# Risk Management Analysis

## Pueblo Chemical Agent-Destruction Pilot Plant (PCAPP) Hydrolysate Transportation Risk Assessment

**Final**

**June 2016**

| Site | Pueblo | Study Number | RM-16-002 | Rev. 0 |
|---|---|---|---|---|

Summary

An evaluation of the risk of transporting treated hydrolysate from PCAPP to the Veolia North America disposal facility in Port Arthur, Texas, was conducted. The regulations for hazardous materials classification, handling, loading, and transport were reviewed for safe transport of the hydrolysate in tanker trucks. The Department of Transportation risk management approach and state-of-the-practice approaches for Transportation Risk Assessments (TRAs) were reviewed and compared with the U.S. Army risk management approach to determine consistency. A TRA was conducted for the PCAPP hydrolysate using the Army approach by determining accident frequency and event consequences for (1) an accident/incident with a release/leak and (2) an accident with a release and a fuel fire. The results indicate that the transportation risk is *Acceptable* and that no mitigation measures are necessary.

**Prepared for**
**U.S. Army Chemical Materials Activity**

## Revision Log

| Rev. # | Date | Summary |
|---|---|---|
| Draft | May 2016 | Initial submittal |
| 0 | June 2016 | No technical changes from initial draft |

# 1. INTRODUCTION

Army Regulation (AR) 385-10 (DA 2013), *The Army Safety Program*, prescribes Department of the Army (DA) policy, responsibilities, and procedures to safeguard and preserve Army resources worldwide, including soldiers, Army civilians, and Army property, against accidental loss. The regulation establishes composite risk management as the Army's principal risk reduction methodology and ensures regulatory and statutory compliance. AR 385-10 provides for public safety during Army operations and activities. The risk assessment described in this paper conforms to the Army policies and procedures referenced in this paragraph.

## 1.1 Objective

The objective of this paper is to assess the risk related to offsite shipment, via a commercial carrier, of treated, agent-free hydrolysate from the Pueblo Chemical Agent-Destruction Pilot Plant (PCAPP) site in Pueblo, Colorado, to a hazardous waste treatment, storage, and disposal facility (TSDF). For the purposes of this study, the Veolia North America (Veolia) facility in Port Arthur, Texas, is assumed to be the TSDF, since this facility has previously processed and disposed of hydrolysate and agent-contaminated secondary waste from other chemical agent disposal facilities. The DuPont Chambers Works facility in Deepwater, New Jersey, which previously processed hydrolysate from a chemical agent disposal facility, was not considered because the facility no longer accepts commercial wastewater for treatment.

Army procedures for system safety management are outlined in Department of Army Pamphlet (DA Pam) 385-16 *System Safety Management Guide* (DA 2013). Paragraph 2-4c(1) of this document specifically excludes from the hazard analysis, systems or operations whose "design meets or exceeds applicable standards." In the context of this statement, hazards related to traffic accidents (i.e., fatalities or injuries directly resulting from a vehicle crash) are excluded from consideration in the hazard analysis if all applicable Department of Transportation (DOT) standards and requirements are met. Although not considered in the hazard analysis that follows, risks related to vehicle accidents are analyzed in Appendix A to this document.

## 1.2 Description of Hydrolysate

The process of mustard agent destruction at PCAPP (NRC 2015) initially involves separating the propellants from the projectiles and removing the bursters and other energetic components at the projectile/mortar disassembly (PMD) machine. The energetic components are sent offsite for destruction. The projectile bodies are drained of agent, washed out in the munitions washout station (MWS) with a high-pressure water stream, and then thermally decontaminated. The clean projectile bodies are shipped offsite for disposal. The mustard agent and washout water are sent to the agent hydrolysis reactors, where the agent is hydrolyzed at an 8.6 weight percent (wt.%) agent concentration in hot water at 194°F. Caustic is added to raise the pH to between 10 and 12 to prevent any reversible reactions back to mustard agent. The resulting product is called the agent hydrolysate. The hydrolysate is analyzed to verify the mustard concentration is below 200 parts per billion (ppb) (agent-free). The hydrolysate is then sent to one of three storage tanks.

Mustard agent hydrolysate is designated as a listed waste code K903 hazardous waste by the State of Colorado. The Department of Public Health and Environment (DPHE) defines K903 as "waste generated from the chemical neutralization of mustard agent by the addition of water and subsequent manipulation to a sustained and stable pH > 10 to ensure destruction of sulfonium ions and TDG-mustard aggregates."

Tables 1-1 and 1-2 summarize the results of the distilled sulfur mustard (HD) and mustard-T mixture (HT) hydrolysate analyses conducted in reference to the PCAPP hydrolysate characterization memo (SAIC 2010). Only constituents with concentrations greater than 0.01% (100 milligrams per liter [mg/L]) are shown. As observed, the principal constituent of the HD or HT hydrolysate is thiodiglycol (TDG), with approximately 95 to 96% solution of water containing sodium salts and sulfur compounds.

Table 1-1. Analysis of HD Hydrolysate

| **Analyte Name** | **CAS No.** | **Method** | **Results (%)** |
|---|---|---|---|
| 1,4-Oxathiane | 15980-15-1 | 8270C CWM | 0.025 |
| 1,4-Dithiane | 505-29-3 | 8270C CWM | 0.015 |
| TDG | 111-48-8 | PCAPP-114 | 4.7 |
| Q-OH; 3,6-Dithia-1,8-octanediol; Ethanol, 2,2'-[1,2-ethanediyl-bis(thio)]bis- | 5244-34-8 | PCAPP-114 | 0.43 |
| Iron | 7439-89-6 | 6020 | 0.0486 |
| Silicon (analyzed as silica) | 7440-21-3 | 6010B | 0.0254 |
| Sodium | 7440-23-5 | 6020 | 1.84 |
| Sulfur | 7704-34-9 | 6010B | 1.38 |
| Chloride | 16887-00-6 | 9056 | 3.53 |

Source: Adapted from SAIC 2010

Table 1-2. Analysis of HT Hydrolysate

| Analyte Name | CAS No. | Method | Results (%) |
|---|---|---|---|
| 1,4-Oxathiane | 15980-15-1 | 8270C CWM | 0.23 |
| 1,4-Dithiane | 505-29-3 | 8270C CWM | 0.017 |
| TDG | 111-48-8 | PCAPP-114 | 3.7 |
| Q-OH; 3,6-Dithia-1,8-octanediol; Ethanol, 2,2'-[1,2-ethanediyl-bis(thio)]bis- | 5244-34-8 | PCAPP-114 | 0.3 |
| bis(2-Chloroethyl)ether | 111-44-4 | 8270C | 0.01 |
| Silicon (analyzed as silica) | 7440-21-3 | 6010B | 0.0254 |
| Sodium | 7440-23-5 | 6020 | 2.02 |
| Sulfur | 7704-34-9 | 6010B | 1.34 |
| Chloride | 16887-00-6 | 9056 | 2.95 |

Source: Adapted from SAIC 2010

# 2. HAZARD CLASSIFICATION OF HYDROLYSATE

## 2.1 DOT Classification for Hazardous Materials

### 2.1.1 DOT Regulations

The DOT regulations address requirements for the safe and secure transportation of hazardous materials (hazmats). Title 49 of the Code of Federal Regulations (CFR) Part 172.101 categorizes hazmats into the following classes:

- Class 1: Explosives
- Class 2: Gases (flammable, non-flammable, or poisonous)
- Class 3: Flammable liquids (and combustible liquids)
- Class 4: Flammable solids; spontaneously combustible materials and dangerous when wet materials
- Class 5: Oxidizers and organic peroxides
- Class 6: Toxic (poison) materials and infectious substances
- Class 7: Radioactive materials
- Class 8: Corrosive materials
- Class 9: Miscellaneous dangerous goods.

49 CFR Part 172 prescribes the requirements for shipping papers, package marking, labeling, and transport vehicle placarding applicable to the shipment and transportation of each class of hazmat. In addition, it prescribes requirements for emergency response, training, and safety and security plans.

49 CFR Part 173 prescribes requirements for preparing the hazmats for shipment, including packaging requirements and quantity limitations.

49 CFR Part 177 prescribes requirements for transportation by public highway by motor vehicle, including inspections, driver training, segregation and separation, and loading and unloading requirements for each class of hazmat.

49 CFR Part 179 prescribes specifications for tank cars, including construction and design requirements, certification requirements, safety features, and testing requirements.

### 2.1.2 DOT Toxic Materials

49 CFR Part 173.132 defines a DOT Division 6.1 *poisonous material* as "a material, other than a gas, which is known to be so toxic to humans as to afford a hazard to health during transportation, or which, in the absence of adequate data on human toxicity."

- Is "presumed to be toxic to humans because it falls within any one of the following categories when tested on laboratory animals (whenever possible, animal test data that has been reported in the chemical literature should be used):
  - (i) *Oral Toxicity.* A liquid or solid with an $LD_{50}$ for acute oral toxicity of not more than 300 mg/kg.
  - (ii) *Dermal Toxicity.* A material with an $LD_{50}$ for acute dermal toxicity of not more than 1000 mg/kg.
  - (iii) *Inhalation Toxicity.* (A) A dust or mist with an $LC_{50}$ for acute toxicity on inhalation of not more than 4 mg/L; or"
- Is a "material with a saturated vapor concentration in air at 20 °C (68 °F) greater than or equal to one-fifth of the $LC_{50}$ for acute toxicity on inhalation of vapors and with an $LC_{50}$ for acute toxicity on inhalation of vapors of not more than 5000 $mL/m^3$; or"
- Is "an irritating material, with properties similar to tear gas, which causes extreme irritation, especially in confined spaces."

### 2.1.3 DOT Corrosive Materials

Per 49 CFR Part 173.136, a "corrosive material" means:

> a liquid or solid that causes full thickness destruction of human skin at the site of contact within a specified period of time. A liquid, or a solid which may become liquid during transportation, that has a severe corrosion rate on steel or aluminum based on the criteria in §173.137(c)(2) is also a corrosive material. Whenever practical, in vitro test methods authorized in §173.137 of this part or historical data authorized in paragraph (c) of this section should be used to determine whether a material is corrosive.

49 CFR Part 173.137 assigns packing groups (PGs) to Class 8 materials as follows:

- PG I – Materials that cause full thickness destruction of intact skin tissue within an observation period of up to 60 minutes starting after the exposure time of 3 minutes or less

- PG II – Materials other than those meeting PG I criteria that cause full thickness destruction of intact skin tissue within an observation period of up to 14 days starting after the exposure time of more than 3 minutes but not more than 60 minutes.
- PG III – Materials, other than those meeting PG I or II criteria:
  - That cause full thickness destruction of intact skin tissue within an observation period of up to 14 days starting after the exposure time of more than 60 minutes but not more than 4 hours; or
  - That do not cause full thickness destruction of intact skin tissue but exhibit a corrosion on either steel or aluminum surfaces exceeding 6.25 mm (0.25 inch) a year at a test temperature of 55°C (130°F) when tested on both materials. The corrosion may be determined in accordance with the UN Manual of Tests and Criteria or other equivalent test methods.

## 2.2 Classification of PCAPP Hydrolysate

Toxicity data are not specifically available for 8.6% HD or HT hydrolysates. However, there are toxicity test results available for 3.8% HD hydrolysate that could be used to provide an indication of the toxicity of 8.6% mustard hydrolysates. Reported toxicity results for 3.8% HD hydrolysate (SAIC 2010) are:

(i) Oral $LD_{50}$ toxicity (rat): No toxic effects observed over a 14-day evaluation period at a 500 milligrams per kilogram (mg/kg) dosage level (ECBC 2000)
(ii) Inhalation $LC_{50}$ toxicity (rat): No toxic effects observed over a 14-day post-exposure period at a 5.4 mg/L dosage level (ERDEC 1998)
(iii) Dermal $LD_{50}$ toxicity (rabbit): No dermal irritation observed over a 14-day evaluation period at a 1,000 mg/kg dosage level (ECBC 2000).

Although test results were for 3.8% HD hydrolysate rather than 8.6% hydrolysate, the lack of any toxic effects for the 3.8% hydrolysate strongly suggests that the 8.6% hydrolysate will have toxicity well below the levels required for classification as a Division 6.1 *poisonous material*, as defined in section 2.1.2.

40 CFR Part 261.24 of the Resource Conservation and Recovery Act (RCRA) defines certain wastes as characteristically toxic as analyzed using the Toxicity Characteristic Leaching Procedure (TCLP) if the concentrations exceed the specified threshold.

The PCAPP research, development, and demonstration (RD&D) permit (PCAPP 2008) describes the hydrolysate as potentially having the following RCRA characteristic TCLP toxic waste codes:

- D004 – D011: TCLP toxic for the following metals: arsenic, barium, cadmium, chromium, lead, mercury, selenium, and silver
- D022: TCLP toxic for chloroform
- D028: TCLP toxic for 1,2-dichloroethane

- D039: TCLP toxic for tetrachloroethylene
- D040: TCLP toxic for trichloroethylene
- D043: TCLP toxic for vinyl chloride.

Based on the results of the analysis of the hydrolysate summarized in section 1.2, the TCLP metals and TCLP organics present in the hydrolysate are in trace amounts and while some of them may exceed the RCRA TCLP toxicity characteristic threshold for RCRA waste coding purposes, they are not in sufficient concentrations to result in the hydrolysate being a DOT *poisonous material,* as defined in section 2.1.2, as confirmed by the testing performed (ERDEC 1998, ECBC 2000).

As stated in section 1.2, the hydrolysate pH will be adjusted to between 10 and 12 after agent is neutralized. Based on the results of dermal toxicity testing described in this section, no dermal irritation was observed over a 14-day evaluation period with the hydrolysate test mixture. The pH of the hydrolysate was 12.2 (ECBC 2000). Therefore, the PCAPP hydrolysate is not expected to meet the definition of a DOT *corrosive material.* However, past precedence indicates that mustard hydrolysate from the Aberdeen Chemical Agent Disposal Facility (ABCDF) was shipped to a TSDF as a DOT Class 8, PG II material. This was based on a decision to conservatively classify the hydrolysate as such. Therefore, the PCAPP hydrolysate will also be considered as a DOT Class 8, PGII material for the purposes of this Transportation Risk Assessment (TRA).

# 3. RISK MANAGEMENT APPROACHES

## 3.1 DOT Risk Management

The DOT Research and Special Programs Administration (RSPA) administers a comprehensive safety program in hazmat transportation for protection against risks to life, property, and the environment. The RSPA has issued a report (DOT 2000) that presents a risk management framework to serve as a resource for self-evaluation by all parties involved in transporting hazmats.

The risk management approach is a generic, stepwise approach that applies generally to a wide range of risk management situations in hazmat transportation, and can be adapted to a single material or process (e.g., transportation of corrosive materials), as necessary. The steps in the process are outlined below:

- Scoping
  – Identify transport activities/materials/programs.
  – Identify interactions with other parties, and potential upstream and downstream risks (e.g., fire, explosion, human health, ecological).
  – Set priorities for analysis and determine risk management objectives and scope.

- Knowledge of Operations
  - Collect data on activities/materials/quantities.
  - Assemble information on baseline programs/policies and established practices (e.g., hazard communication, maintenance, inspections, training, standard operating procedures, emergency preparedness, documentation).
- Assessment
  - Conduct risk analyses, considering a range of consequences and associated probabilities (can be qualitative or quantitative, simple or complex).
  - Assess baseline programs/policies and compare with established practices.
  - Identify risk control points (i.e., risk reduction opportunities).
- Strategy
  - Assess control options and set priorities for risk reduction.
  - Develop tailored risk management strategy (written plan), considering risk, cost, benefits, feasibility, and other factors.
- Action
  - Implement the tailored strategy (e.g., improved maintenance, outreach, technical guidance).
- Verification
  - Verify that strategy is being followed and that specified actions are being taken.
- Evaluation
  - Track incidents and performance data.
  - Periodically assess effectiveness of strategy.
  - Provide feedback, re-examine priorities, and update risk management approach as needed.

The Hazardous Materials Cooperative Research Program (HMCRP), sponsored by the Pipeline and Hazardous Materials Safety Administration, issued a report (HMCRP 2013) that presents the process and findings of a project documenting the current state-of-the-practice for hazmat TRAs. The project included a literature review and extensive interviews with hazmat TRA stakeholders, including an online survey of a wider group of stakeholders. The results were summarized according to the following categories:

- Current uses, users, modes, and decision-making
- Models, tools, methodologies, approaches
- Key sources of data
- Assumptions, limitations, biases, and availability
- Updates
- Risk communication
- Desired improvements
- Implementation barriers.

The results indicated that most of the risk assessment models are based on considering the frequency and probability of hazmat release after an accident, release size, probability of different release types (explosion, toxic gas, etc.), and consequence analysis, including population characteristics along the route, material hazard information, terrain and meteorological conditions, and endpoint impacts that reflect where low-level effects may occur versus those that would result in serious injury or death.

An important recommendation from the project team was to develop a single risk assessment approach across all models using a standard architecture that would include a standard (ideal or baseline) model for addressing hazmat transportation risk. Such a standard approach has been adopted by the Army (see for example, the Bounding TRA [CMA 2014]).

## 3.2 Army Risk Management

### 3.2.1 Army Risk Management Approach

The PCAPP System Safety Program Plan (SSPP) (Bechtel 2013) describes the system safety processes to be used during the life cycle of the PCAPP project. The SSPP provides a systematic approach for identifying potential negative events, defined as those events that could result in release of chemical agent, personnel injury, property damage or loss, and significant equipment downtime. The SSPP was prepared in accordance with AR 385-10, DA Pam 385-61, and MIL-STD-882D.

The risk assessment is conducted by assigning a hazard severity category, hazard frequency level, and corresponding hazard risk assessment code (RAC) to each identified hazard to assess risk and prioritize corrective actions.

The hazard severity categories shown in Table 3-1 are defined to provide a qualitative measure of the worst credible mishaps resulting from personnel error, environmental conditions, design inadequacies, procedural deficiencies, system/subsystem failure, component failure, or malfunction. For the purposes of this TRA, the relevant (shaded) column in Table 3-1 is the *Personnel Injury* column since it relates to consequences of an accident during transport of the energetic materials.

Table 3-1. Hazard Severity (Consequence) Categories

| Severity Level | On-Post Agent Release | Personnel Injury | System Loss |
|---|---|---|---|
| Catastrophic (Level I) | ≥IDLH outside engineering controls | Death or permanent total disability | >25% and/or >1 month to repair |
| Critical (Level II) | ≥VSL and <IDLH outside of engineering controls or in Category E area | Permanent partial disability, or injury or illness resulting in hospitalization | 10% to 25% and >1 week to <1 month to repair |
| Marginal (Level III) | ≥VSL inside non-agent area (Category C area) | Injury or illness resulting in one or more lost work days | <10% and/or <1 week to repair |
| Negligible (Level IV) | <VSL inside non-agent area (Category C area) | Injury or illness not resulting in lost work days | Repairs completed within 1 day |

Notes:

IDLH = immediately dangerous to life and health
VSL = vapor screening level

Source: Bechtel 2013, Table 7.3.1

The hazard frequency is the frequency that a hazard will occur during the life expectancy of the system and is a qualitative assessment based on research of similar items and an evaluation of historical reliability and safety data. The frequency levels are shown in Table 3-2. Again, for the purposes of this TRA, the relevant (shaded) column in Table 3-2 is the *Personnel Injury* column.

Table 3-2. Hazard Frequency Levels (per year)

| Frequency Level | On-Post Agent Release | Personnel Injury | System Loss |
|---|---|---|---|
| A – Frequent | $\geq 10^{-1}$ | $\geq 10$ | $\geq 1$ |
| B – Probable | $\geq 10^{-2}$ but $< 10^{-1}$ | $\geq 1$ but $< 10$ | $\geq 10^{-1}$ but $< 1$ |
| C – Occasional | $\geq 10^{-3}$ but $< 10^{-2}$ | $\geq 10^{-2}$ but $< 1$ | $\geq 10^{-2}$ but $< 10^{-1}$ |
| D – Remote | $\geq 10^{-4}$ but $< 10^{-3}$ | $\geq 10^{-4}$ but $< 10^{-2}$ | $\geq 10^{-3}$ but $< 10^{-2}$ |
| E – Improbable | $\geq 10^{-6}$ but $< 10^{-4}$ | $\geq 10^{-6}$ but $< 10^{-4}$ | $\geq 10^{-6}$ but $< 10^{-3}$ |
| F – Not Credible | $< 10^{-6}$ | $< 10^{-6}$ | $< 10^{-6}$ |

Source: Bechtel 2013, Table 7.3.2

Once hazards are categorized for severity and frequency, they are divided into the four thresholds defined in the hazard RAC matrix of Table 3-3. This matrix maps out the frequency of a hazard's occurrence against the degree of severity for each hazard.

Table 3-3. Hazard RAC Matrix

| Frequency of Occurrence | Hazard Categories | | | |
|---|---|---|---|---|
| | I Catastrophic | II Critical | III Marginal | IV Negligible |
| A – Frequent | 1 | 1 | 1 | 3 |
| B – Probable | 1 | 1 | 2 | 3 |
| C – Occasional | 1 | 2 | 3 | 4 |
| D – Remote | 2 | 2 | 3 | 4 |
| E – Improbable | 3 | 3 | 3 | 4 |
| F – Not Credible | 4 | 4 | 4 | 4 |

Source: Bechtel 2013, Table 7.3.3

Table 3-4 lists hazard prioritization, associated RAC, and required actions that define the hazard decision authority for closing identified hazards.

Table 3-4. Hazard Prioritization and Required Actions

| Hazard Prioritization | RAC | Required Actions/Acceptance Authority |
|---|---|---|
| IA, IB, IC, IIA, IIB, IIIA | 1 | Unacceptable; condition must be resolved/Assistant Secretary of the Army |
| ID, IIC, IID, IIIB | 2 | Undesirable/Program Executive Office Assembled Chemical Weapons Alternatives (ACWA) |
| IE, IIE, IIIC, IIID, IIIE, IVA, IVB | 3 | Conditionally acceptable/ACWA Field Office Site Manager |
| IF, IIF, IIIF, IVC, IVD, IVE, IVF | 4 | Acceptable/Bechtel Pueblo Team Project Manager |

Source: Bechtel 2013, Table 7.4.1

A hazard event remains open until all mitigation/control actions have been implemented.

### 3.2.2 Army TRA Approach

The U.S. Army approach for risk management described in section 3.2.1 was used in developing the Bounding TRA for CMA for transportation of contaminated agent waste to a commercial TSDF (CMA 2014). The TRA approach used is summarized below:

- Investigate and identify a reasonable routing for the representative destination.
- Establish possible truck accident scenarios for evaluation.
- Estimate the truck accident probability using available data and considering mitigation factors.
- Characterize the release scenarios and consequences utilizing the Army dispersion model D2PC, if applicable.
- Evaluate risk of postulated accident scenarios using Army regulation tables for hazard and consequence characterizations.

- Identify those hazards, if any, that require further investigation. Hazards that cannot be readily mitigated through corrective measures will become the focus of more rigorous evaluation methods.

Section 5 provides a detailed discussion of the TRA method as it applies to hydrolysate transport.

### 3.3 Comparison of Army Risk Management Approach to DOT Approach

As described in section 3.1, the DOT risk assessment approach calls for conducting a risk assessment that considers a range of consequences and associated probabilities (frequencies) (can be qualitative or quantitative, simple or complex). The Army approach similarly calls for considering the frequencies and consequences of realistic accident scenarios. The DOT assessment calls for identification of risk control points (i.e., risk reduction opportunities). Similarly, the Army risk assessment calls for establishing priorities for corrective action and resolution of identified hazards. The Army approach of estimating truck accident probability and characterizing the release scenarios is also similar to the state-of-the-practice hazmat TRA approach described in section 3.1. Therefore, the Army TRA approach is consistent with the DOT risk management approach and commercially practiced TRA approach.

## 4. DESCRIPTION OF LOADING, UNLOADING, AND TRANSPORT PROCEDURES

Items to be shipped include the PCAPP mustard agent (HD and HT) hydrolysate. The hydrolysate will be loaded from the hydrolysate storage tanks into tanker trucks for transport to Veolia in Port Arthur, Texas, and disposal.

### 4.1 Description of Requirements During Loading and Unloading

The hydrolysate will be transferred from the hydrolysate storage tanks into the tanker truck in accordance with the PCAPP Standard Operating Procedure (SOP).

General regulatory requirements (49 CFR Part 177.834) applicable during hazmat loading and unloading operations include the following:

- No loading or unloading should occur unless the handbrake is securely set and all other reasonable precautions are taken to prevent motion of the motor vehicle.
- A qualified person must attend the cargo tank at all times during loading and unloading
- A qualified person must be within 25 feet of the cargo tank.
- If the qualified person observes the loading and unloading via video cameras or monitors or instrumentation, these means must meet the operating requirements specified in 49 CFR Part 177.834.
- A containment area must be provided capable of holding the contents of as many cargo tank motor vehicles as might be loaded at any single time.

- Hoses used in the loading and unloading operations must be equipped with features capable of stopping the flow of the material within 1 second without human intervention in the event of hose rupture, disconnection, or separation.
- Prior to each use, each hose must be inspected to ensure it is of sound quality without defects detectable through visual observation.
- Loading and unloading operations must be physically inspected by a qualified person once every 60 minutes.
- Cargo motor vehicles must not be driven unless all manholes are closed and secured, and all valves and other closure devices are closed and free of leaks.

## 4.2 Description of Requirements During Transport

Transport requirements for hazmats are governed by DOT regulations, as described in section 2.1.1. General provisions applicable during the transportation phase (49 CFR Part 177.800) include the following:

- Transport without unnecessary delay, from and including the time of commencement of the loading of the hazmat until its final unloading at destination
- Availability of records, equipment, packaging, and containers under the control of a motor carrier, insofar as they affect safety in transportation of hazmats
- Compliance with safe clearance requirements for highway-rail grade crossings in 49 CFR Part 392.12
- Must not engage in, allow, or require texting while driving, in accordance with 49 CFR Part 392.80
- Must not engage in, allow, or require the use of a hand-held mobile telephone while driving, in accordance with 49 CFR Part 392.82
- Compliance with requirements of hazmat transport restrictions in vehicular tunnels
- Driver training in accordance with 49 CFR Part 177.800 and 49 CFR Parts 390 through 397, including:
  - Pre-trip safety inspection
  - Use of vehicle controls and equipment, including operation of emergency equipment
  - Operation of vehicle, including turning, backing, braking, parking, handling, and vehicle stability
  - Procedures for maneuvering tunnels, bridges, and railroad crossings
  - Requirements pertaining to attendance of vehicles, parking, smoking, routing, and incident reporting
  - Loading and unloading of materials, including compatibility, segregation, package handling, and load securement
  - Specialized training for cargo tanks and portable tanks including emergency control features of the tank, center of gravity, fluid-load surge on braking, properties and

hazards of material transported, and retest and inspection requirements for cargo tanks

- Ensure shipping papers are readily available to authorities in the event of accident or inspection
- Must not move a transport vehicle containing a hazardous waste unless the vehicle is marked and placarded in accordance with 49 CFR Part 172
- In an emergency, must not move a transport vehicle containing a hazardous waste unless:
  – The vehicle is escorted by a representative of a state or local government
  – The carrier has permission from the DOT
  – Movement of the vehicle is necessary to protect life or property.

# 5. RISK ASSESSMENT FOR TRANSPORT OF HYDROLYSATE FROM PCAPP

## 5.1 Transportation Routing

Many different transportation routes could be used to ship the hydrolysate from PCAPP to Veolia in Port Arthur, Texas. The transporter will select a shipment route based on consideration of several factors, such as avoiding major population centers or sensitive land areas and ensuring adequate emergency response capabilities. The transporter will also ensure that the route is selected in accordance with the National Hazardous Materials Route Registry (80 FR 23859).

Using Google Maps, two potential route options are as follows:

- 1,011 miles via US-287 S
- 982 miles via US-287 S and I-45 S

For the purposes of this study, the maximum distance of 1,011 miles was selected.

## 5.2 Truck Accident Frequency Estimation

A baseline frequency for truck accidents was obtained from a Battelle study of hazmat truck shipments (Battelle 2001, Tables 24 and 25). The data from this study were collected from the Hazardous Materials Information System (HMIS), supplemented by the Motor Carrier Management Information System (MCMIS) accident database, as well as Commodity Flow Survey (CFS) data from the U.S. Department of Commerce, the Federal Highway Administration's (FHWA) Highway Statistics, and the RSPA's Office of Hazardous Materials Safety 1998 study on "Hazardous Materials Shipments." Data are provided for accidents involving a vehicle crash and for all incidents related to hazmat transport. Incidents include vehicle crashes as well as non-accident leaks that occur during loading, unloading, and transport. Only releases resulting from vehicle accidents and leaks during transport are considered in the TRA.

The accident rate from the 2001 Battelle study for transportation of Class 8 materials is $1.32 \times 10^{-7}$ accidents per mile. The accident/incident rate (incidents include leaks en route with no accident) from the 2001 Battelle study for transportation of Class 8 materials is $4.092 \times 10^{-7}$ accidents or incidents per mile.

The following scenarios are evaluated in this study:

- Scenario 1 – Accident/Incident occurs, causing a release
- Scenario 2 – Accident occurs, causing a release and a fuel fire.

It should be noted that the hydrolysate is not flammable; therefore, the fire is assumed to be the result of a fuel release. These scenarios are depicted in the event tree shown in Figure 5-1.

| Initiating Event | Release | Fire | Outcome |
|---|---|---|---|
| Accident Occurs | No Release | | Accident – No Release |
| | Release | No Fire | Accident with Release (Scenario 1) |
| | | Fire | Accident with Release and Fire (Scenario 2) |
| Incident Occurs | No En Route Leak | | Incident – No Release |
| | En Route Leak | | Incident – Release (Scenario 1) |

Figure 5-1. Event Tree for Class 8 Materials

The basis for the event frequencies and probabilities is summarized in Table 5-1.

Table 5-1. Basis for Event Frequencies and Probabilities

| Parameter | Reference | Value |
|---|---|---|
| Accident frequency per mile for Class 8 materials | Battelle 2001, Table 24 | $1.32 \times 10^{-7}$ accidents/mile |
| Accident/incident frequency per mile for Class 8 materials (includes leaks en route) | Battelle 2001, Table 25 | $4.092 \times 10^{-7}$ accidents/incidents/mile |
| Event tree conditional probability of a release, given an accident, for Class 8 materials | Battelle 2001, Table 6 | 0.284 |
| Event tree conditional probability of no fire, given a release, for Class 8 materials | Battelle 2001, Table 6 | 0.973 |
| Event tree conditional probability of fire, given a release (fuel), for Class 8 materials | Battelle 2001, Table 6 | 0.027 |
| Number of accidents for Class 8 materials | Battelle 2001, Table 9 | 257 |
| Number of en route incident leaks for Class 8 materials | Battelle 2001, Table 9 | 539 |
| Total number of Incidents plus Accidents for Class 8 materials | Battelle 2001, Table 9 | 4,926 |
| Miles per shipment | Google Maps | 1,011 miles |

The calculation methodology to determine the event frequencies for the scenarios shown in Figure 5-1 is described below.

For Scenario 1, a release can occur as a result of an accident as well as an incident of a leak en route (without an accident). First, the frequency of a release, given an accident, is determined by multiplying the accident rate ($1.32 \times 10^{-7}$) by the conditional probability of a release, given an accident (0.284), multiplied by the conditional probability of no fire, given a release (0.973) (see Figure 5-1), which equals $3.65 \times 10^{-8}$ per mile. Next, the conditional probability of a leak from an en route incident is determined by dividing the number of en route leaks (539) by the total number of accidents and incidents (4,926) minus the number of accidents (257), which equals 0.115. Then, the accident frequency ($1.32 \times 10^{-7}$) is subtracted from the accident/incident frequency ($4.092 \times 10^{-7}$) to give the incident-only frequency of $2.77 \times 10^{-7}$. The frequency of an en route leak is then determined by multiplying the incident-only frequency ($2.77 \times 10^{-7}$) by the conditional probability of an en route leak (0.115) to give $3.19 \times 10^{-8}$ per mile. Finally, the two frequencies ($3.65 \times 10^{-8}$ and $3.19 \times 10^{-8}$) are summed to give $6.84 \times 10^{-8}$, which is the frequency of a release/leak, given an accident/incident, per mile. This value is then multiplied by the shipping distance (1,011 miles) to give the frequency of an accident/incident with a release/leak per shipment to Veolia ($6.9 \times 10^{-5}$).

For Scenario 2, since a fire results primarily from an accident causing a leak or rupture of the fuel tank, the accident rate of $1.32 \times 10^{-7}$ is used. The incident leak rate is not relevant. The conditional probability of a release given an accident is 0.284, as in Scenario 1. The release probability applies to a release of either the cargo contents or the fuel. Thus, the accident rate is multiplied by the conditional rate of release given an accident (0.284), and by the conditional rate of a fire given a release (0.027) and then by the distance (1,011 miles) for shipment to Veolia to give the frequency of an accident with a fuel release and a fire per shipment ($1.02 \times 10^{-6}$).

Table 5-2 summarizes the results of the event frequencies per shipment from PCAPP to Veolia for the three scenarios.

Table 5-2. Calculated Event Frequencies Per Shipment from PCAPP to Veolia

| Event | Scenario 1 Frequency | Scenario 2 Frequency |
|---|---|---|
| Accident/incident per shipment | $6.9 \times 10^{-5}$ | $1.02 \times 10^{-6}$ |

## 5.3 Consequence Assessment

The following types of hazards associated with a tanker truck accident/incident are evaluated:

- Injuries/fatalities due to exposure to a release/leak of hydrolysate
- Injuries/fatalities due to exposure to a fuel-spill fire.

Injuries or fatalities from exposure to a hydrolysate release are based on either the corrosive or toxicity characteristics of the hydrolysate, as determined from the composition and the toxicity of the individual constituents and of the mixture as a whole. A liquid mixture spill releases the more volatile constituents through evaporation. Exposure to individuals occurs through inhalation of the vapors or through dermal contact with the liquid. As discussed in section 1.2, the major constituent of the hydrolysate is TDG. Other organics are present only in trace amounts. 1,4-Oxathiane is listed as having no acute or chronic health hazard (Thermo 2014) and 1,4-Dithiane is listed as not being on any Health and Safety Reporting Lists (Thermo 2008). Table 5-3 lists the composition of the hydrolysate, and provides the vapor pressures and toxicity of the constituents listed.

Table 5-3. Physical and Toxicological Properties of Hydrolysate Constituents

| **Analyte Name** | **CAS No.** | **HD (wt. %)** | **HT (wt. %)** | **Vapor Pressure (at Temperature)** | **Oral $LD_{50}$ (species)** |
|---|---|---|---|---|---|
| TDG | 111-48-8 | 4.7 | 3.7 | 0.003 mm Hg (25°C)[a] | 6,610 mg/kg (rat)[a] |
| 1,4-Oxathiane | 15980-15-1 | 0.025 | 0.23 | 3.6 mm Hg (25°C)[b] | 2,830 mg/kg (rat)[c] |
| 1,4-Dithiane | 505-29-3 | 0.015 | 0.017 | 1.57 mm Hg (25°C)[d] | 2,768 mg/kg (rat)[d] |
| Q-OH; 3,6-Dithia-1,8-octanediol; Ethanol, 2,2'-[1,2-ethanediyl-bis(thio)]bis- | 5244-34-8 | 0.43 | 0.3 | $5 \times 10^{-6}$ mm Hg (25°C)[e] | NA |
| bis(2-Chloroethyl)ether | 111-44-4 | 0 | 0.01 | 1.55 mm Hg (25°C)[f] | 75 mg/kg (rat)[f]<br>126 mg/kg (rabbit)[f] |

Notes:

NA = not available

[a] National Institutes of Health (NIH), *Thiodiglycol*, TOXNET Toxicology Data Network, http://chem.sis.nlm.nih.gov/chemidplus/rn/111-48-8, accessed May 19, 2016.

[b] Yaws, C. L., *The Yaws Handbook of Vapor Pressure: Antoine Coefficients*, 2nd Edition, Elsevier, Oxford, UK, 2015.

[c] Sigma-Aldrich, *Safety Data Sheet for 1,4-Thioxane*, version 5.4, http://www.sigmaaldrich.com/catalog/product/aldrich/131970?lang=en&region=US, accessed May 19, 2016.

[d] National Institutes of Health (NIH), *1,4-Dithiane*, TOXNET Toxicology Data Network, http://chem.sis.nlm.nih.gov/chemidplus/rn/505-29-3, accessed May 19, 2016.

[e] Value estimated using USEPA's EPISuite software, reported online at Chemspider, http://www.chemspider.com/Chemical-Structure.71239.html, accessed May 19, 2016.

[f] National Institutes of Health (NIH), *Bis(2-chloroethyl) ether*, TOXNET Toxicology Data Network, http://chem.sis.nlm.nih.gov/chemidplus/rn/111-44-4, accessed May 19, 2016.

TDG is not a volatile constituent. The vapor pressure of TDG is 0.003 millimeters of mercury (mmHg) at 25°C. By comparison, the vapor pressure of water at 20°C is 17.5 mmHg (http://genchem.rutgers.edu/vpwater.html, accessed on 4/20/16), which is three orders of magnitude greater. This indicates that there will be very little evaporation of TDG during a spill event.

The acute toxicity of TDG is listed as *virtually non-toxic* after ingestion or skin contact, and inhalation of a highly enriched vapor-air mixture represents an *unlikely acute hazard* (BASF 2014). The acute toxicity of TDG is listed as having an oral $LD_{50}$ (rat) of 6,610 mg/kg (*practically non-toxic* as defined by the Hodge and Sterner toxicity scale, [https://www.ccohs.ca/oshanswers/chemicals/ld50.html, accessed on 4/20/16]) and a dermal $LD_{50}$ (rabbit) of 23,600 mg/kg (*relatively harmless*, as defined by the Hodge and Sterner toxicity scale) and no mortality in animal tests was observed after 8 hours of exposure through inhalation. There are no permissible exposure limits (PELs) or time-weighted average (TWA) concentrations established for TDG. Therefore, there is no need to conduct air modeling to determine the concentration of TDG at various interceptor points around the scene of the accident to be compared to PELs or TWAs for health impact.

1,4-Oxathiane and 1,4-Dithiane are *slightly toxic*, while bis(2-Chloroethyl)ether is *moderately toxic* (per the Hodge and Sterner toxicity scale). All three compounds have significantly lower vapor pressures than water. The toxicity of Q-OH was not available; however, the vapor pressure of Q-OH is exceedingly small. Due to the trace quantities, low vapor pressures, and relatively low toxicity, these compounds are not considered significant in evaluating the impact from a hydrolysate spill. The overall hydrolysate mixture exhibits no toxicity, as described in Section 2.2.

Impacts of hydrolysate exposure from dermal contact are not considered significant since testing revealed that there was no dermal irritation observed from exposure to hydrolysate for a 14-day evaluation period (see section 2.2).

Fires occur in a small percentage of accidents involving hazmat releases. In the case of hydrolysate transport, the fire is unlikely to be sustained because the fuel source (truck fuel) would quickly deplete and the fire would be extinguished. Even if the hydrolysate in the tanker truck were subjected to a fire, the liquid would heat very slowly and would reach a maximum at the boiling point of water. This temperature would still be too low to produce a significant downwind hazard, in the event there was also a release of hydrolysate. Therefore, health impacts due to exposure through inhalation will be similar to that described for a hydrolysate release with no fire.

For both scenarios, the resulting consequence falls under the category *Injury or illness not resulting in lost work days*, as per Table 3-1.

## 5.4 Risk Evaluation

The event frequencies given in Table 5-2 are on a per-shipment basis. In order to determine the total frequency and consequence of an accident or incident during hydrolysate transport from PCAPP over the life of the transport operation, it is necessary to multiply each by the total number of planned shipments.

The number of shipments is determined by dividing the estimated hydrolysate generated (8.1 million gallons [Noblis 2008]) by the tanker truck capacity. Tanker truck capacities for chemical transport are usually about 4,500 to 5,000 gallons (http://www.polarservicecenters.com/sales/equipment-inventory/truck-tanks/, accessed 4/20/16). A standard International Organization for Standardization (ISO) tank container nominal capacity is listed as 6,340 gallons (http://www.hooversolutions.com/products/iso-tank-containers/standard-iso-containers.html, accessed 4/20/16), and the working capacity is probably around 6,000 gallons. These capacities translate into 1,800 and 1,350 shipments respectively, as described previously. Noblis 2008, Table B-2 estimates the number of mustard hydrolysate shipments from PCAPP as 1,765. This TRA uses the more conservative value of 1,800 shipments because a higher number of shipments results in a higher risk. The 1,800 shipments would require shipping one tanker truck every day, or multiple tanker trucks every few days, assuming 5 years of transport operations.

Table 5-4 summarizes the results of the total frequencies and consequences.

Table 5-4. Total Frequencies and Consequence Results

| Scenario 1<br>Total Frequency Per Year | Scenario 2<br>Total Frequency Per Year | Consequence Severity |
|---|---|---|
| $2.48 \times 10^{-2}$ | $3.68 \times 10^{-4}$ | Injury or illness, if any, not resulting in lost work days |

Note:

Results are based on 1,800 shipments multiplied by the frequencies in Table 5-2 and divided by 5 years.

Table 5-5 summarizes the information from Table 5-4 in qualitative terms, in accordance with the risk evaluation matrix, Table 3-3. The consequence is listed as *Negligible* since there are no injuries or any illness expected that would result in lost work days.

Table 5-5. Risk Level Determination

| Scenario | Frequency | Consequence | RAC |
|---|---|---|---|
| 1 – Accident/Incident Release/Leak | C – Occasional | IV – Negligible | 4 – Acceptable |
| 2 – Accident with Release and Fuel Fire | D – Remote | IV – Negligible | 4 – Acceptable |

The results indicate that the risk level is *Acceptable.* Therefore, no mitigation of the risk is necessary.

## 6. SUMMARY AND CONCLUSIONS

An evaluation of the risk of transporting treated, hydrolysate from PCAPP to Veolia was conducted. The regulations for hazmat classification, handling, loading, and transport were reviewed for safe transport of the hydrolysate in tanker trucks. The DOT risk management approach and state-of-the-practice approaches for TRAs were reviewed and compared with the U.S. Army risk management approach to determine consistency. The Army TRA approach was found to be consistent with the DOT risk management approach and commercially practiced TRA approach. A TRA was conducted for the PCAPP hydrolysate using the Army approach by determining accident frequency and event consequences for (1) an accident/incident with a release/leak and (2) an accident with a release and a fuel fire. The results indicate that the transportation risk is *Acceptable* and that no mitigation measures are necessary.

## 7. REFERENCES AND SOURCE MATERIALS


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# APPENDIX A
# EVALUATION OF RISK DUE TO VEHICLE CRASHES

Risk related to vehicle crashes can be estimated using DOT fatality and injury risk values for large trucks (DOT 1999, 2015). In the 1999 DOT study, the fatality rate was given as $2.5 \times 10^{-8}$ fatalities per vehicle-mile. The 2015 DOT study lists annual fatality rates for the period from 1975 to 2013. During that period, the fatality rate has decreased substantially from approximately $6 \times 10^{-8}$ fatalities per vehicle-mile at the beginning of the period to less than $2 \times 10^{-8}$ fatalities per vehicle-mile at the end. Over the last 10 years of the period, the fatality rate was $1.7 \times 10^{-8}$ fatalities per vehicle-mile. The 2015 DOT study also lists injury statistics over the 21-year period from 1993 to 2013. Again, the data indicate a decreasing trend in injury rate from approximately $8 \times 10^{-7}$ injuries per vehicle-mile at the beginning of the period to less than $4 \times 10^{-7}$ injuries per vehicle-mile at the end of the period. The average injury rate over the last 10 years was $3.7 \times 10^{-7}$ injuries per vehicle-mile.

The number of fatalities or injuries that would be expected during hydrolysate transport is estimated by multiplying the fatality or injury risk per distance traveled by the total distance traveled over all hydrolysate shipments. Assuming 1,800 shipments and 1,011 miles per shipment, the total distance traveled would be 1.82 million miles. Assuming the fatality and injury rates are $1.7 \times 10^{-8}$ fatalities per vehicle-mile and $3.7 \times 10^{-7}$ injuries per vehicle-mile, respectively, the calculated expected number of fatalities and injuries due to truck crashes are 0.03 fatalities 0.67 injuries, respectively. Thus, there is approximately a 3 percent chance of a fatality and a 67 percent chance of an injury due to a truck crash during hydrolysate transport.

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