Midterm Assignment

by

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Presented to:
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Fate and Transport of Spilled Hazardous Materials

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1.0 Introduction

1.1 Summary
This report includes the summary of the three incidents occurred in the past. It also includes the review of the early warning system that local governments have installed in order to detect hazardous substances in drinking water systems. This report includes the basic information about the location of incident, type and amount of materials involved, characteristics of pollutants, damage and effects caused, number of people involved. The three incidents chosen for the study are as follows.

1. Release of Hazardous Materials From Cargo Tank in Middletown, Ohio

2.0 Case Study 1: Release of Hazardous Materials From Cargo Tank in Middletown, Ohio, on August 22, 2003

2.1 Abstract
On August 22, 2003 a cargo tank half full with the toxic chemical of anhydrous ammonia failed at the AK Steel Corporation in Middletown, Ohio. The analysis shows the probable cause of this accident was the inadequate used of a cargo tank manufactured of quenched and tempered steel to transport anhydrous ammonia containing less than 0.2 % of water by weight. The result was examined to stress-corrosion cracking of the tank failure. Accident was occurred because of the AK Corporation’s failure to inform drivers that ammonia containing less than 0.2 % of water by weight should not be loaded into cargo tanks labelled QT.

Accident No: DCA03MZ002
Transportation Mode: Highway
Location: Middletown, Ohio
Date of Accident: August 22, 2003
Time: 8:20 a.m. eastern daylight time
Carrier: Amerigas Corporation
Shipper: AK Steel Corporation
Vehicle: MC-331 cargo tank
Injuries: 5 people treated and released
Property Damage: About $25,000
Material Released: Anhydrous ammonia, a poisonous and corrosive gas
Type of Accident: Cargo tank head fracture

2.2 Cargo Tank Accident
AK Steel is a steel production facility in Middletown, Ohio which produces its own coke and stores the resulting anhydrous ammonia in stationary tanks (ammonia being a by product of the process of converting coal into coke). Ammonia is then sold to Univar USA, Inc., in Cincinnati, Ohio at a frequency of about six cargo tank per month.
An Amerigas cargo tank semi trailer arrived at the AK Steel Corporation facility in Middletown, Ohio to be filled with anhydrous ammonia from the storage tank. During the gas transfer between storage tanks to the cargo tank, its front head cracked open, releasing vapour. In that moment the cargo tank was a little less than half full, the internal pressure was about 170 psig, and the temperature of the anhydrous ammonia was 80 F. The driver activated the emergency shut off device for the cargo tank.

The accident cargo tank was the only one in which AK Steel transported anhydrous ammonia in the past year. The failure of the tank was likely caused by repeatedly stress-corrosion cracking due to the chemical ammonia. QT (quenched and tempered steel) tanks should transport ammonia only if at least 0.1 % water by weight is added to the anhydrous ammonia to inhibit stress-corrosion cracking in carbon steel. The recommendation of most of the scientist is that a minimum of 0.2 % water must be added to ammonia to inhibit cracking. The record showed that the ammonia loaded in the accident cargo tank during the past 4 months preceding the accident contained less than 0.1 % water.

About 100 employees and contract workers were evacuated from the buildings downwind of the cargo tank and moved to safer locations. Five people were treated for inhalation injuries and released. The cost of repairing and replacing damaged equipment was about $25,000.

### 2.3 Summary of the Accident

1. Date of the accident: August 22, 2003 at 8:20 AM EST
2. Location: AK Steel Corporation Facility located on 703 Curtis ST, Middletown, Ohio, 45044. The closest water body to the accident is the Great Miami River located 0.6 miles west and the lake, located 1.1 miles north of the facility. Figure 1 shows the “G”, location of the AK Steel and Green circle, location of the water bodies.
3. Type of accident: Cargo tank head fracture with spill of anhydrous ammonia (NH$_3$)
4. Quantity spilled by the accident: Maximum amount will be 5300 gallons considering the water capacity of the tank was 10,600 gallons and the tank was little less than half full
5. Cause of the accident: Anhydrous ammonia containing less than 0.2% water by weight was loaded in cargo tanks manufactured of QT (quenched and tempered steel), resulting in stress-corrosion cracking and tank failure
6. Usage: Anhydrous ammonia is a byproduct of the process of converting coal into coke, which is used as a fuel in blast furnaces to produce steel
7. Meteorological Information: Average temp = 75 F, Average wind speed = 4.7 mph, Max Temp = 89 F, Pressure = 29.9 in
8. Emergency Response: 100 employees were evacuated from the buildings downwind of the cargo tank and moved to safer location
9. Injuries: Five people were treated for inhalation injuries and released
10. Costs: The cost of repairing and replacing damaged equipment was about $25,000

2.4 Tools used to calculate from the text book
Air being the main media for the contaminant, it is possible to calculate the degradation of chemical in air using $C_t = C_0e^{-kt}$, where k is the rate constant. Using this I can estimate the concentration of contaminant after the accident.
Very less amount of the contaminant will get into the soil phase and hence I can neglect the calculations partitioning into soil phase. But if I need to estimate the concentration of contaminant in soil, I can make use of partition coefficient (K$_{oc}$) which is listed under contaminant properties section. Once I can find the concentration of contaminant in air or water at a particular location, I can use Henry’s law constant to estimate the
concentration in other phase and the Henry’s law constant value is noted under chemical properties section.

Outdoor air quality or the concentration profile of the contaminant in air can be estimated using ‘Pasquill - Gifford model’ equation (4-16) of text book, where g1 and g2 the Gaussian distribution factors can be obtained by using equations (4-17a) and (4-17b) of textbook. Horizontal and vertical standard deviations can be calculated by using the equations provided in table 4-7 for the identified stability classes from table 4-6.

2.5 Picture

Figure 2: Crack in the tank head (Source: NTSB report)
2.6 Primary Calculation

1. Release of ammonia into the environment

At the time of accident ammonia had the followings physical characteristics:
V = 5300 gal = 20063 L = 20.1 m³
NH₃ liquid at boiling point = 682 kg / m³
Mass = 13708 kg

2. Fugacity calculation: ammonia partitions mostly into the air, but the highest concentration is found to be in fish

HYPOTETICAL ECOSYSTEM
PARTITIONING

AIR  WATER  FISH  FUGACITY  Mair (mol)  Mwater (mol)  Mfish (mol)

<p>| | | | | | | |</p>
<table>
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</tr>
</tbody>
</table>

3. Ammonia concentration in air at the time of the accident

\[ PV = nRT \]

\[
\begin{align*}
PNH3 & = 800 \text{ Kpa} \\
VNH3 & = 5300 \text{ gal} \\
R & = 0.0821 \text{ L*atm/(mol*K)} \\
Tair & = 297 \text{ K} \\
\end{align*}
\]

\[
\begin{align*}
n & = \frac{PV}{RT} \\
& = \frac{6132 \text{ mol}}{10437 \text{ g/m3}} \\
& = 10437 \text{ ppm} \\
\end{align*}
\]

For a hypothetical air volume of 10 m³ (considerate to be around the cargo tank), the ammonia concentration in air at the time of accident is found to be 10437 ppm.

3.1 Abstract
On April 15, 2003 at approximately 11:50 AM central daylight time, a cargo tank used exclusively for agricultural purposes as a nurse tank split open after being filled with anhydrous ammonia at River Valley Cooperative nurse tank filling facility near Calamus, Iowa. About 1,300 gallons of the poisonous and corrosive gas escaped into the atmosphere, seriously injuring two nurse tank loaders, one of whom died from his injuries 9 days after the accident. The total cost of the accident including equipment repair and replacements associated with the accident was about $3,100. The National Transportation Safety Board investigated the accident and identified the following major safety issues: the adequacy of standards for initial qualification and periodic testing of nurse tanks, and the adequacy of River Valley’s emergency procedures.

3.2 Background
Anhydrous ammonia is an important source of nitrogen fertilizer for crops. It is injected into the soil before planting crops (spring season) to increase the soil’s nitrogen content. It is relatively easy to apply and it is largely available, but anhydrous ammonia can have catastrophic results for both plants and farm workers if it is handled improperly. When injected into the soil, the liquid ammonia expands into a gas and is absorbed in the soil moisture. Anhydrous ammonia is a gas formed with one part of nitrogen and three parts of hydrogen. The gas is colourless with a sharp, penetrating odour. It is a poisonous and corrosive gas with a boiling point of -28F. Anhydrous ammonia is caustic and causes severe chemical burns. Body tissues that contain a high percentage of water (eyes, skin, and respiratory tract) are first affected because the water and ammonia quickly combine causing rapid dehydration and severe burns as it combines with the moisture of the body. Also, ammonia is corrosive to certain metals, such as copper, zinc, and their alloys. When used as an agricultural fertilizer, ammonia is compressed into liquid and stored under pressure in special vessels (made by special high-strength steel) strong enough to withstand internal pressures of at least 250 psi (tank cars, cargo tanks, nurse tanks, and cylinders). As the outside temperature increases, the temperature of the liquid in the tank increases and the liquid expands, causing the vapour pressure in the tank to increase. For example, at 60°F, the pressure is 93 psi and at 100°F, the pressure is 197 psi. If released from the pressure vessel, anhydrous ammonia will immediately return to a gaseous state and expand rapidly given a large, white vapour cloud.

3.3 Ammonia Physical Properties
- Boiling point is at -28.17°F
- Freezing point is at -107.9°F with a formation of a white crystalline mass
- Critical temperature is at 270.3°F. Ammonia exists as a vapour, regardless of pressure above this temperature
- Density of NH₃ liquid is 42.57 lb/cu ft at boiling point (Ammonia liquid is lighter than water)
- Density of NH₃ vapour is 0.0555 lb/cu ft at boiling point
Volume: One pound of ammonia vapour occupies a volume of 22.78 cf at 32°F and atmospheric pressure. One pound of ammonia vapour occupies a volume of 22.5 cf and yields 45 cf of dissociated gas at a ratio of 25% nitrogen and 75% hydrogen at 70°F and atmospheric pressure. Ammonia begins dissociating into nitrogen and hydrogen at approximately 850°F.

3.4 Ammonia Exposure Limit
- OSHA Permissible Exposure Limit (PEL) for General Industry is 50 ppm
- National Institute for Occupational Safety and Health (NIOSH) Recommended Exposure Limit (REL) of 25 ppm or 35 ppm STEL (short term exposure limit)

3.5 Ammonia Gas Health Effect
According to the National Institute for Occupational Safety and Health, Ammonia has following health effects.
- Low lethal concentration of anhydrous ammonia for humans is 5000 ppm for a period of 5 minutes
- Immediately dangerous to life or health (IDLH) concentration of anhydrous ammonia is 300 ppm. Humans can detect the odour of anhydrous ammonia at 3 to 5 ppm

Health effects due to exposure to anhydrous ammonia are acute lung damage, asthma, pulmonary fibrosis, bronchiolitis obliterans, body surface area chemical burns, highly irritating to the eyes and respiratory tract. Swelling and narrowing of the throat and bronchi, coughing, and an accumulation of fluid in the lungs may occur. Ammonia causes rapid onset of a burning sensation in the eyes, nose, and throat, accompanied by lacrimation, rhinorrhea, and coughing. Upper airway swelling and pulmonary edema may lead to airway obstruction. Prolonged skin contact (more than a few minutes) can cause pain and corrosive injury.

Anhydrous ammonia is classified and regulated for domestic shipment as a nonflammable gas but is required to be identified as an “inhalation hazard.” Pressure vessels containing anhydrous ammonia must be marked “Inhalation Hazard”. Also the shipping papers for those packages must contain these words.

3.6 Nurse Tank Accident
A cargo tank full with anhydrous ammonia, used by River Valley Cooperative for agricultural purposes as a nurse tank, split open right after being filled. The cause of the sudden failure of the nurse tank at the filling facility was inadequate welding and insufficient radiographic inspection during the tank’s manufacture and lack of periodic testing during its service life. The nurse tank shell split open at the bottom of its front half. The pressure of the escaping gas made several holes in the gravel lot surrounding the platform (the largest was about 7 feet long, 5 feet across, and 30 inches deep). About 1,300 gallons of the poisonous and corrosive gas escaped. Two workers were seriously injured, one of whom died from his injuries 9 days after the accident. At the time of accident vapour pressure of anhydrous ammonia would give an internal tank pressure of 142 psig.
3.7 Summary of the Accident

1. Date of the accident: April 15, 2003 at 11:50 AM CST
2. Location: River Valley Cooperative Anhydrous Station is located about 2 miles east of Calamus on 2417 190 Ave, Grand Mound, Iowa, 52751. The closest water body (Mississippi river) to accident is about 5 miles east of the facility.

3. Type of accident: Spill of anhydrous ammonia (NH₃)
4. Quantity spilled: 1,300 gallons
5. Cause of the accident: inadequate welding and insufficient radiographic inspection during the tank’s manufacture and lack of periodic testing during its service life
6. Meteorological Information: Dry weather, clear sky, and the air temperature were about 81° F. Winds was blowing from the southwest about 19 to 24 mph. The closest city is located 2 miles east of the accident location. The population from this city was not affected by the spill due to the wind direction at that particular moment
7. Emergency Response: At 11:50 a.m., a woman who used this filling facility saw a white vapour cloud emanating from the loading platform area and immediately called 911
8. Injuries: the two tank loaders, the only people at the facility at the time of the accident, suffered more than 50% body surface area chemical burns, eye injuries, and inhalation injuries due to anhydrous ammonia exposure. One of the loader passed away 9 days after the accident due to multiple chemical burns.
9. Costs: Equipment repair and replacement costs associated with the accident = $3,100

3.8 Recommendations by the National Transportation Safety Board

- Periodic nondestructive testing on nurse tanks
- River Valley Cooperative must establish written emergency procedures for employees to follow when anhydrous ammonia releases

3.9 Tools used to calculate from the text book

As most part of the chemical ends up in the atmosphere, I can calculate it’s dispersion profile using ‘Pasquill - Gifford model’ equation (4-16) of text book, where g1 and g2 the Gaussian distribution factors can be obtained by using equations (4-17a) and (4-17b) of textbook. Horizontal and vertical standard deviations can be calculated by using the equations provided in table 4-7 for the identified stability classes from table 4-6. Concentration of constituent in the water in equilibrium with air = Concentration in air/H; If can estimate the concentration of chemical in air we can estimate the concentration in water at that point. Henry’s law constants for different constituents can be obtained from literature (EPA is the best source). I can calculate the degradation of chemical in air using $C_t = C_0e^{-kt}$, Where k is the decay constant which is available in many of the literatures.

3.10 Picture

Figure 5: Accident nurse tank with shell fracture area circled (Source: NTSB report)
3.11 Primary Calculation
1. At the time of accident ammonia had the followings physical characteristics:
   V = 1300 gal = 4921 L = 4.92 m³
   NH₃ liquid at boiling point = 682 kg / m³
   Mass = 3355 kg
2. Fugacity calculation: ammonia partitions mostly into the air, but the highest concentration is found to be in fish

HYPOTETICAL ECOSYSTEM

<table>
<thead>
<tr>
<th>Ecosystem</th>
<th>Volume (m³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Air</td>
<td>1.E+10</td>
</tr>
<tr>
<td>Water</td>
<td>7.E+06</td>
</tr>
<tr>
<td>Fish</td>
<td>3.5</td>
</tr>
</tbody>
</table>

ASSUME

- BCF: 4.4 L/Kg
- Fish density: 1000 Kg/m³
- MW: 17.02 g/mol
- R: 0.0821 L*atm/(mol*K)
- H: 0.0000569 atm*m³/mol
- Tair case 1: 27.2 C

RELEASE: 3355 kg

197147 mol

PARTITIONING

<table>
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<tr>
<th></th>
<th>Mair (mol)</th>
<th>Mwater (mol)</th>
<th>Mfish (mol)</th>
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</thead>
<tbody>
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<td>C (mol/m³)</td>
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<tr>
<td>0.1009</td>
<td>0.00002</td>
<td>0.0066</td>
<td></td>
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</table>

3. Ammonia concentration in air at the time of the accident

PV = nRT

<table>
<thead>
<tr>
<th>PNH3</th>
<th>VNH3</th>
<th>R</th>
<th>Tair</th>
</tr>
</thead>
<tbody>
<tr>
<td>800 Kpa</td>
<td>1300 gal</td>
<td>0.0821 L<em>atm/(mol</em>K)</td>
<td>300.2 K</td>
</tr>
<tr>
<td>7.9 atm</td>
<td>4.92 m³</td>
<td>4921 L</td>
<td></td>
</tr>
</tbody>
</table>

n = PV / RT

<table>
<thead>
<tr>
<th>MW</th>
<th>17.02 g/mol</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mass</td>
<td>26846 g</td>
</tr>
<tr>
<td>Vair</td>
<td>10 m³</td>
</tr>
<tr>
<td>(the space around the tank)</td>
<td></td>
</tr>
</tbody>
</table>

For a hypothetical air volume of 10 m³ (considerate to be around the cargo tank), the ammonia concentration in air at the time of accident is found to be 2685 ppm.
4.0 Case Study 3: Meat-Packing Plant has Ammonia Spill Jun 20, 2008

4.1 Abstract
Sacramento Metropolitan Fire District officials reported that a pipe failure in a Rio Linda meat-packing plant Thursday evening caused 50 gallons of anhydrous ammonia spill. According to Greg Mugartegui, Sac Metro assistant fire chief, in this accident, no injuries or evacuations were reported from the spill at the Stafford Meat Co., near 16th and Q streets and there were eleven workers in the plant when the pipe burst around 7 pm. Some of workers were sent home and others returned to work after the incident. Approximately 50 gallons of the anhydrous ammonia was spilled before the safety valve in the pipe closed down. Members of the Sacramento County Hazardous Materials Unit were checking the plant as a precaution.

4.2 Summary of the Accident
1. Date of the accident: Jun 20, 2008 at 7:00 PM PST
2. Location: Stafford Meat Co. is located 1545 Q Street Rio Linda, CA 95673 and the nearest water body is the creek located about 0.2 miles east from the site
3. Type of accident: Spill of anhydrous ammonia (NH3)
4. Quantity spilled: 50 gallons
5. Cause of the accident: Pipe failure, but the detail cause is not known yet
6. Meteorological Information: Average temperature was 82°F. Maximum and minimum temperature was 100°F and 64°F. There was no precipitation on that day and the average wind velocity was 6mph.

7. Emergency Response: No evacuations were reported from the spill at the Stafford Meat Co

8. Injuries: No injuries reported

9. Cost: Information is not available right now

4.3 Tools used to calculate from the textbook

Travel time in Creek: the time required for a chemical to travel a distance can be calculated using $T = \frac{L}{V}$, where $V$ is the velocity which can be calculated by using Manning’s equation or Chezy equation. In the case I can estimate how far the product has been travelled. I can calculate the how much distance is really the chemical flume is travelled in next 24 hours form the incident. Pulse injection technique in Creek: To find concentration of a chemical at a given point $C(x,t) = \frac{M(e-(x-Vt)/4DLt))}{(sqrt(4*pi*t)}$, DL is Fickian mixing coefficient and it can be obtained by using equation 2-7 in the textbook. Concentration of constituent in the water in equilibrium with air = Concentration in air/H; If can estimate the concentration of chemical in water I can estimate the concentration in air at that point. Henry’s law constants for different constituents can be obtained from literature (EPA is the best source). Bio-accumulation can be estimated from the partition coefficients such as Koc, Kow, BCF, which are listed in many literatures (EPA is the best source). Retardant of the constituents can be estimated by using equations 3-22, 3-24a and 3-24b of textbook. These calculations needs partition coefficient values.
5.0 Early Warning System for the Drinking Water System

5.1 Summary
PipelineNet is a monitoring system which monitors and project the potentially introduced contaminates fate and transport in water distribution system. It is considered as early warning system, which is very essential in current day life where there a high threat from militant operations. This report is prepared based on the case study conducted on PipelineNet monitoring system at East Bay Municipal Utility District (EBMUD) in Oakland, California. The study area for PipelineNet represents 13% of the 122 pressure zones in the EBMUD.

Figure 9: EBMUD Water distribution system (Source: EPA water security division)

5.2 Objectives
The system uses three types of data in its function and it work is combination of three different steps with each step dealing with three individual data types. The data consists of hydraulic model inputs, PipelineNet model outputs and GIS data. The system consists of three tools which enhances its function for emergency response, mitigation and normal operations. The three tools consists of ‘Consequence Assessment Toll’, which provides the ability to identify and quantify the population, infrastructure and resources at risk form contaminants. The second tool of the system ‘Isolation Toll’, which helps in change the status (open or close) of any pipe in the distribution system, and the third tool ‘Spatial Database Display Toll’ helps in developing the monitoring regimes for routine screening of distribution system water quality, and track the fate and transport of contaminants in the system to effectively respond to a purposeful contamination incident.
References

2. Course website, www.eng.ua.edu/~rpitt
3. Case study for a Distribution System Emergency Response Tool, Bahadur et.al., 2003, EPA