

Consequence and risk assessment: Case study of an ammonia storage facility

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Abstract

This paper presents the results obtained by quantitative risk assessment performed for an ammonia storage facility. The storage facility was found to belong to the “highly hazardous category” based on qualitative Hazard Analysis (HAZAN) technique, which involved a detailed Fire, Explosion and Toxicity Index studies (FETI) and Hazard and Operability (HAZOP) analysis. Subsequently, Fault Tree Analysis (FTA) was used to identify all the failure modes, which could result in the occurrence of the undesirable incident more commonly known as the “top event”. Subsequently, both probabilistic and fuzzy logic techniques were employed to determine the probability of occurrence of this top event. The application of fuzzy set logic resulted in a range of probabilities, which took into account the uncertainties associated with the occurrence of the basic events. Recommendations regarding the maintenance/operator training were suggested and detailed sensitivity analysis was performed to determine the effect of incorporating the modifications on system safety. Detailed consequence analysis carried out for different cases of instantaneous release of ammonia from pressurized vessel indicate that the damage potential of this unit was “high”. Risk analysis, based on the top event probabilities and damage calculations indicate that in case of an accidental release of ammonia, its impact would permeate far beyond the plant boundaries thereby causing damage to the nearby areas. Nevertheless, these situations could be averted if the operators are trained and are sensitized to practice relatively simple safety measures.

Keywords: Ammonia, HAZOP, Risk Analysis, Fault Tree Analysis, Consequence Analysis

1. Introduction

With increase in the number of industries handling hazardous chemicals, there has been an equivalent increase in the number of accidents as well as their magnitude in terms of adverse consequences. This has led to a greater awareness of the imperative need for systematic identification and assessment of the potential hazards and associated risks in the industries handling hazardous chemicals [1]. Over the years, risk assessment has evolved as an important branch of science, which has been defined as a process, which includes both qualitative and quantitative determination of risks and their social evaluation [2]. This risk assessment tool can be used for estimating the risks associated with storage and use of hazardous chemicals. One such hazardous chemical is ammonia, which has been used in large volumes, particularly as a nitrogen feedstock, refrigerant and even as a sustainable fuel for power generation [3]. Ammonia has a

low IDLH (300 ppm) and TLV-TWA (25 ppm) values, which are indicative of its highly hazardous nature [4,5]. There are several reports on accidents involving ammonia [6-9] and hence it has been a subject of many risk assessment studies [10]. In fact even minor exposures to ammonia is believed to be harmful to human body and may cause some serious symptoms such as headaches, burns, and even permanent damage to the eyes and lungs [11]. Keeping in view the increasing use of ammonia and the extremely hazardous nature of this chemical, we attempt to perform a quantitative risk assessment study for a typical ammonia storage facility using a fuzzy logic based theoretical approach.

Anhydrous ammonia exists in the gaseous phase under ordinary temperatures and pressures and it may be liquefied by reducing temperature or by increasing pressure. Due to obvious reasons, it is stored as a liquid in various types of containers, the choice primarily depending on the quantity to be stored. Three types of storage commonly encountered are: (a)

storage at ambient temperature and equivalent pressure in cylindrical vessels, (b) storage under pressure in spherical vessels and (c) storage at atmospheric pressure under cryogenic conditions [12]. Usually the risk in such storage facilities results from the failure of the vessel at ground level, which leads to evolution of large amounts of ammonia. Such releases can result in serious consequences, including fatalities and injuries depending on the concentration of ammonia to which the plant workers and the surrounding public are exposed [13,14].

In the storage facility under investigation, ammonia is stored under pressurised conditions at ambient temperatures. The storage area is on the outer periphery of operating plant so that the supply tankers do not have to enter the main plant area. This however implies that any ammonia release can easily travel across the boundary and affect the nearby habitation. This paper presents the results of risk analysis for the case of an instantaneous accidental release of ammonia under different prevalent weather conditions from a pressurized vessel.

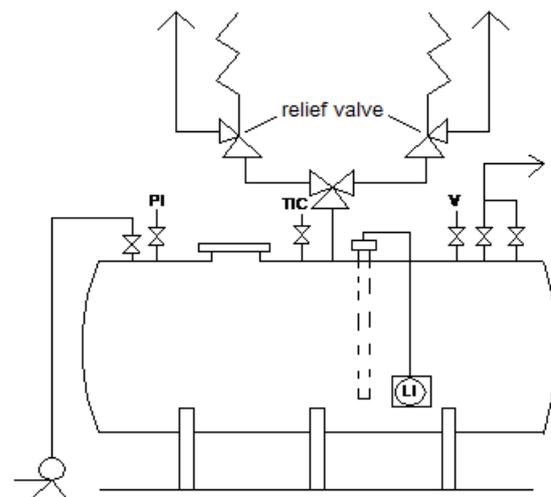
2. Methodology

Analysis of the risk posed by the storage facility was carried out in several steps. The first step was the identification of factors, which can contribute to the occurrence of the potential accident scenarios. This was performed by HAZAN technique. The HAZAN techniques employed were Fire Explosion and Toxicity Index (FETI) for hazard ranking and Hazard and Operability Studies (HAZOP) for identifying the probable hazards, their associated causes and consequences at every stage of the process. This is followed by a detailed fault tree analysis, which depicts all possible routes for the occurrence of the probable scenario, commonly referred to as the top event. The top event probability was calculated using both probabilistic approach as well as the fuzzy logic approach. The most important aspect of the fuzzy logic approach is the way in which imprecision is handled.

Fault Tree Analysis (FTA) leads to all possible minimum combinations of basic human, instrument and equipment failures called minimal cut sets, which could lead to the occurrence of the "top event". The end result of this analysis is a set of critical basic failure

events and the failure rates of each of these events significantly affect the failure rate of the overall system. The analysis gives the system designers a set where the effort in improvement can be best focused. In this paper, fuzzy set theory has been used to define the probabilities of various basic events. The probability of the top event calculated, thus takes into account the uncertainties associated with the basic events. Importance of fuzzy set theory in fault tree analysis has been demonstrated with respect to failure analysis of structures [15]. This is followed by sensitivity analysis to check the effect of recommendations on the top event probability. The results obtained from the studies based on the above methodology for an ammonia storage facility is presented in the following sections.

Figure 1. Schematic sketch of ammonia storage facility



V: vent line; PI: pressure indicator; LI: level indicator; TIC: temperature indicator

3. Case Study: Ammonia Storage Facility

In the ammonia storage facility under investigation, four tanks each of 50 metric tonnes are filled to 80% of their working capacity. A schematic of a representative storage tank is presented in Fig 1. Each of these tanks is 10 m long and has a diameter of 2.74 m. The chemical is stored at ambient temperature and 13 kg/cm² pressure, and under these conditions, it exists as pressurized liquid. The tanks are made of carbon steel and are saddle supported (3 no) at a height of 1m. The ground underneath is composed of soil and small stones and a concrete path is provided all around the storage section. All the four tanks are

interconnected and each of these tanks is provided with two bayonet heaters in which hot water at 50-90°C is used as the heating medium. A cooling system is also present to avoid

overheating which may result in pressure buildup. Ammonia is transferred to the nearby sections through insulated pipelines.

Figure 2a. Fault tree for release of ammonia from storage tank

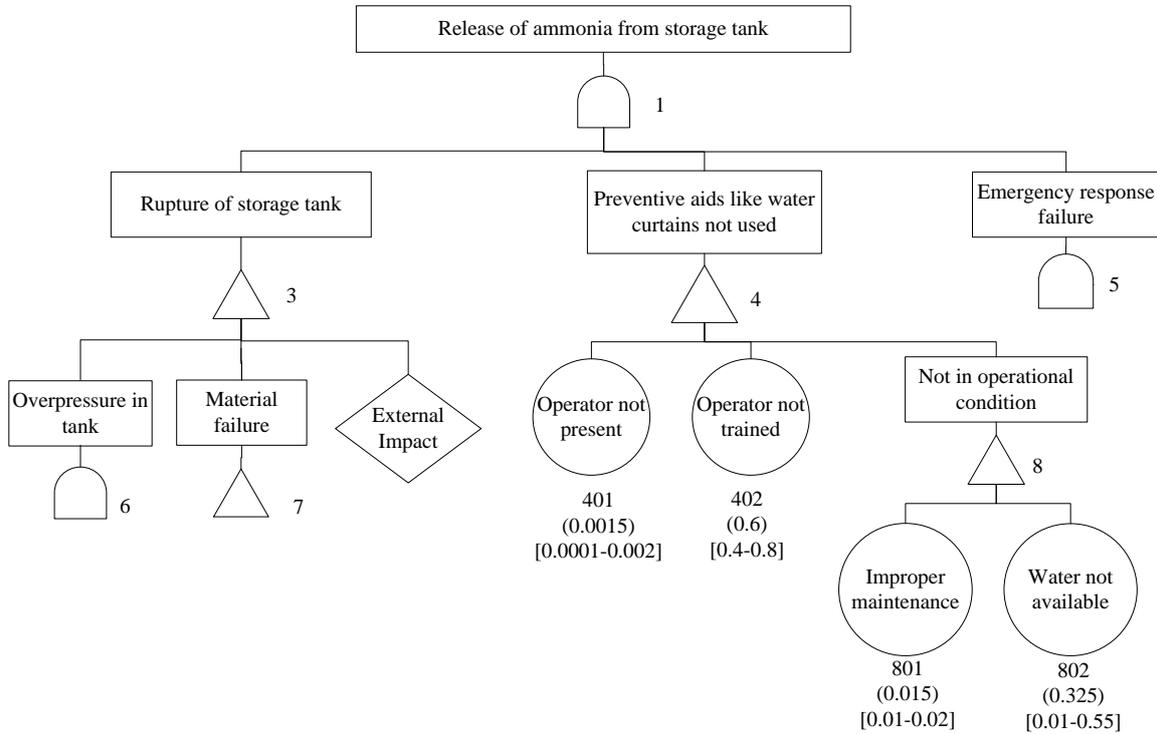
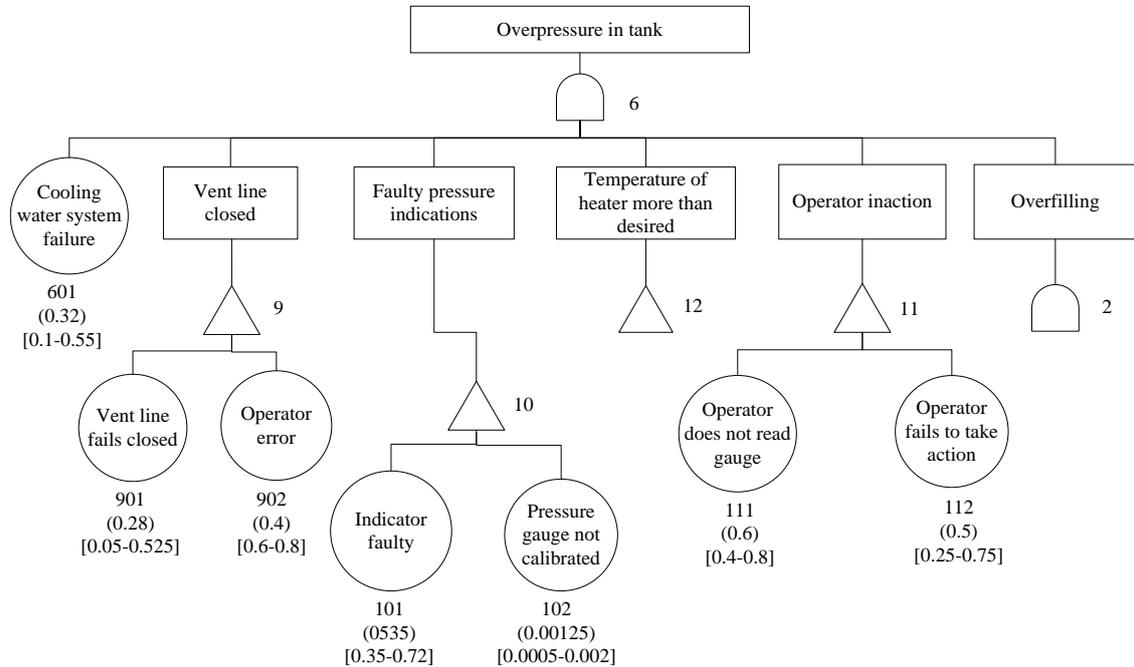


Figure 2b. Fault tree for release of ammonia from storage tank



3.1. Hazard Identification

The flammable limits of ammonia are 16-25% by volume in air with an ignition temperature of 651°C. Ignition of such mixtures is improbable under ordinary conditions, but if

it occurs in a confined space, it could result in an explosion. The probability of this event is low and therefore ammonia installations are not regarded as significant fire hazards.

Formalised technique of estimating Fire & Explosion Index (F&EI) and Toxicity Index (TI)

was used for hazard identification. The F&EI obtained was 105.8 and TI was 10.4, which places the storage facility in an overall hazard category of III (high hazard). Moreover, the inventory of the material is large, thereby increasing the damage potential. Therefore, this facility was subjected to a detailed qualitative and quantitative assessment. The major hazard identified from the Hazard and Operability studies (HAZOP) is “Release of ammonia due to spillage/leakage caused by catastrophic rupture of storage tanks”. Both probabilistic and consequence analysis was carried out for the resulting scenario and the risk was quantified.

Figure 2c. Fault tree for release of ammonia from storage tank

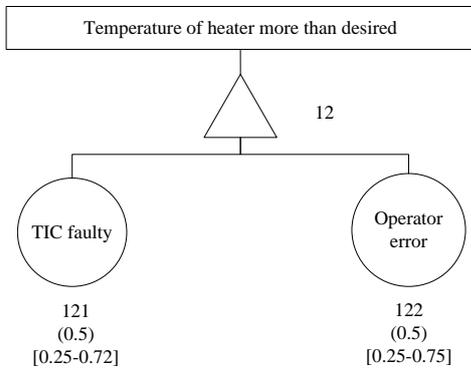


Figure 2d. Fault tree for release of ammonia from storage tank

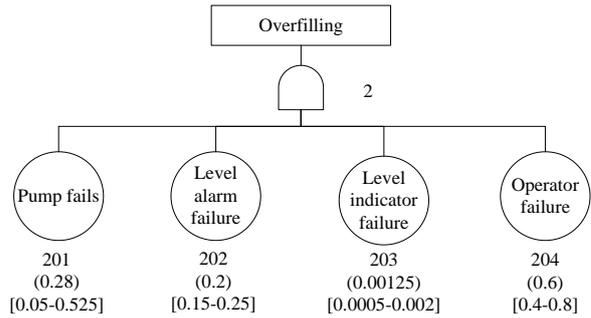


Figure 2e. Fault tree for release of ammonia from storage tank

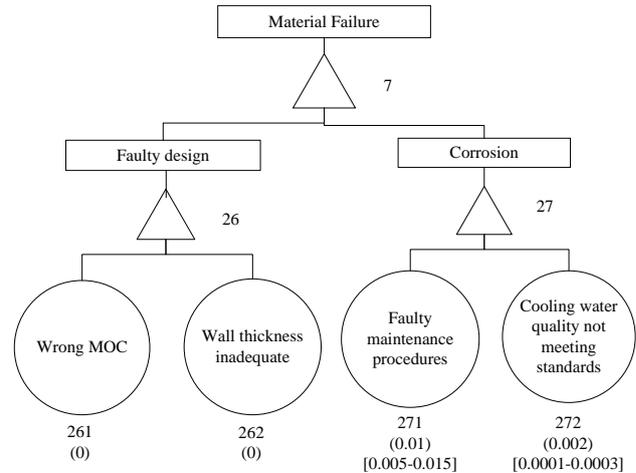
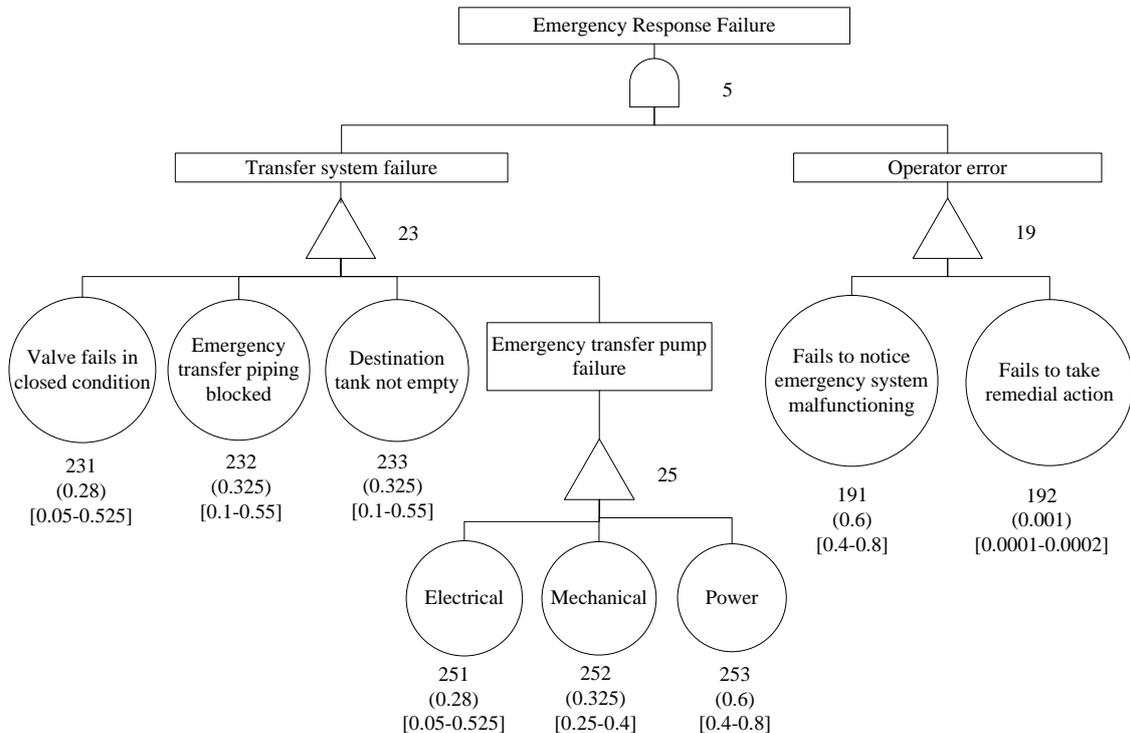


Figure 2f. Fault tree for release of ammonia from storage tank



4. Fault Tree Analysis

The fault trees for the most hazardous event has been developed and presented in Fig 2a-2f. The failure rates of the events are based on the data from several sources [16,17], suitably modified, where necessary to account for country conditions.

The total number of minimal cut sets for this fault tree was computed to be 480. The minimal cut sets in order of decreasing probability of occurrence of top event are listed in Table 1. A combination of basic failures- faulty maintenance procedures (271), cooling water not meeting standards (272), operator not trained (402), power failure (253) along with operator error in not noticing the emergency system malfunctioning (191) was found to be the most catastrophic and resulted in the highest probability for top event occurrence.

However, while using the conventional probabilistic approach for fault tree analysis, considerable amount of uncertainty builds up in the calculation of top event probability. The basic failure rates of the individual components are usually available as a range of values. Uncertainty exists as to where the actual failure rate lies within that range. This makes the conventional rigid mathematical technique not suitable in most of the cases. The probabilistic approach as a whole lacks adequate mechanism for tackling the problem of uncertainties associated.

4.1. Fuzzy Set Theoretical Approach

Fuzzy set theory offers a frame of analysis which models the imprecision in the input failure probabilities used in FTA, given the failure probabilities and the lower and upper bounds at the failure nodes [18-20]. A numerical code for fuzzy fault tree was developed and applied to the present case in order to estimate the fuzzy top event probability range. The code used a trapezoidal model in which the sides of the trapezoid represent the reasonable bound of the component failure probability. The fuzzy logic application is dependent on the membership function. The choice of the membership function is usually problem dependent and is often determined heuristically and subjectively. This approach offers a fuzzy top event probability range.

4.2. Evolving Fuzzy Membership Functions

Fault tree basically consists of many nodes placed in some hierarchical order and each of the node is either a Basic/Leaf node or an Intermediate node. The Basic/Leaf nodes are characterized by three inputs: Lower Bound probability, Upper Bound probability and the probability at particular instant. The intermediate nodes are characterized by two inputs: the first one represents either an AND gate or an OR gate and the second is the number of children it has which is actually equivalent to number of causes for the occurrence of that event. For each of the leaf node a fuzzy membership function is constructed using the given lower bound probability and upper bound probability. Then, a membership value μ is evaluated using the probability of occurrence of that event at a particular instant.

4.3. Comparison of Probabilistic and Fuzzy Set Approach

The most critical cut sets associated with the maximum probabilities (in decreasing order of likelihood), leading to the top event "Release of ammonia from storage tank" are presented in Table 1. It can be seen that the probability of the top event was calculated to be 4.46E-7 using the conventional probabilistic method and it could actually vary between 3.2E-8 to 2.3E-6 (as estimated by fuzzy set approach). Assuming 300 working days per year, the corresponding conventional and fuzzy failure rates was calculated as 1.34E-4 per year and {9.6E-6 per year to 6.9E-4 per year} respectively. It can be seen that operator related basic events could lead to disastrous consequences. What is more important to note is that most of the previous studies indicate [21,22] the more common nature of operator related failures as compared to instrument failures and due to their unpredictability, the complexity of the situation increases manifold. On the basis of the observations brought forward by the fault tree analysis in the present study, recommendations regarding the maintenance/operator training were suggested and a detailed sensitivity analysis was performed to determine the effect of incorporating the suggested modifications on system safety.

Table 1. Minimal cutset's associated with the maximum probability obtained by fault tree analysis of the top event "Release of ammonia from storage tank"

S. No	Minimal cut sets	Conventional probability	Fuzzy probability range
1	(271)(402)(253)(272)(191)	4.3E-7	(3.2E-8 - 2.3E-6)
2	(271)(802)(253)(272)(191)	2.3E-7	(8.0E-9 - 1.6E-6)
3	(271)(402)(233)(272)(191)	2.3E-7	(8.0E-9 - 1.6E-6)
4	(271)(402)(232)(272)(191)	2.3E-7	(8.0E-9 - 1.6E-6)
5	(271)(402)(231)(272)(191)	2.0E-7	(4.0E-9 - 1.5E-6)
6	(271)(402)(251)(272)(191)	2.0E-7	(4.0E-9 - 1.5E-6)
7	(271)(802)(252)(272)(191)	1.2E-7	(5.0E-9 - 7.9E-7)
8	(271)(802)(233)(272)(191)	1.2E-7	(2.0E-9 - 1.1E-6)
9	(271)(802)(232)(272)(191)	1.2E-7	(2.0E-9 - 1.1E-6)
10	(271)(802)(231)(272)(191)	1.1E-7	(1.0E-9 - 1.0E-6)

5. Sensitivity Analysis

The sensitivity analysis was performed using both the approaches i.e. probabilistic as well as fuzzy set theoretical approach. The results of the analysis are shown in Table 2. It is apparent

from the table that incorporation of the suggested modifications can bring down the conventional failure rate from 1.3E-4 to 3.6E-7 per year, thereby causing several orders of improvement in system safety.

Table 2. Sensitivity analysis results

Basic event	Recommendation	Top event occurrence ^a		Top event occurrence ^b	
		Before	After	Before	After
Power failure	Generator for auto take off	1.34E-04	2.16E-06	9.6E-06 to 6.9E-04	2.4E-08 to 8.6E-05
Operator error	Operator training for using preventive aids like water curtains	2.16E-06	3.6E-07	2.4E-08 to 8.6E-05	6.0E-10 to 1.6E-05

a. Probabilistic approach

b. Fuzzy set theoretical approach

6. Consequence Analysis

The objective of consequence analysis is to quantify the harmful impacts in case of occurrence of the potential top event. Toxicity is the major hazard associated with the accidental release of this chemical. Ammonia stored at pressure possess considerable potential energy and should a rupture of the primary container occur, the liquid will flash into a vapour spontaneously as the thermodynamic state of the ammonia adjusts itself to the diminished pressure. Since this adiabatic flash evaporation takes place almost instantaneously, most of the contents of the ruptured pressure vessel will enter the atmosphere either as a vapor or as a fine aerosol. For this reason, the design of the primary container should meet international

standards, which virtually eliminates the possibility of a major failure.

6.1. Dispersion of Ammonia: Model Description

Ammonia although being lighter than air has been modeled using the heavy gas dispersion model. "Heavy gases" belong to that category of gases that form vapor clouds that are heavier and denser than air. Heavy gases include not only gases with molecular weights heavier than air, but also those that are stored liquefied under pressure. Liquefied gases typically escape from storage as a cold, heavy cloud containing a mixture of gas and fine aerosol droplets. A release of such a mixture is called a two-phase flow. The aerosols weigh the cloud down and

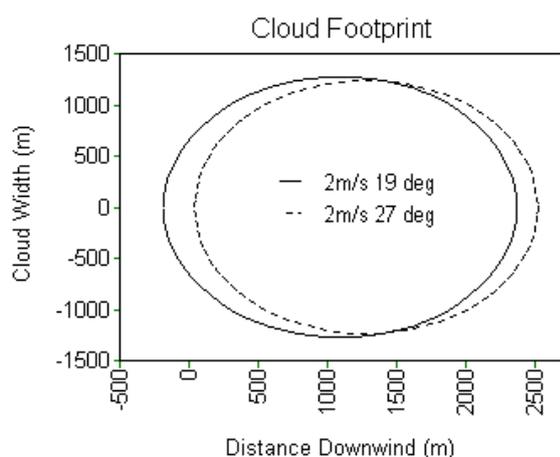
make it denser, and their evaporation cools the cloud.

Heavy gases behave in a complex manner when they escape from storage. A heavy gas cloud first slumps away from the source in all directions, then flows downwind like water, propelled by the wind, gravitational slumping, and its forward momentum. As it moves downwind, air is stirred into the cloud, and it becomes less and less dense, eventually behaving like a neutrally buoyant gas.

6.2. Dispersion Calculations

Safeti software (Safeti micro 6.21) has been used to assess the effect of ammonia dispersion into surrounding atmosphere. The dispersion calculations were carried out for different scenarios (weather conditions and amount released) and the results are reported in Tables 3 and 4. These tables report the maximum distance to IDLH concentration. The IDLH gives an estimate of the maximum concentration in air to which a healthy worker could be exposed for about 30 min without suffering permanent health effects. The tables also report the upwind distance as a function of the released mass, which has maximum impact due to initial expansion [22]. This area should be evacuated all around the release point. Figure 3 gives the dispersion to the IDLH level in case of an accidental release of 50 T of ammonia under the prevailing weather conditions.

Figure 3. Dispersion to IDLH level



As expected, the distance to which the IDLH plume travels increases with the amount released, implying higher risks with larger inventories. The stability class also appreciably affects the distance traveled by the plume. It was however interesting to note that variation in wind velocity has only marginal effect on the

dispersion while temperature conditions can change the dispersion length by an order of 100-400 m.

6.3. Effect of Day and Night Conditions on Dispersion

Tables 3 and 4 also present the dispersion results for day and night conditions. Due to a wide variation in the weather conditions vis a vis temperature and stability class the effect of the released mass in terms of distance IDLH plume travels, is significantly higher for night conditions. This implies that any significant release of ammonia inventory during the night shift is likely to spread over larger areas and result in larger number of people being exposed to higher risks.

6.4. Analysis of the Meteorological Data

The weather data provided by the local meteorological department (one year data) was analysed. The year was divided into two seasons namely summer (April to September) and winter (October to March) as there was substantial change in the wind direction and temperature in these two seasons. The wind directional probability was calculated for both summer and winter season. The calculated probability of wind direction is reported in Tables 5 and 6. Based on the wind rose pattern, the predominant wind direction during summer (51 % of the time) is NE so probability of ammonia dispersing in this direction is maximum. During winters, the wind direction changes with the plume pointing towards SW (52% of the time).

7. Incident Outcome Frequency Calculations

The frequency of release of ammonia due to storage tank rupture is $1.3E-04$ /yr. Based on this figure and the directional wind probability, the incident outcomes for both summer as well as winter season have been calculated [22] as given in equation (1)

$$\text{Incident outcome} = \text{Top event frequency} \times \text{directional wind probability} \quad (1)$$

The results for summer and winter season are summarized in Tables 5 and 6 respectively. Since the storage is in an open area, the wind direction will appreciably affect the dispersion pattern of the released gas.

Table 3. Distances to IDLH level (300 ppm) for instantaneous release of ammonia in relation to released mass and atmospheric conditions (Day scenario)

Weather category	Wind speed (m/s)	Temperature (°C)	Relative Humidity	Released mass (Ton)					
				10T		30T		50T	
				Down wind distance (m)	Back distance (m)	Down wind distance (m)	Back distance (m)	Down wind distance (m)	Back distance (m)
B	1	40	0.8	1141	295	1704	306	2005	512
B	2	40	0.8	1105	99	1735	25	2000	103
B	1	25	0.9	1195	151	1745	351	2102	391
B	2	25	0.9	988	149	1626	121	1839	324
A	1	40	0.8	1049	191	1536	468	1823	611
A	2	40	0.8	903	181	1439	234	1837	106
A	1	25	0.9	1056	187	1585	280	1901	483
A	2	25	0.9	834	187	1347	241	1565	346

Table 4. Distances to IDLH level (300 ppm) for instantaneous releases of ammonia in relation to released mass and atmospheric conditions (Night scenario)

Weather category	Wind speed (m/s)	Temperature (°C)	Relative Humidity	Released mass (Ton)					
				10T		30T		50T	
				Down wind distance (m)	Back distance (m)	Down wind distance (m)	Back distance (m)	Down wind distance (m)	Back distance (m)
D	1	27	0.8	1282	254	1925	366	2256	410
D	2	27	0.8	1197	135	1942	88	2353	105
D	1	19	0.9	1284	260	1996	254	2355	411
D	2	19	0.9	1234	100	1882	94	2360	-68
E	1	27	0.8	1284	300	1943	450	2334	528
E	2	27	0.8	1256	169	2133	35	2582	-35
E	1	19	0.9	1268	353	1902	327	2262	667
E	2	19	0.9	1267	130	1900	178	2449	94

Table 5. Incident outcome and risk associated with the storage of ammonia in summer season^a

Wind direction	Directional probability	Population affected ^b	Incident outcome before recommendation	Risk in fatalities/year before recommendation	Incident outcome after recommendation	Risk in fatalities/year after recommendation
N	8.7	-	1.13E-05	-	3.13E-08	-
NE	51	-	6.63E-05	-	1.84E-07	-
NW	0.5	3000	6.50E-07	1.95E-03	1.80E-09	5.40E-06
E	14.7	1000	1.91E-05	1.91E-02	5.29E-08	5.29E-05
W	1.6	10000	2.08E-06	2.08E-02	5.76E-09	5.76E-05
S	3	-	3.90E-06	-	1.08E-08	-
SE	5.4	1000	7.02E-06	7.02E-03	1.94E-08	1.94E-05
SW	14.2	1500	1.85E-05	2.77E-02	5.11E-08	7.67E-05

a: Before recommendation: incident frequency per year (1.34E-04). After recommendation: incident frequency per year (3.6E-07)

b: Area considered for affected population = 4.8 Km²

Table 6. Incident outcome and risk associated with the storage of ammonia in winter season^a

Wind direction	Directional probability (%)	Population affected ^b	Incident outcome before recommendation	Risk and fatality before recommendation	Incident outcome after recommendation	Risk and fatality after recommendation
N	7	-	9.10E-06	-	2.52E-08	-
NE	14	-	1.82E-05	-	5.04E-08	-
NW	1	3.00E+03	1.30E-06	3.90E-03	3.60E-09	1.08E-05
E	5	1.00E+03	6.50E-06	6.50E-03	1.80E-08	1.80E-05
W	16	1.00E+04	2.08E-05	2.08E-01	5.76E-08	5.76E-04
S	3	-	3.90E-06	-	1.08E-08	-
SE	-	1.00E+03	-	-	-	-
SW	52	1.50E+03	0.0000676	1.01E-01	1.97E-07	2.80E-04

7.1. Damage Calculations

The effect calculations give the extent of the IDLH plume while the probability calculations give the directional probability of the incident outcome. Their damage potential is calculated based on the extent of IDLH plume and its superimposition on the layout of the plant and the surrounding areas. Tables 5 and 6 give the area of exposure and population at risks during summer and winter season. If effective measures are instituted to evacuate the affected public (exposed to IDLH concentration) within a radius of 2.5 km in the wind direction within 30 min, then the damage will come down to the personnel present in the immediate vicinity of the ammonia storage facility within the plant. Assuming this figure to be 5, the damage will come down to 5 fatalities per incident. Onsite and offsite emergency plans need to be formulated and all district level agencies involved in emergency planning should be sensitized to the plans and participate in mock drills to aid evacuation. Placing appropriate sensors for determining the concentration of ammonia at different places can be very helpful [23] in reducing the top event probability.

8. Risk Assessment

From the probability calculations as well as the effect and damage calculations, the risk has been calculated as follows.

$$\text{Risk (fatalities/yr)} = \text{Probability (events/yr)} \times \text{Damage (fatalities/event)} \quad (2)$$

In the storage section, the individual risk for both the summer and winter season have been estimated and the results are summarized in Tables 5 and 6. The total individual risk (Fatalities /year) as seen from these tables is 7.6 E-02 per year during summer and 3.1E-01 per year during winters. However after incorporation of the recommendations suggested, the fatalities will be brought down to 2.1E-04 per year and 8.8E-04 per year for summer and winter season respectively. Similar risk calculations were performed using the fuzzy probability range and the results are tabulated in Table 7.

According to Table 8, the frequency of 1.3E-04 per year (before implementing recommendation) belongs to “Remote” category, while the damage falls under “Catastrophic” category. Thus the risk falls under “B” category -Undesirable and management needs to take a decision as to continuation of operation under existing conditions. After incorporating the recommendations the frequency could be brought down to 3.6E-07 per year, which falls under the improbable category, resulting in the reduction of the risk to C category - “Acceptable with review”. After implementation of protective measures i.e. evacuation and assuming only 5 plant personnel present at the site, the damage could be brought down to “Marginal” category.

Table 7. Fuzzy Risk values

	Risk and fatality	
	Before recommendation	After recommendation
Summer	{0.5E-03 - 0.41}	{3.5E-07 - 9.5E-03}
Winter	{2.4E-02 - 1.7}	{1.5E-06 - 3.9E-02}

Table 8. Risk Assessment matrix

Frequency of occurrence		Hazard category			
		Catastrophic > 100	Critical 10 - 100	Marginal 1 - 10	Negligible < 1
Frequent	0.01	A	A	A	C
Probable	0.001	A	A	B	C
Occasional	0.0001	A	B	B	D
Remote	E-4	B	B	C	D
Improbable	E-6	C	C	C	D

9. Conclusions

A quantitative risk assessment was performed for an ammonia storage facility using both probabilistic and fuzzy set approach. Based on the hazard identification analysis, the storage section was found to belong to “high” hazard category with respect to both F&EI and TI. Since ammonia is stored under pressurized conditions, accidental rupture would lead to instantaneous dispersion of ammonia into the surrounding atmosphere. The release of ammonia into the atmosphere resulting from rupture of the storage vessel was identified as the top or unwanted event. Fault tree analysis technique was used to identify the combination of basic events responsible for the top event occurrence. The top event probability was calculated using both the conventional probabilistic approach as well as the fuzzy set theory approach. The former gave the top event probability while the latter approach resulted in the fuzzy top event probability range, which gives a more realistic picture as it takes care of the imprecision in the failure rate data, which is the basis of these calculations. Based on the dispersion behavior of the plume, the threat zone was found to extend to an inhabited area of 4.8 km² in the case of the worst case scenario. Since this extends well beyond the plant boundary, appropriate onsite and offsite emergency plans were formulated to aid the evacuation in the event of ammonia release.

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