

Evaluation of Hazards by Event Tree Analysis and Assessment of Toxicity Index using Aloha In Pharma Industry

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Abstract – Chemicals are highly hazardous in nature. Starting from the initial stage of manufacturing till the storage of raw chemicals is dangerous to human life. This study has been done in pharma industry where the workers are exposed to hazardous chemicals such as chlorine dioxide, hydrogen peroxide, methanol and the same. The physical and chemical properties of the chemicals are studied. The second step is Checklist analysis where the needed data are gathered which are going to be used for further steps. At next step, to select a highly hazardous chemical, Toxicity Index Calculation is used to rank the chemicals based on the data collected from checklist. After the selection of the hazardous chemical, the next step is to find out what is the next event going to happen if there is a release. For which, Event Tree Analysis (ETA) is used in this step. The next step after finding the final event from ETA is to find the how it is dispersed into atmosphere and how much distance it covered. It can be easily found out using the ALOHA Dispersion Software. The next step is human health and safety loss calculation using the distance found out by software and compensation amount gathered from law. The final step is to make the precautionary & preventive measures to avoid the toxic dispersion into atmosphere and the emergency preparedness should be prepared for what should be done during the toxic release.

Keywords- ALOHA, Event Tree Analysis, Emergency Response Planning,etc.

I. INTRODUCTION

Medilux Laboratories is manufacturer of world-class bulk drugs intermediates and fine chemicals. Its inception in 1988 to earning the status of 100% export oriented unit. The management is headed by well-qualified professionals from the pharmaceutical industry who have helped the company consistently met quality and delivery commitments..Today Medilux is the "preferred supplier" for various intermediates to many reputed multinational pharma companies and is fast emerging as a reliable global manufacturer of basic drugs. An ISO 9001:2000 certified company. Medilux produces more than 85 different products and also provides customized solutions. Eighty percent of Medilux's business is repeat business. Medilux offers a comprehensive and flexible package of chemical development and manufacturing services to meet customer needs. Exports constitute almost 99% of its sales. A head office at Pithampur, Madhya Pradesh in India.

II.LITERATURE REVIEW

Review of Literature

Hu Si (2012) et al stated that QRA model involves that probability calculations for leakage, derivative accidents to identify the likelihood and frequency of these

accidents. It also calculates the influence range to identify who and how much people are involved. Loss calculations includes Personnel direct economic loss, Material direct economic loss, and total economic loss for quantitative analysis. Acceptable risk level analysis is done by comparing the standards with calculated risks by plotting graphs. By this, poisoning of toxic release pose high risks comparing than fire and explosion by using above factors. After finding this, suitable suggestion was made to revoke or reduce it to control it within an acceptable range [1].

O. Sanguino (2013) et al stated that predicting release rates is the first step, and a crucial step, in consequence analysis. The dispersion modeling of acid gas was calculated using PHAST software by applying various parameters. Effects of quantification can be done using probit functions. By plotting death rate with hole size in a graph, the author concluded that Mostly intermediate hole sizes (50mm) can cause more consequences [4-5-6].

Juan A. Vilchez (2012) et al explained that each sequence will lead to a final accident scenario, the severity of which will range between "no outcome" (no consequences or negligible consequences for people and property) and a "major accident". In this paper, the authors used the EC labeling and CPR 18E for finding

the exact probabilities of accidental events occurring. The author concluded that which is more hazardous and what needs immediate attention by probability and event trees [7-8-9].

PerriZeitzRuckart (2012) et al stated that to find the significant difference between using chlorine and its derivatives uses, data of chemical release are gathered from Hazardous Substances Emergency Events Surveillance (HSEES) system organized by US EPA. Paper manufacturing was involved in 32.3% of the chlorine releases, resulting in 122 injured persons (5.9% of all injured persons in chlorine releases). Hydrogen peroxide had fewer injured persons per release with injured persons and fewer injured persons for all releases: chlorine had 3.9 and 1.3, respectively, and hydrogen peroxide had 2.0 and 0.2, respectively. Hydrogen peroxide resulted in a higher proportion of reports of gastrointestinal problems and headaches (12.2% each) than chlorine (8.1% and 3.1%, respectively). Evacuations were more likely to be ordered for chlorine (26.2%) releases than for releases involving hydrogen peroxide (9.5%). Using alternatives instead of chlorine can reduce the hazardous exposure at certain level [10-11-12].

Q. Yu (2009) et al stated that a safety criterion based on frequency and consequence of major hazard accidents was set up for consequence analysis. The author used both Consequences analysis and Risk assessment were used to find optimum safety distance for people to take shelter. And also it explains that low frequency occurrence cause serious threat than high frequency occurrences.

J.M. Tseng (2012) et al explained the consequences analysis by using two scenarios which have common factors such as chemical released as Chlorine (Cl). It is found that the ERPG I and ERPG II conditions for scenario 1 and 2 are more or less same for both summer and winter but IDLH for scenario 2 at winter is different, so the temperature and climate plays significant role in chemical dispersion [14-15].

III. PROBLEM STATEMENT

From the literature review, the following inferences are obtained,

- Poisoning of toxic release pose high risks comparing than fire and explosion.
- The frequency of the toxic release is less, but when it occurred, it cause more impact on human health and safety.
- Use of software instead of manual calculation has more efficient result within short duration.
- Consequences analysis can provide better safe distance from hazardous release.

- The most of the chemicals used in the pharma industry are toxic in nature. So, the likelihood toxic release in this industry is inevitable at such scenario. And also the company does not have the Offsite emergency plan yet. Bhopal Gas disaster 1984, which opens the eyes of every nation to assess the safety of people and their vulnerability to the toxic release. It caused the total death of 6, 046 people and 5, 58,125 of various injuries confirmed by Government of Madhya Pradesh and Government of India. The same scenario is likely to be happening in the pharma industry situated at urban area due to the usage of various hazardous chemicals and high population around the industry. To avoid this to be happening in future, the following objectives are made in this project work [16-17].
- To analyze the Consequences of chemical release
- To calculate the Safe and Threat Zone which can be used by emergency responders?
- To take Preventive and Precautionary measures
- To prepare the Emergency Preparedness Plan.

IV. METHODOLOGY

The following methodology are used in step by step procedure to do this project work, which are,

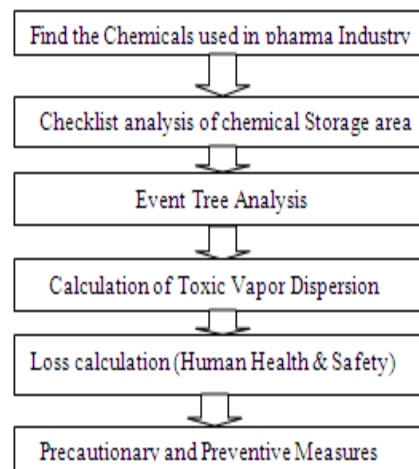


Fig.1 Flowchart For The Methodology of The Project. The above methodology helps in finishing this project successfully and quickly. In which, the first step is to know about the chemicals used in pharma industry. The second step is Checklist analysis where the needed data are gathered which are going to be used for further steps. At next step, to select a highly hazardous chemical, Toxicity Index Calculation is used to rank the chemicals based on the data collected from checklist.

After the selection of the hazardous chemical, the next step is to find out what is the next event going to happen if there is a release. For which, Event Tree Analysis (ETA) is used in this step. The next step after finding the final event from ETA is to find the how it is dispersed into atmosphere and how much distance it covered. It









can be easily found out using the ALOHA Dispersion Software.

The next step is human health and safety loss calculation using the distance found out by software and compensation amount gathered from law. The final step is to make the precautionary & preventive measures to avoid the toxic dispersion into atmosphere and the emergency preparedness should be prepared for what should be done during the toxic release [18-19].

V. HAZARD IDENTIFICATION

1. Hazardous Chemicals Used

Table No.1 List of hazardous chemical used in Pharma Industry

S.No	Chemical	TLV (in ppm)	IDLH (in ppm)	Hazards
1.	Chlorine Dioxide	0.1	10	
2.	Hydrogen Peroxide	1	75	
3.	Sulphuric acid	1	15	
4.	Methanol	200	2000	
5.	Sulphur Dioxide	2	100	
6.	Liquid oxygen	-	-	
7.	Sodium Chlorate	10	-	
8.	Caustic Lye	2	10	

In pharma industry lot of hazardous chemicals are used to prepare chemical products. In the below table the chemicals are listed with their TLV, IDLH and NFPA values. In NFPA value the blue numbers are for health hazard, red number is for fire and explosion hazard, white colour is for special hazards and yellow colour is for reactivity hazard.

2. Checklist Analysis

The next step of this project is Checklist analysis from which the data needed for this project can be gathered. Checklist is a type of informational job aid used to reduce failure by compensating for potential limits of human memory and attention. The checklist is one of the main tool available to assist in hazard identification. It is should be used for just one purpose. It is more effective if the questions can be answered by a simple 'yes' or 'no' but require some thought in formulating an answer.

It is one of the most simplistic tools of hazard identification is the checklist. Like a standard or a code of practice, a checklist is a means of passing on lessons learned from experience. It is impossible to envisage

high standards in hazard control unless this experience is effectively utilized. The checklist is one of the main tools available to assist in this.

Checklists are applicable to management systems in general and to a project throughout all its stages. Obviously the checklist must be appropriate to the stage of the project, starting with checklists of basic materials properties and process features, continuing on to checklists for detailed design and terminating with operations audit checklists.

3. Event Tree Analysis

After the chemical selection by using Toxicity Index numbering, what is the likelihood and possible event when there is a release of ClO₂. It can be done by using Event tree Analysis (ETA). An event tree analysis involves the development of the consequences of an event. It starts with a particular event such as power failure or ruptures of vessels and is developed from the bottom up. It is constructed by defining an initial event and the possible consequences which flow from this.

The initial event is usually placed on the left and branches are drawn to the right. The branches should be only the safety functions. When the event goes up it results success and if down results in failure of the safety function. The event tree analysis of chlorine dioxide leak from vessel, due to rupture. It is said as loss of containment and the safety function used are leak detector, manual shutdown and DCS automatic shut off which are shown below.

From these Event tree analyses, no safety function can hold of the toxic release. So when there is a release, it will quickly forms vapor and disperse into atmosphere as toxic vapor which can be hazardous to workers nearby. If the vapors escape out of industrial area, it will definitely affect the people nearby and upto certain distances based on the different criteria.

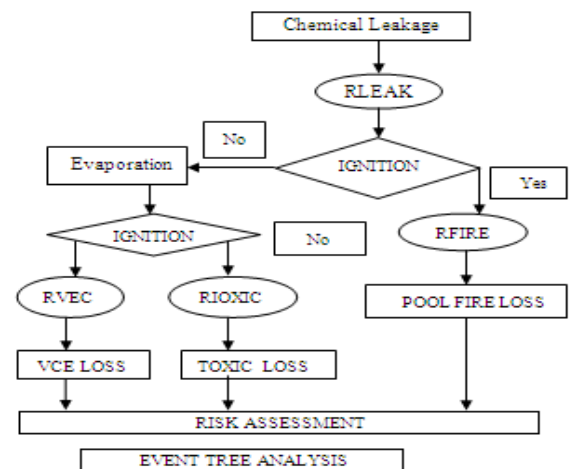


Fig.2 Flow Diagram of Event Tree Analysis.

VI. HUMAN HEALTH AND SAFETY LOSS CALCULATION

Human health and safety loss is the loss due to the occurrence of fatalities and/or injuries resulted from a failure of a system or subsystem. Human life resulting from an accident can be counted in terms of the number of people injured or killed when accidents occur.

The reference to 'people injured' by an accident is justifiable since, many times, it is not only the product users but also people who were near the scene are injured when an accident occurred. Injuries suffered may vary from light scratches to fatalities. A simple method to calculate the human health is by using damage radii and population density which is simply shown in fig.no: For toxic release calculations, the below three should be considered, which are:

- Possible death effects: number of people inside the damage radius to whom deaths could be induced. This radius corresponds to the ERPG-3 (Emergency Response Planning Guidelines) concentrations for toxic release.
- Possible injuries: Number of people inside the damage radius to whom injuries could be induced. This radius corresponds to the ERPG-2 concentration for toxic release.
- Possible annoyance: Number of people inside the damage radius that slight injuries, annoyance or other slight reversible effect could be induced. This corresponds to the ERPG-1 concentration for toxic release.

VII. RESULT AND SIMULATION

1. Population density:

Population density is defined as the number of people living in per square kilometer of that area/ district. Here the company is located at edge of pithampur. Therefore for the calculation we have to consider both population density by taking average of it.

- Population density of Indore District.
- Population density of Dhar District.
- Final Population density used for calculation: 5204 persons/km² (avg.)

2. Cost of injuries and life:

According to section. 2 of Public Liability Insurance Act 1991, the accident which cause death, injury, damage etc. liable to give relief by owner who used hazardous chemical. He should take one or more policies throughout the period of usage of hazardous chemical which should not be less than 50 cores. The other expenses for aforesaid are given in the below.

By using the above cost data and damage radius from dispersion, HHSL can be calculated. The final cost of HSSL is Rs. 9.44 cores (approx.) during day time and Rs. 8.93 cores (approx.) during night time. When

calculating the loss, the cost of death is taken from the law but the cost of value is costless where it can be said as the value of statistical life (VSL).

Table No 2 Compensation Amount according to Public Liability Act 1991

S.No.	Type of Damage/Injury	Compensation amount(Rs.)each
1.	Medical expenses only	12,500
2.	Fatal accidents (in case along with Medical expenses)	25,000 + 12,500
3.	Permanent partial disability & sickness	12,500
4.	Total permanent disability	25,000
5.	Temporary partial disability (at least 3 days hospitalized & above 16 yrs)	1,000 /person for 3 Months
6.	Property Damage	6,000

In India, the value of statistical life is Rs.10 lakhs. When the VSL is taken into account, the loss will be Rs.164.67 cores (approx.) during day time and Rs.164.16 cores (approx.) but in this project the compensation cost is based on the law.

And also, the company workers also inside the red zone which will cause more life loss, compensation cost should be considered and the experienced workers are one of the important asset of the company but the above said is not included. And there is also an indirect cost such as recruitment of new workers, experienced workers and training for them etc. The loss of reputation due to the accident is inevitable and irreparable which needs more time to change that bad reputation.

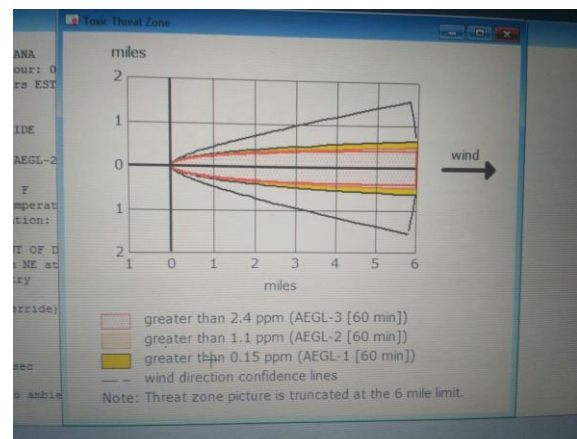
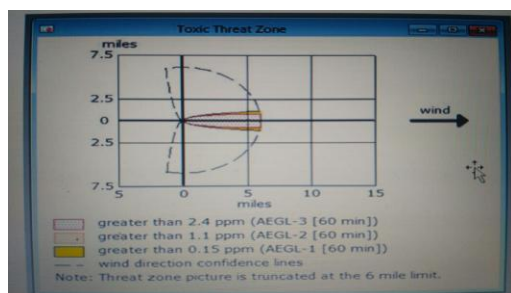


Fig.3 A. Aloha Software Wind Maximum Region. : 9718 persons/km²[11]



B. Area Covered.

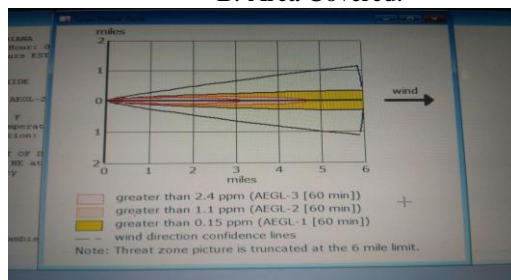
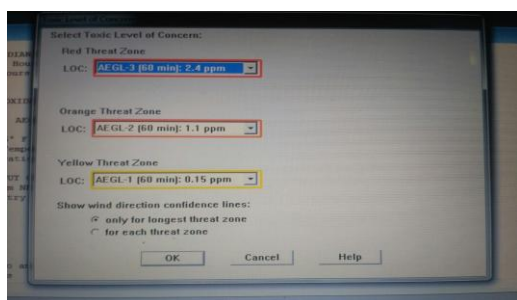


Fig.4 A. ALOHA Software wind minimum region.



B. Area covered different zone.

2. Precautionary measures- This type of accident cannot be controlled without effective precaution measures to avoid the dispersion into atmosphere. It can be controlled by diluting the dispersed gas. This can be done by using the same method while producing Chlorine dioxide solution in which the gaseous ClO₂ produced is scrubbed with water to make the ClO₂ solution. The same method is considered here but Spray curtains are going to be used because it is suitable to mitigate the risk connected to this accidental event.

The mixing and dispersion of dense gas clouds are often much slower than those of buoyant clouds and, consequently, it is desirable to increase their natural dispersion by enhancing the dilution rate. In this respect, spray curtains can represent an effective method to control the spreading of a cloud and mitigate the toxic effects.

The effectiveness of the barrier depends on the characteristics of the liquid solution and, particularly, on the reagent concentration. In here, the Chlorine dioxide can be easily soluble in water, sulfuric acid and alkalis. When comparing water with other two compounds,

make the water as a safe substance used in spray barrier. The spray barrier which works exactly like sprinkler system but here it dilutes the toxic vapor produced from the pool. The water droplets from the spray has affinity to attract the ClO₂ vapor. By this, the toxic vapor cannot be let into atmosphere. Spray barrier has to be constructed around the storage area at the dyke wall. It should cover all the sides to avoid the toxic vapor escape.

VIII. CONCLUSION

The consequences analysis of hazardous chemical Chlorine dioxide (ClO₂) release from the storage has been done in this project. For which, this project used Toxicity Index to rank the hazardous chemical with the data gathered from checklist. It resulted in Chlorine Dioxide (ClO₂) as rank 1st with Toxicity Index as 12.18. In Event Tree Analysis (ETA), the loss of containment of ClO₂ results in toxic dispersion into atmosphere and there is no safety function already available can't hold it. By using the ALOHA Software, this project can easily and quickly identify the threat and safe zones when there is a hazardous ClO₂ release. The final result of ALOHA software with alternate ERPG level for both day and night are 3.6 kms (ERPG 3 (RED) = 32ppm), 7.5 kms (ERPG 2 (ORANGE) = 10 ppm), 11 kms (ERPG 1 (YELLOW) = 5 ppm) & 3.6 kms (ERPG 3 (RED) = 32ppm), 6.9 kms (ERPG 2 (ORANGE) = 10 ppm), 9.9 kms (ERPG 1 (YELLOW) = 5 ppm) respectively. After the simulation, the losses incurred here Human Health and Safety Loss (HHSL) is considered and calculated as 9.44 crores (approx.) during day time and 8.93 crores (approx.) during night time and also the reputation of the company is lost. Spraybarrier is only the effective measures to avoid the ClO₂ dispersed into the atmosphere, this is one of the laboratory scale up method but in the coming years it will be implemented in every toxic storages with different substances used to neutralize the released chemical. Eventhough use of corrosion resistant Fibre glass Reinforced Plastic (FRP) tank, it still may fails due to ageing and not regular monitoring and low maintenance on FRP. For these, the action plan has to be made in which there is regular monitoring, inspection and maintenance have to be included. Emergency preparedness for the ClO₂ spill are given to act when there is such scenario to avoid confusion and delay to act because of unavailability of pre action plan. By implementing the spray barrier and following the precautionary and preparedness measures can avoid the major confusion and losses when there is a Chlorine dioxide release from the storage tank.

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