

Separation Processes

Safety Module 1: *Ammonia Release due to Hydraulic Shock at Millard Refrigeration System, August 23, 2010*

Problem Statement: On August 23, 2010, 32,100 pounds of anhydrous ammonia were released into the atmosphere because a hydraulic shock in the pipe caused it to rupture. The resulting vapor cloud that formed travelled a quarter mile towards 800 workers. The workers had no place for shelter to prevent themselves from exposure to ammonia. 153 workers were exposed to the toxic ammonia cloud, many requiring hospitalization.



Watch the Video: (<https://www.youtube.com/watch?v=icf-5uoZbc>)

Incident Report Available At: (<https://www.csb.gov/file.aspx?DocumentId=5933>)

(Relevant pages: Pg.3-4, Pg.10-14)

- (a) It is important that chemical engineers understand of 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 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:

- (b) A multi-stage absorber is installed to clean the incoming air into the “Safe Room”. The gas entering the “Safe Room” from the atmosphere would first be sent through this absorber. If pure water is used to absorb ammonia in the air, estimate the number of stages in a counter-current absorber that should be installed to reduce concentration of ammonia from 100ppm to 10ppm. Also estimate the water flow rate (in dm^3/s) that would be required in the unit. Assume the system to be dilute.

Additional Information

Assume that the air flow rate into the “Safe Room” is $500 \text{ dm}^3/\text{s}$
 Absorber is at 1atm. Operation is such that the ratio of the water-to-gas flow rate is 1.15 times the minimum value of the ratio. ($(L/V) = \alpha \times (L/V)_{\text{min}}$) ($\alpha=1.15$).
 Henry’s Law Constant for ammonia-water system = $1.414 \text{ atm/mol fraction}$
 $\rho_{\text{air}} = 1.23 \text{ kg/m}^3$. $\rho_{\text{water}} = 997.05 \text{ kg/m}^3$

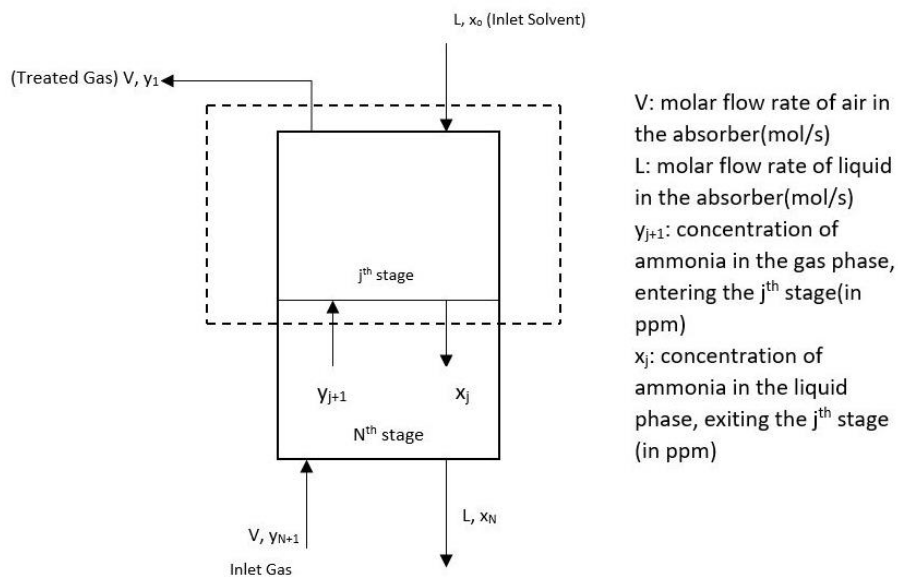
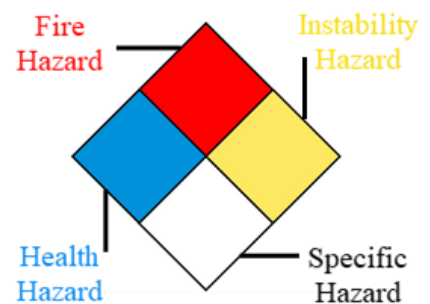


Figure 1. Gas Absorber

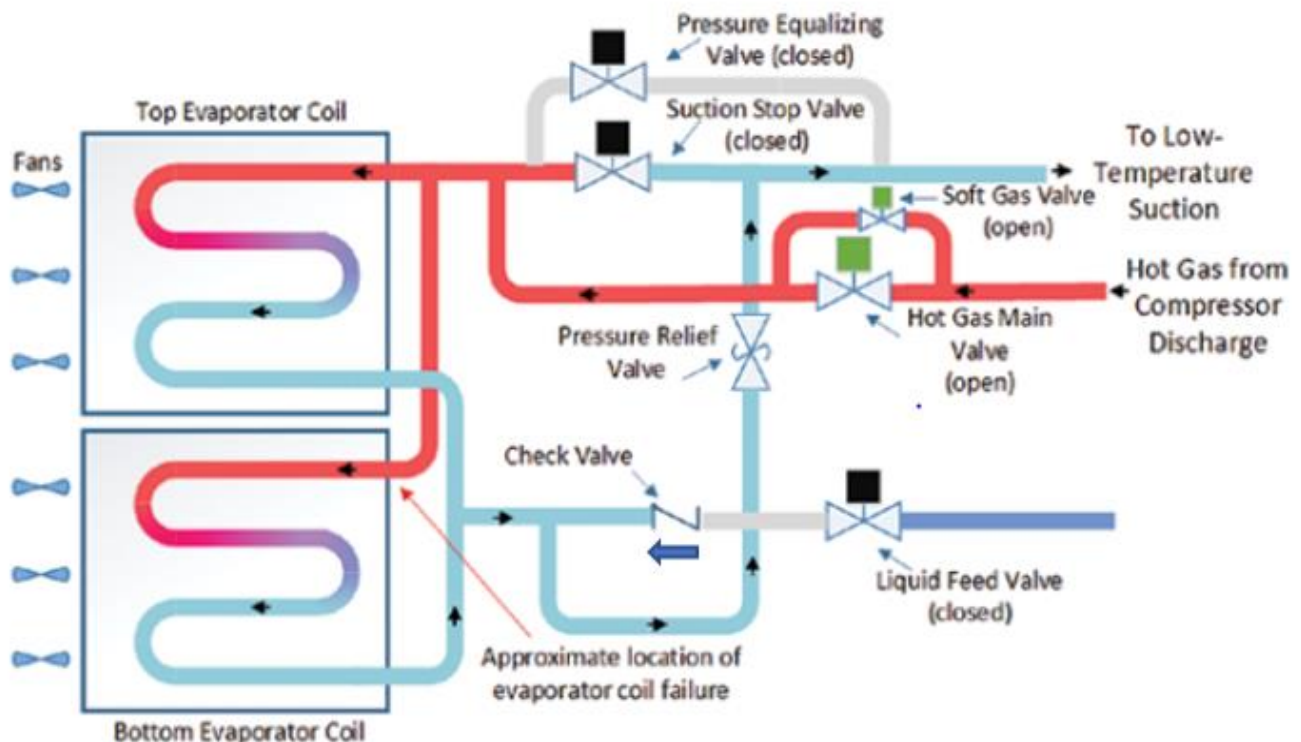
- (c) Review the information in the [NFPA Diamond tutorial](#). After reviewing the information, visit the [CAMEO Chemicals website](#) and fill out the blank NFPA Diamond below for ammonia..



Parts (d)-(f) 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.*

- (d) Review the explanation of the components of a BowTie diagrams found [here](#). After reviewing the information, create a BowTie diagram for the Millard Refrigeration incident.
- (e) 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 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
<i>More</i> 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	Have password protected systems so that only authorized personnel can modify the control system logic
<i>More</i> flow of hot high-pressure gas to the low-temperature suction line			(same Safeguards for all Deviations)	
<i>Low (Less)</i> Pressure in the evaporator coils				
<i>Residual</i> liquid ammonia in the defrost cycle	Low pump-out times which are not sufficient to remove the liquid ammonia			
<i>Other (Start-up</i> 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.

(f) 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 x PFD ₂ x ...	
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-IPL ₁ , P-IPL ₂ , ...	
	P-PFD = P-PFD ₁ x P-PFD ₂ x ...	
MCF	MCF = FOIE x PFD x P-PFD	
	Category of MCF:	
Risk	Type of risk:	
	Acceptable / Unacceptable?	

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

MATLAB

Click [here](#) to download the MATLAB file.

To run the code, you can download the latest version of MATLAB [here](#).

Click [here](#) to view the MATLAB tutorial.

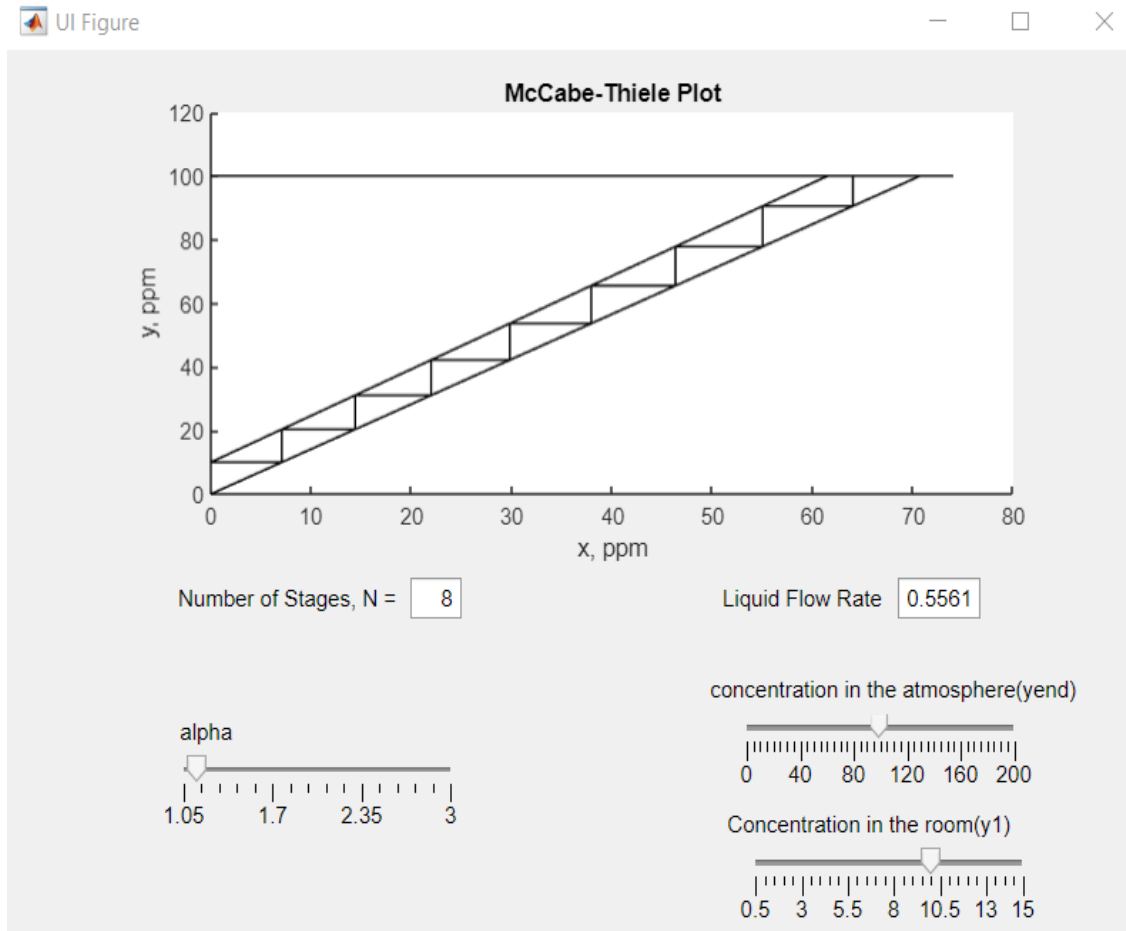


Figure 2. Output of the MATLAB code: McCabe Thiele plot

- (i) Vary α and comment on its effect on the number of stages and liquid flow rate.
- (ii) Vary *concentration of ammonia in the atmosphere* (y_{N+1}). How does this affect the number of stages and liquid flow rate?
- (iii) Vary *concentration of ammonia in the room* (y_1). How does this affect the number of stages and liquid flow rate?
- (iv) Suppose the *concentration of ammonia in the atmosphere* (y_{N+1}) is 120 ppm and the value of α is 1.2. Find the number of stages (N) that would bring down the *concentration of ammonia in the room* (y_1) to 0.5 ppm. Due to budget cuts, an absorber with only $N/2$ stages can be afforded. What range of y_1 can the absorber achieve for the same y_{N+1} ?
- (v) Write a short conclusion based on your experiments in parts (i)-(iv).

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

Relative Volatility: A measurement that compares the vapor pressures of different substances in a mixture. The symbol α is typically used to denote relative volatility and can be mathematically solved using the following equation $\alpha_{ij} = \frac{K_i}{K_j}$ where K is the equilibrium constant of the i or j component

Stage/Tray: A surface inside of a distillation column that helps in the separation between the vapor and liquid. A sieve tray is the most common and has various holes throughout to let the vapor rise up as the liquid flows down.

Table of nomenclature

Symbol	Name	Units
L	Liquid (water) flow rate	dm ³ /s
V	Gas (air) flow rate	dm ³ /s
α	Alpha – the factor multiplied to the minimum value of the ratio (L/V)	No units
y	Molefraction of ammonia in air	mol/mol
x	Molefraction of ammonia in water	mol/mol
N	Number of stages	No units
ρ_{air}	Density of air	kg/m ³
ρ_{water}	Density of water	kg/m ³

ⁱIn collaboration with Kara Steshetz, University of Michigan and Triesha Singh, Indian Institute of Technology, Bombay