzed cleavage (hydrolysis) of the P-S bond. Cleavage of the P-S bond destroys the characteristic toxicity of this nerve agent. The fundamental chemistry of VX destruction (caustic hydrolysis) is well known and occurs according to the following general reaction scheme:

\[
\text{VX} + 1.9 \text{ NaOH} \rightarrow 0.9 \text{ EMPA-Na} + 0.9 \text{ RS-Na} + 0.1 \text{ EA2192-Na} + 0.1 \text{ EtOH}
\]

\[
0.1 \text{ EA2192-Na} + 0.2 \text{ NaOH} \rightarrow 0.1 \text{ MPA-Na}_2 + 0.1 \text{ RS-Na} + 0.1 \text{ H}_2\text{O}
\]

\[
0.9 \text{ EMPA-Na} + 0.9 \text{ NaOH} \rightarrow 0.9 \text{ MPA-Na}_2 + 0.9 \text{ EtOH} \text{ (Slow Reaction)}
\]

The major reaction involves the attack of OH\(^-\) on phosphorus and the cleavage of the P-S bond to form the sodium salt of ethylmethylphosphonic acid (EMPA) and thiolamine. The minor reaction involves the cleavage of the P-O bond to form the intermediate compound, EA2192, which is subsequently hydrolyzed at elevated temperatures to methylphosphonic acid (MPA) and thiolamine.

The overall reaction requires more than 2 moles of NaOH per mole of VX and can be written as:

\[
\text{VX} + 2.1 \text{ NaOH} \rightarrow \text{RS-Na} + 0.9 \text{ EMPA-Na} + 0.1 \text{ MPA-Na}_2 + 0.1\text{H}_2\text{O}
\]

---


The term 8% NCH refers to the hydrolysis product obtained by the reaction of VX and aqueous hydroxide solution in the weight ratio of 8.0 to 92.0. The term 16% NCH refers to the hydrolysis product obtained by reaction of VX and an aqueous solution of sodium hydroxide in the weight ratio of 16.0 to 84.0. Both reactions have excess sodium hydroxide in aqueous solution which is sufficient to totally convert the VX and leave an excess of 1.0 mole of sodium hydroxide per 1000 grams in the final solution.

2.2 Mixing

The caustic neutralization of VX will be performed in semi-batch reactors containing hot caustic at NECDF. The reactors will be mixed by in-vessel turbines to ensure there are no stagnant regions in the vessel and will be equipped with a continuous recirculation loop with an in-line mixer. The VX will be fed into hot recirculating caustic directly upstream of the static mixer at a rate only slightly greater than its rate of destruction.

The mixing requirements for effective VX dispersion during the caustic hydrolysis reaction were reported in “Analysis and Scale-up of Mixing for VX Neutralization University of Louisville Mixing Study”, October 1999. The test program at the University was conducted in equipment similar in scale to the proposed reactors at NECDF. The studies demonstrate that the in-vessel and recirculation loop provide excellent mixing and created a high surface area dispersion that enable the hydrolysis reaction to proceed to completion. The recirculation loop and in-vessel mixing were shown to result in the droplet size required for efficient VX neutralization and ensure complete uniformity of composition within the vessel.

---

2.3 Rate of Reaction

There are several values in the literature for the reaction rate of VX at a variety of temperatures and sodium hydroxide concentrations. Rate constants of 0.6m⁻¹ and 35.65m⁻¹ have been reported for 0.1M and 1.0M NaOH, respectively⁹. There are no reported values at the higher concentrations of sodium hydroxide that will be used at NECDF in the destruction process. The reaction rate at the higher NaOH concentration would be expected to be as fast as or faster than the rate at 1.0 M for a given reaction temperature and initial VX concentration. To be extremely conservative, the rate constants for 0.1 M NaOH were used to calculate the concentration of VX present at the end of the reaction.

The pseudo first order rate constant at 90°C is 0.6m⁻¹ (at 0.1 M NaOH)⁹. The final concentration of a first order reaction may be defined by¹⁰:

\[ C(t) = C(0) e^{(-kt)} \]

where \( C(t) \) is the concentration at time t, \( C(0) \) is the initial concentration, and k is 0.6m⁻¹, the first order rate constant.

The concentration of VX will decrease rapidly under these reaction conditions and will be reduced from an initial concentration of 0.3 moles/liter (80,000 ppb) to non-detect (<20 ppb) within the first 30 minutes of the reaction (Figure 2).

---


Figure 2: Calculated VX concentration vs. time for the caustic hydrolysis of VX at a temperature of 90°C and initial concentration of 0.3 moles/L

![Graph showing VX concentration vs. time](image)

The final VX concentration at 150 minutes, and a temperature of 90°C (the minimum reaction time and temperature which will be used at NECDF) with an initial VX concentration of 0.3 moles/L was calculated to be:

\[
C(150) = 0.3 \text{ moles/liter} e^{-0.6 \times 150} = 2 \times 10^{-40} \text{ moles/liter}
\]

This VX concentration (2 x 10^{-40} moles/liter) is equivalent to 6.6 x 10^{-32} ppb (µg/L) VX or 2.1 x 10^{22} molecules of VX/L of NCH. The anticipated concentration of VX in the NCH after caustic hydrolysis is significantly less than the 20 ppb clearance level.

This is an approximation because the concentration equation is not linear at very low reactant concentrations. However, because the rate constant used was extremely conservative and because the calculated VX concentration is extremely low (10^{-40} moles/liter), even if the concentration were off by several orders of magnitude the final VX concentration would be so low that it cannot be accurately measured and would not produce an adverse effects on people or the environment, in other words the concentration would be the “practical equivalent of zero”.
2.4 NCH Clearance at NECDF

The destruction of VX is verified by a highly sophisticated analytical procedure designed to provide an extremely small probability of giving a false negative result. The CDC, in its report “Review of the U.S. Army Proposal for Off-Site Treatment and Disposal of Caustic VX from the Newport Chemical Agent Disposal Facility” found that “The current analytical methods for the analysis of VX agent and EA 2192 in 8% VX loaded, DIC-stabilized Caustic VX hydrolysate (CVXH) are adequate to detect and quantify the established clearance levels for VX”11.

The GC-ITMS detection of VX requires the evaluation of three ions, M/Z 128, 139 and 167. These three ions can be thought of as a "fingerprint" for the detection of VX. Although there are specific criteria for clearance or conversely criteria for a positive detection of VX, the most controversy or confusion lies in the discussion of the 128 ion. In order for a batch to fail clearance, the signal from the 128 ion must be greater than three times the signal to noise ratio. Since the 128 ion is also an ion of other hydrolysate products, it can be thought of as a "fail safe". Detection of the 128 ion at levels greater then three times the standard deviation of the noise will require the hydrolysate to be held at high temperature to continue the reaction until the 128 ion is cleared, even if the detection is due only to the hydrolysis products, and not VX.

2.5 Storage of NCH at NECDF

After destruction at NECDF, the NCH will be stored in a solution of excess sodium hydroxide and maintained in a reactive matrix until final treatment at DuPont SET. The term reactive matrix is used to indicate that agent will not survive, and cannot reform, under these conditions. In the presence of hydroxide ion, water reacts with agent to form the products of hydrolysis of agent. The reverse reaction, to reform agent from its hydrolytic degradation products, would also reform the water consumed in the hydrolysis reaction. Consistent with the principal of mass action, the large excess of water and hydroxide ion forces this reaction in the direction of hydrolysis, rather than the reverse direction to form agent and water. In a reactive matrix, if any agent were present, it would continue to undergo hydrolytic degradation.

11 Department of Health and Human Services Centers for Disease Control and Prevention; Review of the U.S. Army Proposal for Off-Site Treatment and Disposal of Caustic VX from the Newport Chemical Agent Disposal Facility; April 2005, page 12.
3.0 Transportation of NCH

In 2004, DuPont completed a Transportation Safety Assessment and Risk Management Plan for the shipment of hazardous wastewater from the NECDF. This assessment was reviewed in 2005 by the Centers for Disease Control and Prevention (CDC) in collaboration with the Department of Transportation (DOT). The key findings from the CDC review stated that the DuPont Transportation Plan, "appropriately addresses key risk management considerations, as well as DOT regulations for transporting hazardous materials." Furthermore, the report goes on to conclude that the "precautions used to manage the corrosivity hazard characteristic in the event of a spill are adequate to protect response personnel".

The corrosive wastewater to be transported for this proposed project is classified as a medium-hazard material (Corrosive, PGII) by the DOT and does not pose any unique or new concerns in transportation. The transportation risks for this material along the four identified routes are very low to populations, employees, emergency response personnel and the environment. DuPont has carefully selected the routes, carriers and equipment to further reduce the risk of accident or release of material. DuPont's risk management plan includes the use of a carrier with "best in industry" safety qualifications and dedicated equipment with driver teams to reduce transit time, layover and improve the security of the shipment. All equipment will meet or exceed DOT regulations, be equipped with speed governors, and trailers will be built to American Society of Mechanical Engineers (ASME) boiler code standards. To further enhance the communications and security of the shipments, Global Positioning Systems (GPS) will be utilized in the dedicated trucks.
4.0 Newport Caustic Hydrolysate (NCH): Combined Pretreatment and Biotreatment

The NCH from NECDF received at SET will undergo oxidative pretreatment, precipitation, and biological treatment at the DuPont Secure Environmental Treatment (SET) facility in Deepwater, NJ, prior to discharge. The pretreatment process proposed by DuPont utilizes an aggressive chemical oxidation stage to destroy thiolamine and convert EMPA to MPA. The MPA is removed in the precipitation stage and the effluent is sent to the SET wastewater treatment facility for additional treatment by the two-stage PACT® biotreatment system. The treatment is over 95% effective in the removal of phosphonates (EMPA and MPA) and over 99% effective in the removal of thiolamine.

4.1 Overall Process Description

The full-scale combined pretreatment process is proposed to be a semi-batch procedure, to allow for testing of each batch before releasing to the next process step. The Secure Environmental Treatment (SET) wastewater treatment facility recommends receipt and storage of the Newport Caustic Hydrolysate (NCH) in a 100,000 gallon agitated tank with emissions controls. NCH will be pumped directly from this tank to the pH adjustment step. Twenty percent sulfuric acid will be utilized to adjust NCH to a neutral pH via a two-stage pH adjustment step. The first stage is an in-line mixer and the second stage is a continuous stirred tank reactor with pH controls.

The neutral NCH and sodium persulfate solution will be fed into the chemical oxidation reactor along with other potential oxidants or catalysts. The reactor temperature will be raised to 80°C and the oxidation reaction will be allowed to proceed for 30 minutes. Additional sodium persulfate solution then will be fed into the reactor and the oxidation reaction will be allowed to proceed for 2 ½ hours at 80°C. The temperature will then be increased to 90°C for an additional 30 minutes. Organic constituents, including thiolamine and EMPA, will be fully oxidized via this pretreatment.

The reaction mass will be cooled and a lime slurry and ferric chloride will be injected to increase the pH and precipitate out MPA. The liquid phase, or pretreated effluent, will then be pumped to a large holding tank to be sampled and analyzed for key constituents such as thiolamine, EMPA, and MPA. If treatment specifications are not met, the material will be sent back to the chemical oxidation reactor for reprocessing. Solids from the precipitation stage will be collected, tested, and managed in the SET Resource, Conservation and Recovery Act (RCRA) Subtitle C secure on-site landfill.
The pretreated effluent will be sent to the wastewater treatment plant (WWTP) for additional treatment by the two-stage PACT® biotreatment. The WWTP plant maintains rigorous process controls on standard wastewater parameters. The combined pretreatment process will allow tight control of the oxidation reaction and precipitation steps, and ensure safe and effective treatment of the NCH such that the organics are effectively destroyed and the phosphonates are removed.

The GC/MS analyses of the 16% NCH DIC hydrolysate “as received”, and after oxidation are shown in Figures 3. The GC/MS analysis demonstrates the organic components in the hydrolysate “as received” are destroyed after the sodium persulfate oxidation stage. A small amount of acetic acid generated during the oxidation of NCH (DIC), is removed in the precipitation stage. Both the 8% and 16% GC/MS scans are similar and are available in the phosphonate removal treatability studies posted on the SET website (www.set.dupont.com). The GC/MS data indicates that organic components in the hydrolysate are effectively destroyed and removed during the combined pretreatment process. Both the 8% and 16% GC/MS scans show similar destruction and removal of organics.
Figure 3: GC/MS Analysis of 16% NCH (DIC) “as received” and after the oxidation step of the Combined Pretreatment Process.

GC/MS of “as received” 16% NCH (DIC) before oxidation

GC/MS Chromatogram of Oxidized 16% NCH (DIC)
4.2 Combined Pretreatment Details

4.2.1 8% NCH (DIC) - Removal of Thiolamine, EMPA, and MPA

The following section provides the details around concentration and mass load for the treatment of 8% NCH. The mass loading calculation accounts for the effects of dilution in the wastewater treatment plant.

8% NCH DIC “as received” has a density of 1.09 g/ml and contains approximately 36,109 mg/L EMPA, 2,297 mg/L MPA, 20,900 mg/L thiolamine and <100 mg/L PO₄. The NCH is pH adjusted to a pH of approximately 6-7 with 20% sulfuric acid solution at a treatment ratio of 2.76:1 NCH:H₂SO₄ (w:w). This pH adjustment stage reduces the concentration of constituents in the NCH by a factor of 1.35 on a volume basis.

Sodium persulfate is dissolved in deionized water and added to the pH adjusted NCH at a treatment ratio of 0.38 sodium persulfate:NCH (w:w). This is equivalent to a sodium persulfate/EMPA weight ratio of 13.9. The oxidation stage destroys the thiolamine and other organic components and results in essentially the complete conversion of EMPA to MPA. The oxidized sample contained 40 mg/L EMPA, 11,731 mg/L MPA and 131 mg/L PO₄. The oxidation stage reduces the concentrations of the remaining constituents by 1.98.

Ferric chloride solution is added to the oxidized solution to a final concentration of 20,000 mg/L and the pH of the solution is adjusted to a pH of 5 by the addition of lime slurry. In laboratory studies, additional deionized water is added to the sample to adjust the final volume of the sample to twice its initial volume to facilitate comparison of treatment conditions and precise calculation of MPA removal efficiencies. In a pilot or full-scale operation this deionized water addition may be omitted from the process. The precipitation stage results in a reduction in the MPA concentration of the sample. The effluent from the precipitation stage contained <10 mg/L EMPA, 157 mg/L MPA and < 5 mg/L PO₄. This represents a reduction of 99.7% and 97.3%, for EMPA and MPA, respectively, and an overall phosphonate removal of 99.6% for the combined pretreatment process relative to the initial compound concentrations.

The pH adjustment and combined pretreatment technology results in an overall dilution (or mixing ratio) of 5.3 for the NCH sample “as received” (Note: this mixing ratio will be lower in the full-scale facility where it is anticipated the additional water is not added to the precipitation stage).
The effluent from the combined pretreatment process is fed to the SET biotreatment facility at a rate of 5,000 to 10,000 gallons per day (GPD) “as received” or 53,460 GPD from the combined pretreated effluent. The minimum plant flow rate is anticipated to be 10 MGD. The biotreatment stage of the treatment process results in the removal of organic components of the wastewater using a two-stage PACT® system. The mixing ratio associated with the two-stage biotreatment with a 53,460 GPD pretreated NCH stream (equivalent to 10,000 GPD “as received”) and 10 million gallons per day (MGPD) plant flow is 187. (Note: Mixing ratio for “as received” NCH is 1:1000)

The effluent from the WWTP (10MGD) is mixed with non-contact water before discharge to the Delaware River. The total plant outfall flow is 26 MGD. The mixing ratio associated with the non-contact water is 2.6 “as received” and 0.486 “pretreated”.

The expected concentration of EMPA, MPA, and PO₄ in the discharge to the Delaware River are <0.02, 0.3 and 0.006 mg/L, respectively, at the 10,000 GPD 8% NCH treatment rate. The associated mass loading to the river is calculated to be <3.8, 60, and 1.3 lbs/day, respectively. Figures 4 and 5 show the concentration (mg/L) and mass loading (lbs/day) of EMPA, MPA and thiolamine through the combined pretreatment and PACT® processes for 8% NCH at a treatment rate of 10,000 GPD.

**Figure 4:** Concentrations of EMPA, MPA and Thiolamine through the Combined Pretreatment and PACT® Processes in the Treatment of 8% NCH. (See Figure 1 for locations denoted B, C, D and E)
4.2.2 16% NCH (DIC) – Removal of Thiolamine, EMPA, MPA and Phosphate.

The EMPA conversion, MPA removal efficiency, thiolamine destruction and overall phosphonate removals for the 16% NCH samples were comparable to the 8% NCH results. To better understand the overall phosphorus balance, phosphate (PO$_4$) was accounted for in the 16% NCH.

16% NCH DIC “as received” contains approximately 81,346 mg/L EMPA, 6,792 mg/L MPA, 72,400 mg/L thiolamine and 290 mg/L PO$_4$. The NCH is pH adjusted to a pH of approximately 6-7 with 20% sulfuric acid solution and reduces the concentration of constituents in the NCH by a factor of 1.5 on a volume basis.

Sodium persulfate is dissolved in deionized water and added to the pH adjusted NCH at a treatment ratio of 1.08 sodium persulfate:NCH “as received” (w:w). The oxidation stage destroys the thiolamine and other organic components and results in essentially the complete conversion of EMPA to MPA. The oxidized sample contained <50 mg/L EMPA, 10,829 mg/L MPA, <5 mg/L thiolamine and <50 mg/L PO$_4$. The oxidation stage reduces the concentrations of the remaining constituents by 3.1.
Ferric chloride solution is added to the oxidized solution to a final concentration of 20,000 mg/L and the pH of the solution is adjusted to a pH of 5 by the addition of lime slurry. The precipitation stage results in a reduction in the MPA concentration of the sample. The effluent from the precipitation stage contained <50 mg/L EMPA, 180 mg/L MPA and <50 mg/L PO₄. This represents a reduction of >99.7% and 95.8%, for EMPA and MPA, respectively, and an overall phosphonate removal of >96.6% for the combined pretreatment process relative to the initial concentration.

The pH adjustment and combined pretreatment technology results in an overall dilution (or mixing ratio) of 11.9 for the 16% NCH sample “as received”. The effluent from the combined pretreatment process is fed to the SET biotreatment facility at a rate of 5,000 to 10,000 gallons per day (GPD) “as received” or 119,000 GPD from the combined pretreated effluent. The minimum plant flow rate is anticipated to be 10 MGD. The biotreatment stage of the treatment process results in the removal of organic components of the wastewater using a two-stage PACT® system. The mixing ratio associated with the two-stage biotreatment with a 119,000 GPD pretreated NCH stream (equivalent to 10,000 GPD “as received”) and 10 million gallons per day (MGPD) plant flow is 84.

The expected concentration of EMPA, MPA, and PO₄ in the discharge to the Delaware River are <0.2, 0.7 and <0.2 mg/L, respectively, at the 10,000 GPD 16% NCH treatment rate. The associated mass loading to the river are calculated to be <42, 153, and <42 lbs/day, respectively. Figures 6 and 7 show the concentration (mg/L) and mass loading (lbs/day) of EMPA, MPA, thiolamine and PO₄ through the combined pretreatment and PACT® processes for 16% NCH (DIC) at a treatment rate of 10,000 GPD.

Figure 6: Concentrations of EMPA, MPA, Thiolamine and Phosphate through the Combined Pretreatment and PACT® Process in the Treatment of 16% NCH (DIC). (See Figure 1 for locations denoted B, C, D and E)
Figure 7: Mass Loads of EMPA, MPA and Thiolamine through the Combined Pretreatment and PACT® Processes in the Treatment of 16% NCH (DIC).
5.0 Newport Caustic Hydrolysate (NCH): Effect of Combined Pretreatment on VX and EA2192 in Hydrolysate

The combined pretreatment process utilizes an aggressive chemical oxidation stage to destroy the organic constituents of the NCH and convert EMPA to MPA. The chemical oxidation stage of the combined pretreatment was evaluated in response to a question posed by the CDC regarding the effect of the DuPont oxidation process on VX and EA2192. The studies were conducted at NECDF with the oversight of a DuPont chemist\(^\text{12}\).

Samples of 16% (wt.%) NCH were spiked with 200 ppb VX and 1,000 ppb EA2192 and analyzed for these compounds before and after the oxidative pretreatment. To confirm starting levels of VX, the spiked samples were analyzed and VX concentrations ranged from 124 to 195 ppb. After oxidation, all samples were non-detect for VX using detection levels of 20 ppb. The 128 ion, as discussed in 2.4, was also not detected.

Similarly, to confirm starting levels of EA2192, the spiked samples were analyzed for EA2192 and the concentrations ranged 923 to 1,130 ppb. After oxidation, all samples were non-detect for EA2192.

The results of the spiking experiment demonstrate that the oxidation process destroys trace quantities of VX and EA2192 in 16 wt.% hydrolysate. Since this oxidative destruction of VX proceeds through a different mechanism than the treatment at NECDF, it provides another layer of assurance that VX will be thoroughly destroyed and not impact the Delaware River.

---

6.0 Newport Caustic Hydrolysate (NCH): Aquatic Toxicity Testing of Combined Pretreatment and Treatability Reactor Effluents.

The acute and chronic aquatic toxicity testing was to conduct to determine if there was significant toxicity associated with the effluent from the treated NCH mixture. The results show effluents from combined pretreatment (oxidation and precipitation) or biotreatability reactors. The toxicity testing was robust, in that the testing encompassed three species of biota covering three trophic levels. The toxicity testing showed the treatment of the NCH mixture by the proposed SET treatment plan will cause no adverse effects to the Delaware River.

Acute whole effluent toxicity (WET) testing of the bioreactor effluents was conducted with *Pimephales promelas* (fathead minnow) using the test methodology outlined in US EPA-821-R-02-012 Methods for Measuring the Acute Toxicity of Effluents and Receiving Waters to Freshwater and Marine Organisms, 5th Edition. Chronic aquatic toxicity studies of the combined pretreatment and bioreactor effluents were completed using *Pimephales promelas* (fathead minnow), *Ceriodaphnia dubia* (water flea) and for the 16% NCH samples, *Pseudokirchneriella subcapitata* (green algae). The chronic toxicity studies used the test methodology outlined in US EPA-821-R-02-013 (October 2002) Short-Term methods for Estimating the Chronic Toxicity of Effluents and Receiving Waters to Freshwater Organisms, 4th Edition. EA Engineering Science and Technology, Sparks MD performed the acute and chronic toxicity testing.

Acute and chronic toxicity were measured using a multi-concentration or definitive test, consisting of a control and a minimum of five effluent concentrations. The tests were designed to provide dose-response information, expressed as the percent effluent concentration that affects mortality, growth, and/or reproduction. The results of the acute tests were statistically determined as the concentration of effluent that caused mortality in 50% of the organisms (fathead minnow), defined as the LC50. The criterion for judging the LC50 results was the current NJPDES permit limit requiring LC50 > 50%.

The results of the chronic tests were expressed in terms of the highest concentration that had no statistically significant observed effect on those responses when compared to the controls, defined as No Observable Effect Concentration (NOEC). The criterion for judging the NOEC results was assurance that the NOEC value was greater than the in-stream waste concentration (IWC) that has been drafted by the Delaware River Basin Commission (DRBC). The IWC is defined by EPA as the concentration after mixing of an effluent in the receiving water. The DRBC has determined that the IWC for the site outfall is approximately 1%. Since the WWTP discharge comprises about 40% of the site discharge, the IWC for the WWTP discharge is 0.4%.
Chronic testing was performed on the effluents from the Combined Pretreatment Process with 8% NCH (DIC) and 16% NCH (DIC, DCC and DIC/DCC). Acute and chronic testing were performed on the effluents from the laboratory-scale 2-stage PACT® biotreatability reactors receiving the equivalent of 5000 GPD and 10,000 GPD of the pretreated 8% NCH (DIC) and 16% NCH (DIC, DCC and DIC/DCC) that had been subject to the Combined Pretreatment Process.

The effluent from the control and NCH biotreatability reactors for both 8% and 16% NCH did not adversely affect survival in the acute whole effluent toxicity studies (Table 1).

Table 1: Bioreactor Acute Whole Effluent Toxicity Testing with Fathead Minnow (*Pimephales promelas*) with 8% NCH (DIC) and 16% NCH (DIC, DCC and DIC/DCC)

<table>
<thead>
<tr>
<th>NCH Stabilizer</th>
<th>NCH Loading GPD</th>
<th>96-Hour LC50</th>
</tr>
</thead>
<tbody>
<tr>
<td>Control</td>
<td>N/A</td>
<td>&gt;100%</td>
</tr>
<tr>
<td>8% NCH DIC</td>
<td>5,000</td>
<td>&gt;100%</td>
</tr>
<tr>
<td>8% NCH DIC</td>
<td>10,000</td>
<td>&gt;100%</td>
</tr>
<tr>
<td>16% NCH DIC</td>
<td>5,000</td>
<td>&gt;100%</td>
</tr>
<tr>
<td>16% NCH DCC</td>
<td>5,000</td>
<td>&gt;100%</td>
</tr>
<tr>
<td>16% NCH DIC/DCC</td>
<td>5,000</td>
<td>&gt;100%</td>
</tr>
</tbody>
</table>

Table 2, below, provides a summary of the fathead minnow, *Ceriodaphnia* and green algae chronic toxicity testing results on the 8% and 16% NCH samples subjected to the combined pretreatment process only (*i.e.*, without PACT® biotreatment). In all cases, the NOEC values were 100% for both the fathead minnow and green algae, indicating no chronic toxicity to these species. The NOEC values observed for *Ceriodaphnia* in the 8% NCH testing ranged from 25 % to 50%, yielding a margin of safety of two orders of magnitude compared with the in-stream waste concentration (IWC) of 0.4%. The *Ceriodaphnia* NOEC values in the 16% NCH testing ranged from 3.1 to 6.25%, yielding a margin of safety of about an order of magnitude compared with the IWC.
The chronic aquatic toxicity test results for the 8% and 16% NCH biotreatment effluents are provided in Table 3. The effluent from the 8% NCH (DIC) reactors did not adversely affect growth and survival in the fathead minnow studies. There was no statistical difference between the control and NCH treatability reactors receiving either 5,000 or 10,000 GPD pretreated 8% NCH (DIC) in the Ceriodaphnia studies. Similarly, there was no statistical difference in NOEC values between the control and NCH treatability reactors receiving 5000 GPD loading rate in either the fathead minnow or the Ceriodaphnia studies. At the 10,000 GPD loading rate, chronic NOECs for the biotreatment effluents were 12.5-50% for the fathead minnow and 3.1-25% for Ceriodaphnia. The NOEC values obtained in all tests were approximately an order of magnitude, or more, greater than the expected in-stream waste concentration.

Table 2: Chronic Toxicity Testing Results for the Effluent from the Combined Pretreatment Process with 8% and 16% NCH containing the DIC, DCC or both DIC/DCC stabilizers

<table>
<thead>
<tr>
<th>NCH</th>
<th>Stabilizer</th>
<th>Fathead Minnow NOEC</th>
<th>Ceriodaphnia dubia NOEC</th>
<th>Green Algae NOEC</th>
</tr>
</thead>
<tbody>
<tr>
<td>8% NCH</td>
<td>DIC</td>
<td>100%</td>
<td>50%</td>
<td></td>
</tr>
<tr>
<td></td>
<td>DCC</td>
<td>100%</td>
<td>25%</td>
<td></td>
</tr>
<tr>
<td></td>
<td>DIC/DCC</td>
<td>100%</td>
<td>50%</td>
<td></td>
</tr>
<tr>
<td>16% NCH</td>
<td>DIC</td>
<td>100%</td>
<td>6.3%</td>
<td>100%</td>
</tr>
<tr>
<td></td>
<td>DCC</td>
<td>100%</td>
<td>3.1%</td>
<td>100%</td>
</tr>
<tr>
<td></td>
<td>DIC/DCC</td>
<td>100%</td>
<td>6.3%</td>
<td>100%</td>
</tr>
</tbody>
</table>
Saltwater solutions were prepared containing the major salt components of the biotreatability effluents from 8% and 16% NCH testing including calcium, magnesium, sodium, chloride, sulfate and bicarbonate. The salt levels had no apparent effect on chronic toxicity to fathead minnow, for 8% and 16% NCH at the 10,000 GPD rate. However, at these salt levels, the *Ceriodaphnia* NOEC was 50% at the salt loading equivalent to the 10,000 GPD rate of 8% NCH, and 12.5% at the salt loading equivalent to the 10,000 GPD rate of 16% NCH. By comparison with the results in Table 3, it can be seen that the simple salt levels in the wastewater can explain a major portion of any chronic toxicity observed in *Ceriodaphnia*.

The acute and chronic toxicity results of the effluents from the combined pretreatment process and biotreatability reactors indicated that the discharge from the proposed pretreatment process, consisting of chemical oxidation, precipitation and biotreatment, resulted in effluents that will cause no adverse effects to the Delaware River.

### Table 3: Chronic Toxicity Testing Results of Biotreatability effluents with 8% NCH (DIC) and 16% NCH (DIC, DCC and DIC/DCC) at loading rates of 5,000 and 10,000 GPD.

<table>
<thead>
<tr>
<th>Reactor</th>
<th>Stabilizer</th>
<th>NCH Loading GPD</th>
<th>Fathead Minnow NOEC</th>
<th>Ceriodaphnia dubia NOEC</th>
</tr>
</thead>
<tbody>
<tr>
<td>Control</td>
<td>N/A</td>
<td>25%</td>
<td>50%</td>
<td>50%</td>
</tr>
<tr>
<td>8% NCH</td>
<td>DIC</td>
<td>5,000</td>
<td>50%</td>
<td>50%</td>
</tr>
<tr>
<td>8% NCH</td>
<td>DIC</td>
<td>10,000</td>
<td>50%</td>
<td>50%</td>
</tr>
<tr>
<td>Control</td>
<td>N/A</td>
<td>12.5%</td>
<td>25%</td>
<td>25%</td>
</tr>
<tr>
<td>16% NCH</td>
<td>DIC</td>
<td>5,000</td>
<td>25%</td>
<td>25%</td>
</tr>
<tr>
<td>16% NCH</td>
<td>DCC</td>
<td>5,000</td>
<td>50%</td>
<td>25%</td>
</tr>
<tr>
<td>16% NCH</td>
<td>DIC/DCC</td>
<td>5,000</td>
<td>50%</td>
<td>25%</td>
</tr>
<tr>
<td>Control</td>
<td>N/A</td>
<td>50%</td>
<td>25%</td>
<td>25%</td>
</tr>
<tr>
<td>16% NCH</td>
<td>DIC</td>
<td>10,000</td>
<td>25%</td>
<td>3.1%</td>
</tr>
<tr>
<td>16% NCH</td>
<td>DCC</td>
<td>10,000</td>
<td>50%</td>
<td>25%</td>
</tr>
<tr>
<td>16% NCH</td>
<td>DIC/DCC</td>
<td>10,000</td>
<td>12.5%</td>
<td>25%</td>
</tr>
</tbody>
</table>
7.0 Summary

The treatment of NCH at the DuPont SET facility in Deepwater, New Jersey was evaluated using a systems approach called Layers of Protection Analysis (LOPA). The analysis included the fundamental hydrolysis chemistry, operational parameters, analytical certification of VX and EA2192 concentrations, and the effect of the combined pretreatment process on effluent phosphonate (EMPA and MPA) concentrations and thiolamine. An additional study was conducted that verified that the SET process is capable of destroying trace levels of VX and EA2192. In addition, a series of toxicity studies was performed to assess whether there would be environmental effects from the treatment of the hydrolysate mixture.

A summary of the conclusions from this analysis is provided below.

- The destruction of VX is rapid and driven to completion under the proposed reaction conditions at NECDF. Studies at the University of Louisville demonstrated that the proposed reactor provided excellent mixing and ensured uniformity within the vessel.

- The reported rate constants from the reaction indicate the concentration of VX will be decreased to <20 ppb within the first 30 minutes of the hydrolysis reaction. The hydrolysis reaction will be run for at least 150 minutes (5 times as long) to ensure maximum destruction of VX and EA2192.

- NCH will be stored and shipped in a reactive solution, containing an excess of sodium hydroxide.

- The concentration of VX and EA2192 in hydrolysate will be verified non-detect for VX and EA2192. DuPont will review the operating conditions and analytical quality control data for each batch prior to clearance. Any batch outside the acceptance criteria will not be shipped for treatment to DuPont.

- The DuPont Transportation Plan adds additional layers of protection to prevent spills or transportation incidents, by requiring two drivers, GPS capability, and transport containers that exceed DOT requirements.

- DuPont has thoroughly evaluated the hazards of NCH and established to ensure the safety of workers and contractors at Chambers Works. DuPont safety systems and processes will be thoroughly followed in all aspects of this treatment program.

- The NCH wastewater will be treated at DuPont’s SET facility by a combined pretreatment process that uses aggressive chemical oxidation and precipitation. This is followed by two stages of PACT® - combined biological
and carbon treatment. This treatment scheme is effective in destroying and removing organics and phosphonates (EMPA and MPA) present in the NCH mixture.

- The chemical oxidation stage of the DuPont combined pretreatment process destroyed the VX and EA2192 spiked into NCH samples.

- The combined pretreatment process resulted in the removal of approximately 99.6% and > 96.6% of the total phosphonates in the 8% and 16% NCH (DIC) samples, respectively. The resulting mass loading of phosphorus to the Delaware Estuary is not expected to result in over stimulation of algal biomass.

- Acute and chronic toxicity testing with fish, invertebrates, and algae, in conjunction with environmental fate and treatability data demonstrate that NCH treatment by the SET facility would result in no adverse effects to the Delaware River.