Mass and Heat Transfer
Safety Module 4: *Dispersion of Ammonia, Millard Refrigeration System, August 23, 2010*

Problem Statement: Over 32,000 pounds of anhydrous ammonia was released into the atmosphere from a pipe rupture resulting from a hydraulic shock in a refrigeration piping system. The resulting vapor cloud traveled a quarter mile towards 800 workers. 153 workers were exposed to the toxic ammonia cloud, many requiring hospitalization.

Photo: csb.gov

Watch the Video: (*https://www.youtube.com/watch?v=_icf-5uoZbc*)

Incident Report Available At: (*https://www.csb.gov/file.aspx?DocumentId=5933*)
(Pages 2-5 and 13-14)

(a) It is important that chemical engineers understand what the accident was, why it happened and how it could have been prevented in order ensure similar accidents may be prevented. Applying a safety algorithm to the accident will help achieve this goal. In order to become familiar with a strategy for accident awareness and prevention, view the Chemical Safety Board video and read the incident report on the hydraulic shock at Millard Refrigeration System and fill out the following algorithm. See definitions on the last page. If necessary, view the incident report.

Safety Analysis of the Incident

Activity: ____

____

Hazard: ____

____

Incident: ____

Initiating Event: ____

Preventative Actions and Safeguards: ____

____

Contingency Plan/ Mitigating Actions: ____

____

Lessons Learned: ____

Additional Information:

Density of liquid ammonia at 240 K and 15.2 psi (104.8 kPa) , ρ^1 = 681.75 kgm^{-3}
Diameter of pipe, d = 12 inch (0.3048m)
Discharge coefficient for release, C_o = 0.61
Area of the ruptured orifice in the pipe, A_r = 0.003 m^3
Point of release from the roof of the Millard facility from ground level, H = 50 ft (15.24 m)
Molecular weight of ammonia = 17 g/mol

(b) Due to hydraulic shock, the pipe ruptured and resulted in release of liquid ammonia to the atmosphere. Liquid ammonia immediately flashes in the surrounding at ambient temperature, T_{amb} = 298 K and atmospheric pressure, P_{atm} = 14.7 psi (101.35 kPa). Determine the mass flow rate of leaking ammonia, Q_m, through the ruptured pipe. Also estimate the amount of ammonia that escaped in 10 minutes.

Assume liquid ammonia is flowing at 50 kgs^{-1} in the pipe at 240 K and 15.2 psi (104.8 kPa).

(Hint: First solve for exit velocity of liquid ammonia using Bernoulli's equation. Then multiply exit velocity with discharge coefficient to incorporate frictional losses.)

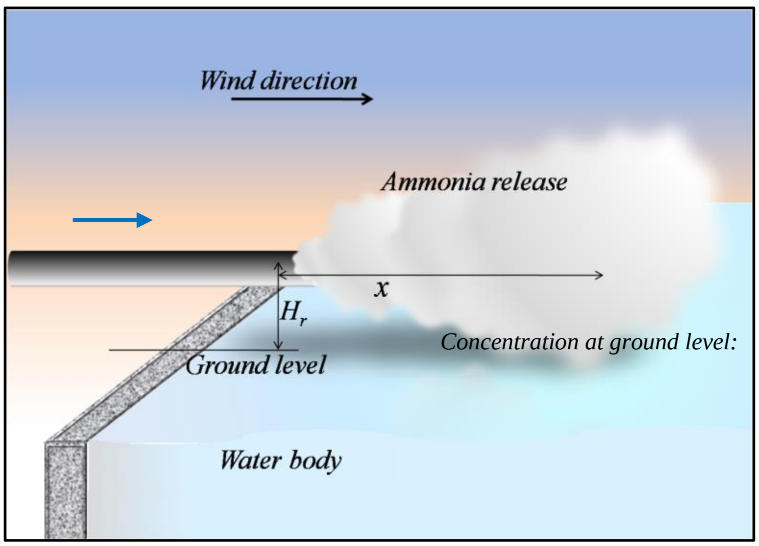


Figure 1.1. Schematic diagram of the ammonia vapor cloud

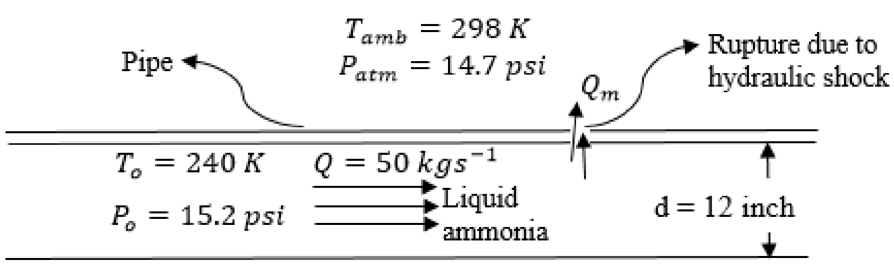


Figure 1.2: Liquid ammonia escaping and getting flashed immediately in the surrounding

(c) Anhydrous ammonia released from the leak on the roof of the facility was carried by wind blowing at 3.5 mph (1.56 m/s) in southerly direction across the Theodore Industrial Canal towards contract employees working at the Deepwater Horizon (DWH) vessel and boom decontamination

[1]From https://webbook.nist.gov/cgi/cbook.cgi?ID=C7664417

site which was about 0.25 mile (0.4 km) from the Milliard facility. Determine concentration of ammonia (in ppm) to which the workers were exposed to.

For a plume with continuous and steady state source (the ammonia release on the roof) at height, H_r, above the ground level with the wind moving in x direction at constant velocity, w, the ground level(z=0) concentration of ammonia vapor at a distance x, C(x), from the source (Milliard facility) is given by[2]

$$C(x) = \frac{Q_m}{\pi \sigma_y \sigma_z w} exp\left[-\frac{1}{2}\left(\frac{H_r}{\sigma_z}\right)^2\right] \quad \text{(c-1)}$$

where, Q_m is the mass flow rate of ammonia vapor through the leak

σ_y, σ_z are dispersion coefficients that define how much the plume of ammonia would deviate from the centerline in y and z directions, respectively.

Q_m can be taken equal to the one calculated in part (b) as liquid ammonia is immediately flashes in the surrounding.

Assuming the radiation intensity of the sun to be moderate and given that the wind speed is less than 2 ms^{-1}, the atmospheric stability class for the ammonia plume will be B. For plume of class B, the dispersion coefficients are given by[3]

$$\sigma_y = 0.337x^{0.88} \quad \text{(c-2)}$$

for x between 100 m – 500m,

$$\sigma_z = 0.135x^{0.95} \quad \text{(c-3)}$$

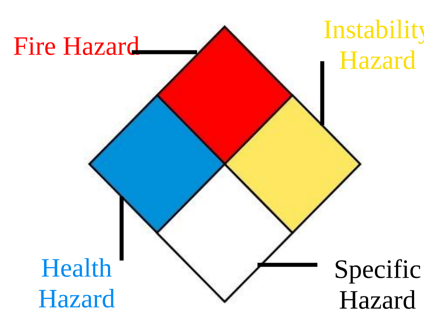
For vapors, mg/m^3 (mg of vapor per m^3 of air) conversion to ppm (molecules per 10^6 molecules of air) is given by,

$$Concentration\ \left(\frac{g}{m^3}\right) = Concentration\ (ppm) * \frac{M}{V_{molar}} \quad \text{(c-4)}$$

where V_{molar} is the molar volume calculated using ideal gas equation in m^3/mol, and M is the molecular weight in g/mol.

(d) As given in the incidence report, the Immediately Dangerous to Life or Health (IDLH) exposure limit for anhydrous ammonia established by the National Institute of Occupational Safety and Health is 300 ppm for 30 minutes of exposure.[4]Taking this as reference, comment on the concentration of ammonia obtained in part (c).

(e) Review the information in the NFPA Diamond tutorial. After reviewing the information, visit the CAMEO Chemicals website and fill out the blank NFPA Diamond to the right for ammonia.



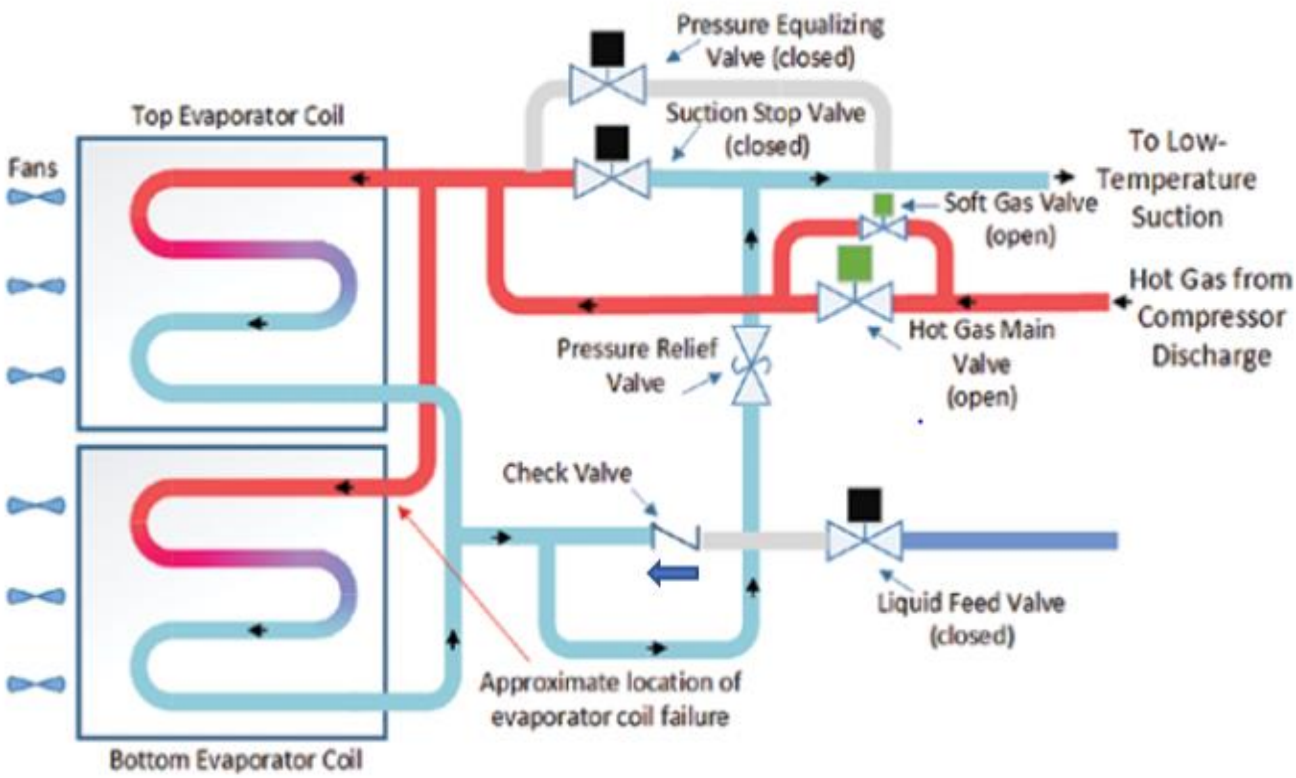
[2]From D. A. Crowl and J. F. Louvar, *Chemical Process Safety: Fundamentals with Applications*, 1st ed.(Englewood Cliffs, N. J.: Prentice Hall), p. 143
[3]From D. A. Crowl and J. F. Louvar, *Chemical Process Safety: Fundamentals with Applications*, 1st ed.(Englewood Cliffs, N. J.: Prentice Hall), p. 139
[4]From Incident Report, p. 8

Parts (f)-(h) are based on industry practices used to assess process safety. For more information on process safety and its importance in chemical engineering, please visit the University of Michigan SafeChE website here. *It is recommended that professors only assign 1-2 of the following parts due to the similar nature of the questions.*

(f) Review the explanation of the components of a BowTie diagrams found here. After reviewing the information, create a BowTie diagram for the Millard Facility incident.

(g) A HAZOP study is structured analysis of process design to identify potential vulnerabilities in a facility. Review the background on how to conduct a HAZOP study here before completing one for the following system. It is important to note that not all guidewords and parameters will be relevant for different systems. Some information is given here for guidance:

System to consider: The evaporator undergoing a defrost cycle



Hot gas is passed through the evaporator coils. Valves are present to control the flow of the gas and stop the flow of the cold liquid to the coils. The check valve allows only flow from the liquid feed valve to the evaporator coil (right to left) and prevents flow in the reverse direction (left to right). In the defrost cycle, the hot gas main valve, the soft gas valve and the pressure relief valve are open, while the suction stop valve and the pressure equalizing valve are closed. There is a manual stop button present which shuts down all the compressors and pumps, and de-energizes the valves. It is recommended that you go through pages 8-9 of the incident report for more background on this system.

Process parameters to consider: Flow of liquid ammonia to evaporator, Flow of hot high-pressure gas to suction line, Pressure, Amount of liquid ammonia in defrost cycle, Start-up procedure after interruption

(i) Fill out the boxes and the blanks in the HAZOP chart as shown in the tutorial. Some information has been filled out here for you.

Guideword + Parameter = Deviation	**Causes**	**Consequences**	**Safeguards**	**Recommendations**
More flow of liquid ammonia to the evaporator	Opening of the Liquid feed valve due to human error or programming error	Presence of hot gas and cool liquid → Hot gas condenses to create vacuum → high acceleration of liquid → _____ → Release of Ammonia	1. High ammonia detector alarm 2. Manual stop button that shuts down the entire operation (same Safeguards for all Deviations)	Have password protected systems so that only authorized personnel can modify the control system logic
More flow of hot high-pressure gas to the low-temperature suction line				
Low (Less) Pressure in the evaporator coils				
Residual liquid ammonia in the defrost cycle	Low pump-out times which are not sufficient to remove the liquid ammonia			
Other (Start-up after a process interruption)	Power Outage			

(ii) Write a short conclusion on some takeaways from completing a HAZOP for this system and recommendations you would make.

(h) A Layers of Protection Analysis (LOPA) is a semi-quantitative study to identify available safeguards and determine if the safeguards sufficiently protect against a given risk. Review the background on how to conduct a LOPA study here before filling the table out for the system described in this module. Some information is given for guidance:

- Assume that the plant can only accept a minor risk
- Frequency of restarting the process after a disruption is 1/year
- Release of ammonia caused 32 people to be hospitalized and business losses between $1-10 million

LOPA Study for Millard Refrigeration Hydraulic Shock		
Initiating Event	Cause:	Operator Error (Clearing all alarms during start-up)
	Consequence:	Release of ammonia gas
	FOIE:	
IPL(s)	Description of IPL_1, IPL_2, ...	
	$PFD = PFD_1 \times PFD_2 \times ...$	
MCF	MCF = FOIE x PFD	
	Category of MCF:	
Severity	Impact:	Multiple injuries that required a hospital stay
	Category:	
Risk	Type of risk:	
	Acceptable / Unacceptable?	
If risk evaluated above is unacceptable, please continue below:		
Proposed IPL(s) (P-IPL(s))	Description of $P\text{-}IPL_1$, $P\text{-}IPL_2$, ...	
	$P\text{-}PFD = P\text{-}PFD_1 \times P\text{-}PFD_2 \times ...$	
MCF	MCF = FOIE x PFD x P-PFD	
	Category of MCF:	
Risk	Type of risk:	
	Acceptable / Unacceptable?	

(i) Describe what was the most unsettling to you about the incident.

Wolfram

Click here to download Wolfram CDF Player for free.

Click here to view CDF installation tutorial.

Click here to download Wolfram code for this module.

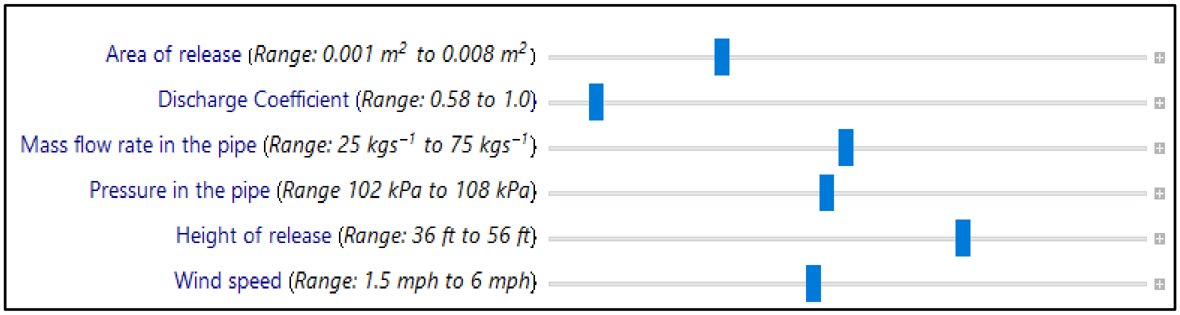


Fig 4.3 Wolfram sliders

Wolfram graph:

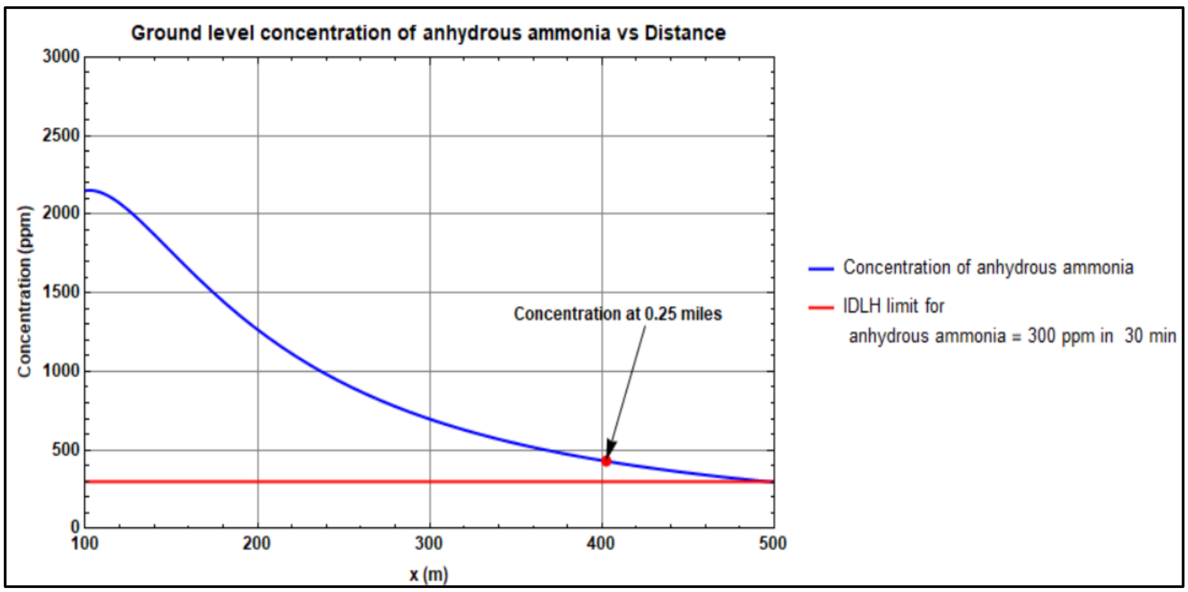


Fig 4.4 Concentration profile

(i) Vary the following parameters: pressure in the pipe, height of release, area of release and wind speed. Describe how they affect the ground level concentration profile of anhydrous ammonia.

(ii) For what set of values of the parameters mentioned in (i) would the concentration at 400m be lower than the IDLH limit?

(iii) Consider a pipe with a pressure of 102 kPa and a mass flow rate of 25 kg/s with a discharge coefficient of 0.58. Find the maximum area for which the concentration at 400 m is always below the IDLH limit independent of wind speed and height of release.

(iv) Based on your experiments in parts (i)-(iii), write a set of conclusions.

Definitions

Activity: The process, situation, or activity for which risk to people, property or the environment is being evaluated.

Hazard: A chemical or physical characteristic that has the potential to cause damage to people, property, or the environment.

Incident: What happened? Description of the event or sum of the events along with the steps that lead to one or more undesirable consequences, such as harm to people, damage to property, harm to the environment, or asset/business losses.

Initiating Event: The event that triggers the incident, (e.g., failure of equipment, instrumentation, human actions, flammable release, etc.). Could also include precursor events, (e.g., no flow from pump, valve closed, inadvertent human action, ignition). The root cause of the sum events in causing the incident.

Preventative Actions and Safeguards: Steps that can be taken to prevent the initiating event from occurring and becoming an incident that causes damage to people, property, or the environment. Brainstorm all problems that could go wrong and then actions that could be taken to prevent them from occurring.

Contingency Plan/ Mitigating Actions: These actions occur after the initiating event. They are steps that reduce or mitigate the incident after the preventative action fails and the initiating event occurred.

Lessons Learned: What we have learned and can pass on to others that can prevent similar incidents from occurring

BowTie Diagram: A qualitative hazard analysis tool through which potential problems and consequences associated with a hazard are studied through a pictorial representation. Necessary preventive and mitigating barriers are determined to reduce the process safety risk.

Hazard and Operability Study (HAZOP): A qualitative hazard analysis tool that uses a set of guide words to determine whether deviations from design or operating intent can lead to undesirable consequences. The existing safeguards are evaluated and if required, actions are recommended to mitigate the consequences.

Layer of Protection Analysis (LOPA): A semi-quantitative study that determines initiating event frequency, consequence severity, and likelihood of failure of independent protection layers (IPLs) to calculate the risk of a scenario. If the existing risk is intolerable, then additional IPLs are suggested to bring down risk to an acceptable level.

Module Specific for Hydraulic Shock at Millard Refrigerated Services

Hydraulic Shock: A sudden localized pressure surge in piping or equipment resulting from a rapid velocity change in the flowing liquid

Table of Nomenclature:

Symbol	Description	Units
Q_m	Mass flow rate of ammonia vapor through the leak	kg/s
σ_y, σ_z	Dispersion coefficients	
C(x)	Ground level concentration of ammonia vapor at a distance x	kg/m^3
H_r	Height above ground level	m
V_{molar}	Molar volume calculated using ideal gas equation	m^3/mol
w	Velocity of wind	m/s