

“RESULTS AND DISCUSSION OF CHEMICAL HAZARD AND TOXICITY REDUCTION WITH PRODUCTION QUALITY IMPROVEMENT”

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ABSTRACT

In general, chemicals are very toxic. The handling of raw chemicals is hazardous for human existence from the first steps of the produce. In the pharmaceutical sector, this research has been carried out where the staff is subjected to hazards like chlorine dioxide, hydrogen peroxide, methanol etc. The physical and chemical properties of chemicals were tested. The second step is to take the checklist and then obtain the appropriate data to be used for additional measures. The Toxicity Index Measure is used to identify the product based on obtained data from the checklist in the next phase in the identification of a particularly harmful material. The next move would be to figure out what the next occurrence would be if the release happens after discovery of the dangerous chemical. In this stage, Event Tree Analysis (ETA) is used. Following the final ETA case, the fourth step is to find out how and how widely it is spread in the environment. The ALOHA dispersion program can be quickly elaborated. The pre-final step is the estimation of human health and protection damages dependent on technical distance and legal liability. The last move is to take precautionary and preventative steps in order to prevent chemical dispersion into the environment and plan the emergency management measures for the chemical release.

1. INTRODUCTION

Medilux Laboratories is manufacturer of high class best quality drugs intermediates and fine chemicals.

- It is an ISO 9001:2000 certified company.
- Head office of company is at Pithampur, Madhya Pradesh in India.
- Inception of company found in 1988 to earning the status of 100% export oriented unit.
- Choosing the right contract chemical manufacturer is a key business decision that is critical to the rapid and successful commercialization of drug products.

- It produces more than 85 different products and also provides customized solutions.

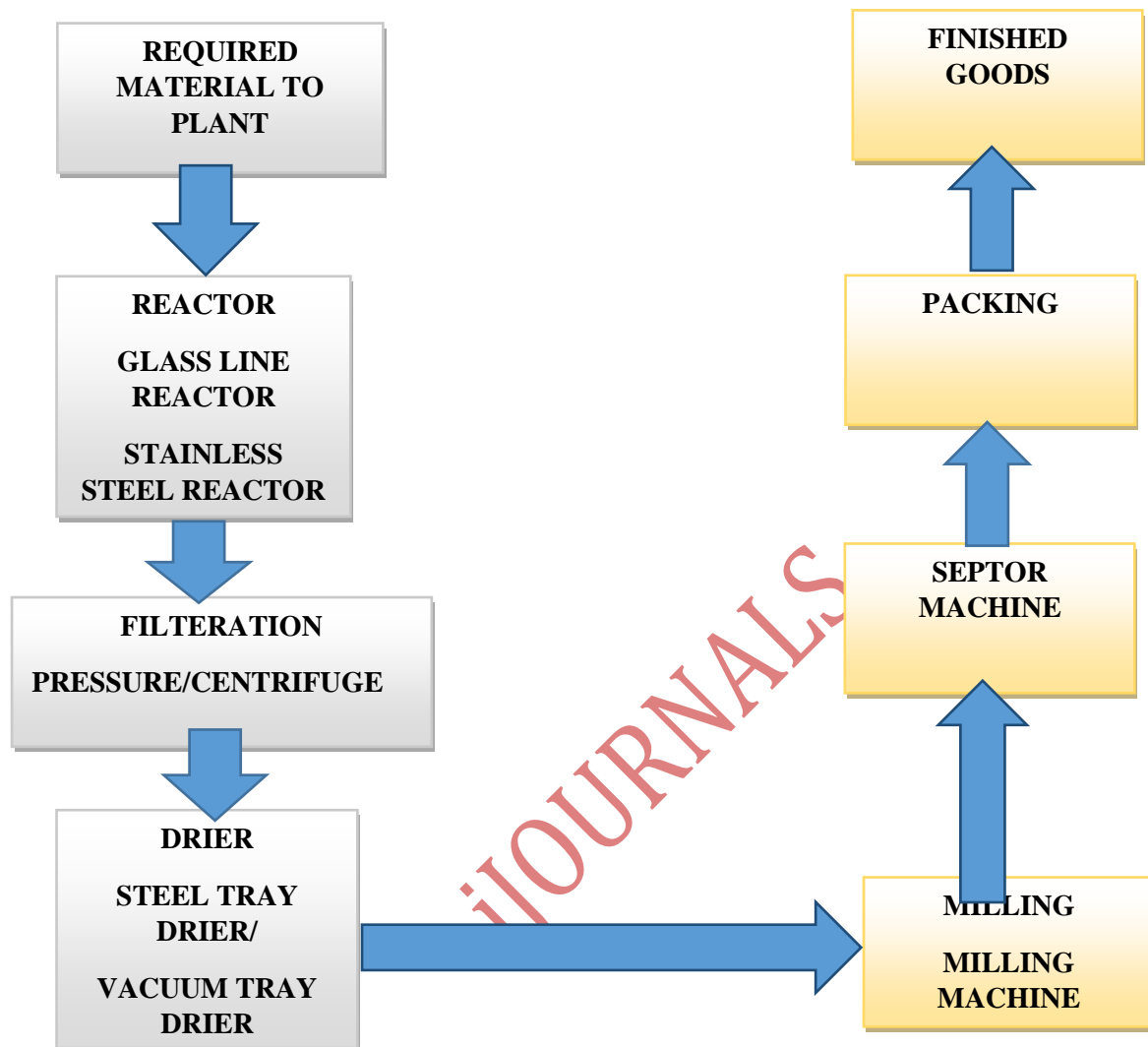


Fig 1 Process flow block diagram.

Accidents such as Bhopal tragedy in 1984 involved hazardous material releases constitute an important concern in industrial related risk assessment. They can lead to consequences of large magnitude since the hazardous cloud can spread widely across distances of kilometers and pose a hazard to both human health and the environment. Besides, such incidents in urban areas present an extremely hazardous scenario in terms of the magnitude of consequences, exacerbated by the high population densities present in these areas. In pharma industries and the process involves the use of various hazardous chemicals such as Methyl Alcohol, Chlorine dioxide, Hydrogen Peroxide, Sulfuric acid, Sulfur dioxide and it is tabulated in According to the Manufacture, Storage and Import of Hazardous Chemical Rules (MSIHCR), 1989, when there is a use of any hazardous chemical in industrial activity which either above or below the threshold quantity, the occupier must have to prevent such major accidents and to limit their consequences to persons and the environment. And the occupier of the factory with the help of concerned authority should prepare both Onsite and Offsite Emergency Plan and update it frequently by concerning the nature, extent and likely effects of possible major accidents. Severe

damage to human life and health caused by industrial accidents prompt orienting emergency management from simple post-event response to preventive preparedness.

The extent of the field of effect of the unintended release of a toxic material depends on a variety of factors pertaining to the modality of release being taken into account, the external circumstances (meteorological, geological, terrain form, etc.) and the material itself (physical characteristics and toxicity). Consequence estimation is a very time-consuming phase and is only done in very few situations, although certain solutions, for example reducing the measurement to the worst circumstances, are used in most implementations.

To assist in preparing emergency plan and evacuation procedure for the worst case scenarios and for quick calculation, dispersion modeling software is used which can calculate the maximum concentration and threat zone. This analysis can be used by emergency responders and other officials to help during emergency situations. This project is aimed to avoid the mass casualties and to reduce the cost for the damages such as human health and safety losses by hazardous chemical release from Pharma Industry.

QEEHS POLICY:

We at SPB committed to continually improve Quality, Environment, Energy, Occupational Health and Safety management systems with a view to promote:

1. Trust of customers and other stakeholders
2. Abatement of pollution
3. Efficient use of energy and other resources
4. Wellbeing of employees and safety of occupational workplace
5. Competence and effective participation of all employees and service providers and
6. Compliance of applicable legal and other requirements.

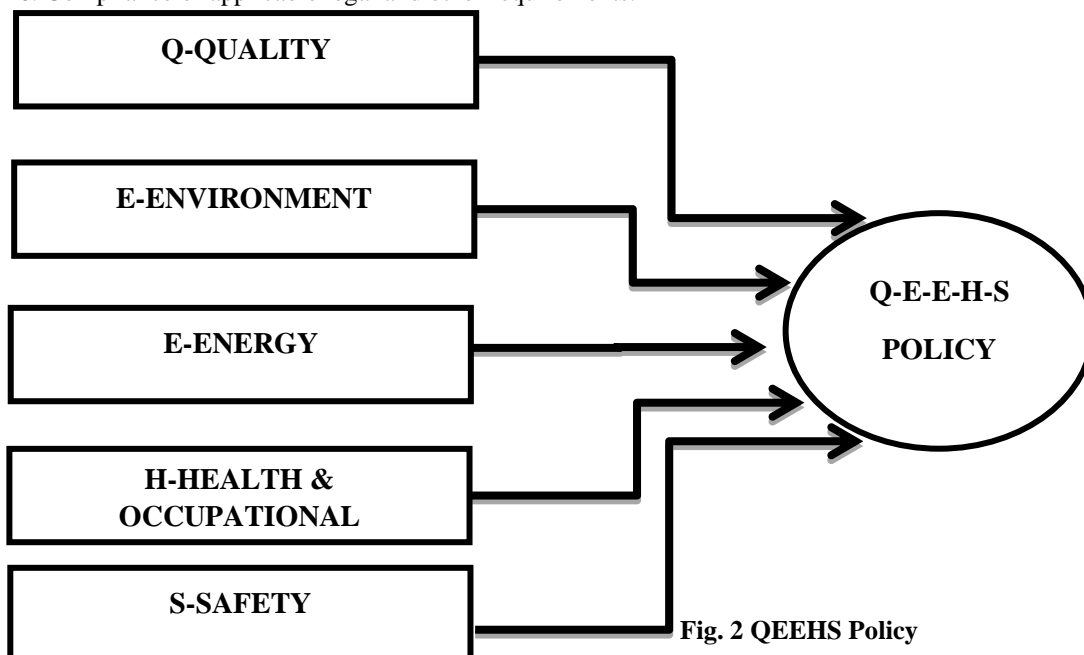


Fig. 2 QEEHS Policy

2. LITERATURE REVIEW

Hu Si (2012) et al: The QRA model includes the calculation of risk for leakage as well as indirect incidents in order to identify the likelihood and duration of those incidents. It also measures the range of influence to identify the people concerned and how much. Damage estimates include direct financial losses of employees, direct financial loss of resources and overall financial loss for quantitative analysis. Analysis of appropriate danger thresholds is carried out by matching expectations with measured hazards by graphs. By using these considerations, toxic release toxicity poses a high risk as opposed to fire and explosion. Once this was noticed, it was recommended that it should be abolished or reduced in an acceptable scope for regulation.

Juan A. Vilchez (2012) et al: Explained that each series would contribute to a final accident scenario whose occurrence varies from "no impact" (no repercussions for persons and property or marginal implications) to a "serious accident." The authors used the EC and CPR 18E marking in this paper to determine the exact probability of unexpected accidents. The investigator argued that this is more dangerous and that the likelihood and occurrence trees require urgent attention.

Perri Zeitz Ruckart (2012) et al: The data collected for chemical releases from the Hazardous Substances Emergency Events Surveillance (HSEES) system organized by U.S. EPA were collected to detect the significant difference between the use of chlorine and its derivatives usage. The production of paper involved 32.3 percent of the release of chlorine, resulting in 122 persons being injured (5.9 percent of all chlorine-release wounded). The proportion of complaints of GM issues and headache (12.2% respectively) was greater than the proportion of chlorine reported by hydrogen peroxide (8.1% and 3.1% respectively). Chlorine releases (26.2 percent) were more likely to be requested as evacuations relative to hydrogen peroxide releases (9.5 percent). Alternatives may minimize harmful exposure to some amounts instead of chlorine.

O. Sanguino (2013) et al: It claimed that the first step, and key, in consequence analysis is the estimation of release rates. 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.

Wilfried Sanchez (2018) et al the application of TIE (toxicity identification evaluation) approach which combines bioassays and chemical analysis, allowed to identify the androgenic compounds implicated in aquatic environment contamination such as androstenedione. Several effluents of domestic and industrial water treatment plants discharging into environment, exhibited also androgenic activities linked to the occurrence of various androgenic EDCs such as testosterone, dehydrotestosterone, androsterone, and trembolone.

G. Badri Narayanan (2018) et al extends the GTAP (Global Trade Analysis Project) framework to aid in the analysis of changes to public procurement policies. It develops a modeling framework to analyze the impact of trade policies on sustainable development in India. Sustainability has multiple dimensions, but we focus on four broad ones among them in this chapter: economic growth, food security, emissions, and inequality. Trade liberalization and integration among countries can lead to both enhancement and deviation from some of the Sustainable Development Goals.

Sarah Habran (2019) et al In response to the Walloon Environment and Health Program, the Scientific Institute of Public Services (ISSeP) developed an integrated approach of environmental exposure assessment in the Walloon region, Belgium. In parallel, a spatial web tool based on **GIS (Geographic Information System)** was developed to enable a flexible and weighted combination of the normalized indicators by computing the resulting composite index online. This tool designed for policy makers and experts eases the spatial analysis of results in order to identify geographic areas where hotspot exposures are a potential risk to human health. The next steps of this work aim to integrate more environmental indicators and some sociodemographic and health indicators in order to detect vulnerable populations.

Elson Silva Galvao (2020) et al As a start point, the knowledge of the main PM (Particulate Matter) contributors is fundamental. Receptor models are frequently used for the identification and apportionment of local sources, nevertheless, some features of these models must be considered. In this work, it is presented some study of cases showing some strengths of the **chemical mass balance model (CMB)**, such as to infer specific sources acting over specific locations in a same region, and its weaknesses for separating collinear sources.

3. METHODOLOGY

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

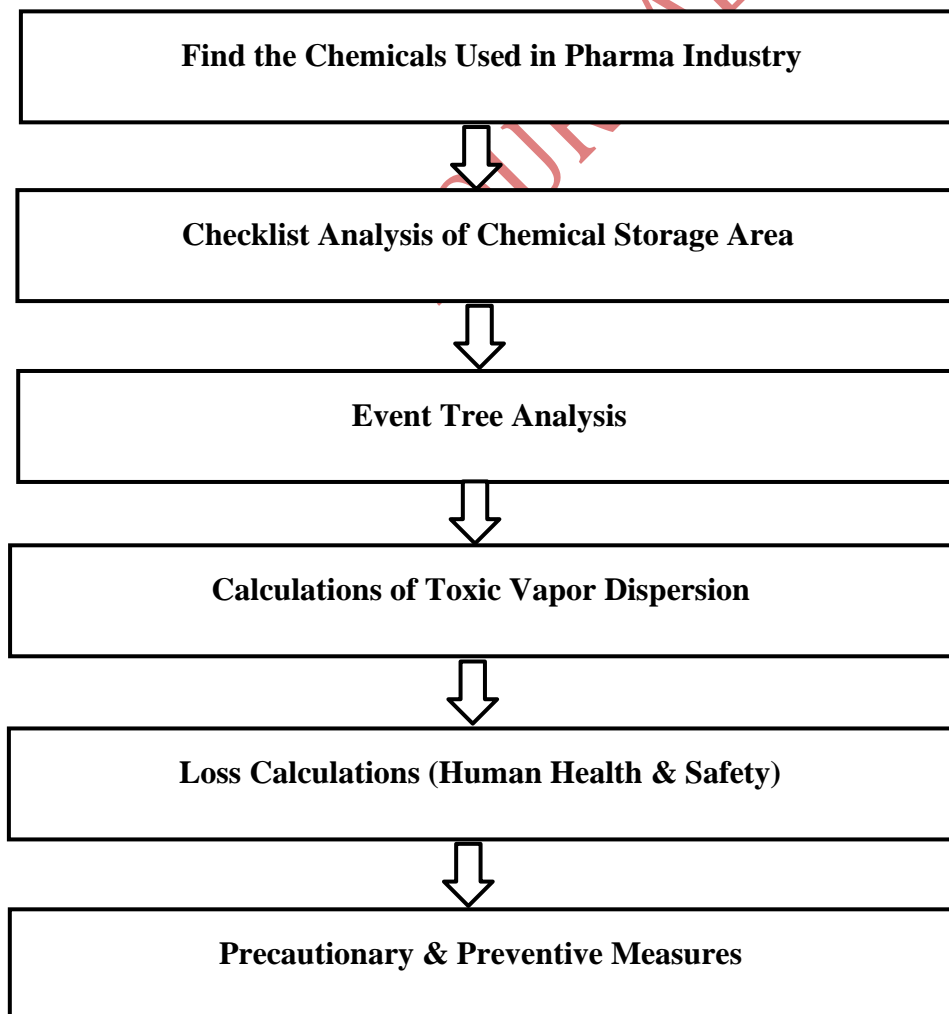


Fig 3 Flowchart for the Methodology of the Project

The above approaches lead to a effective and swift completion of this undertaking. The first step is to consider the chemicals used in the pharmaceutical industry. The second step is to review the checklist and obtain the appropriate details to be used for additional measures. The Toxicity Index Measure is used to identify the product based on obtained data from the checklist in the next phase in the identification of a particularly harmful material. The next move would be to figure out what the next occurrence would be if the release happens after discovery of the dangerous chemical. In this stage, Event Tree Analysis (ETA) is used. Following the final ETA case, the next step is to figure out how and how widely it is distributed through the environment. The ALOHA dispersion program can be quickly described. The next step is the estimation of human health and protection damages dependent on technical distance and legal liability. The last move is to take precautionary and preventative steps in order to prevent chemical dispersion into the environment and plan the emergency management measures for the chemical release.

4. INTRODUCTION ABOUT ALOHA SOFTWARE:

ALOHA (Aerial Locations of Hazardous Atmospheres) is the first software which is developed by US Environment Protection Agency (EPA) and National Oceanic and Atmospheric Administration (NOAA) to model how the released hazardous chemical vapors dispersed into the atmosphere. It is the part of CAMEO software suite, a system of software applications widely used to plan for and respond to chemical emergencies. It uses the Gaussian distribution for calculating the dispersion in atmosphere. The software also integrates Chemical database and a method to manage the data, air dispersion model and a mapping capability characteristics which it gets from CAMEO Chemicals which is the database of most of chemicals used for industrial purposes. It allows the user to estimate the downwind dispersion of a chemical cloud based on the toxicological/physical characteristics of the released chemical, atmospheric conditions and specific circumstances of the releases. ALOHA can estimate threat zones associated with several types of hazardous chemical releases, including toxic gas clouds, fires and explosions. Threat zones can be plotted on maps to display the location of other facilities storing hazardous materials and vulnerable locations such as hospitals, schools. ALOHA helps to make decision about the degree of hazard posed when there is a hazardous chemical release. The steps to work the ALOHA software is explained by below flowchart.

4.1 INPUT NEEDED FOR SOFTWARE SIMULATION:

To do a simulation in ALOHA software, this project needs the following things which are site data, chemical data, atmospheric data and source of release data.. It explained by simply taking up a scenario explained in section 4.5.1.

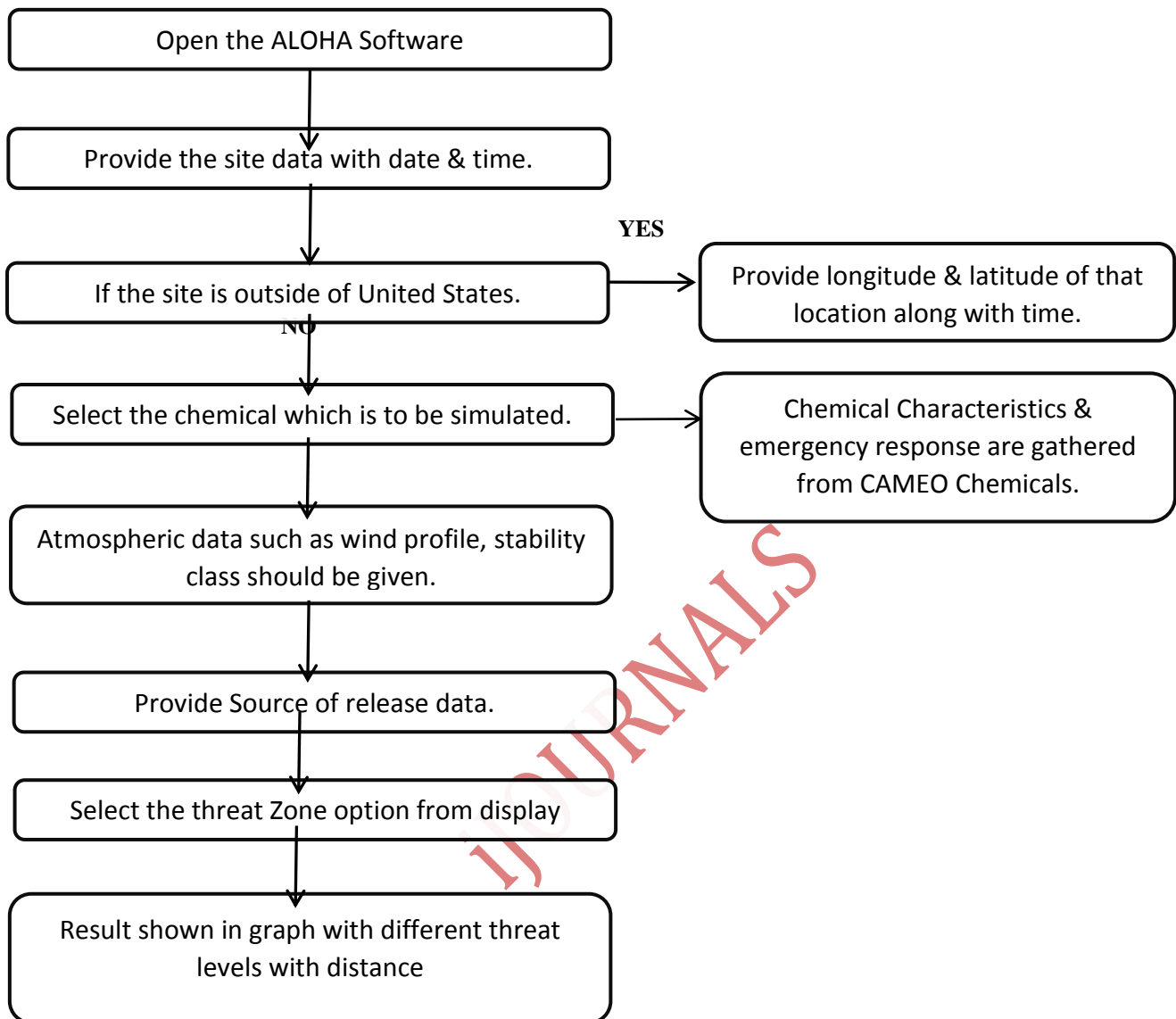


Fig 4.5.1: Flowchart for Working ALOHA S/W

5. RESULTS OF ALOHA SIMULATION:

The result from ALOHA showed that the release duration is 1 hour and then release rate of chemical is estimated around 1560 kgs/min. The ALOHA result showed that the results for all three threat zone, the dispersion is over 10.45 kms (6 miles) which are shown in the below figure. no: 10.3 & 10.4 and truncated to 10.45 kms in graphical representation. The above result is also same for during night time release.

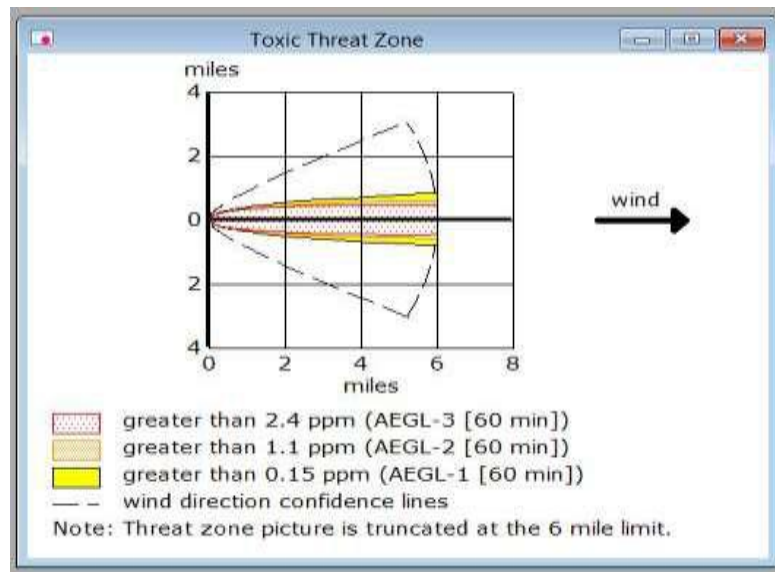


Fig.4 Release of Chlorine dioxide from the storage tank during day time.

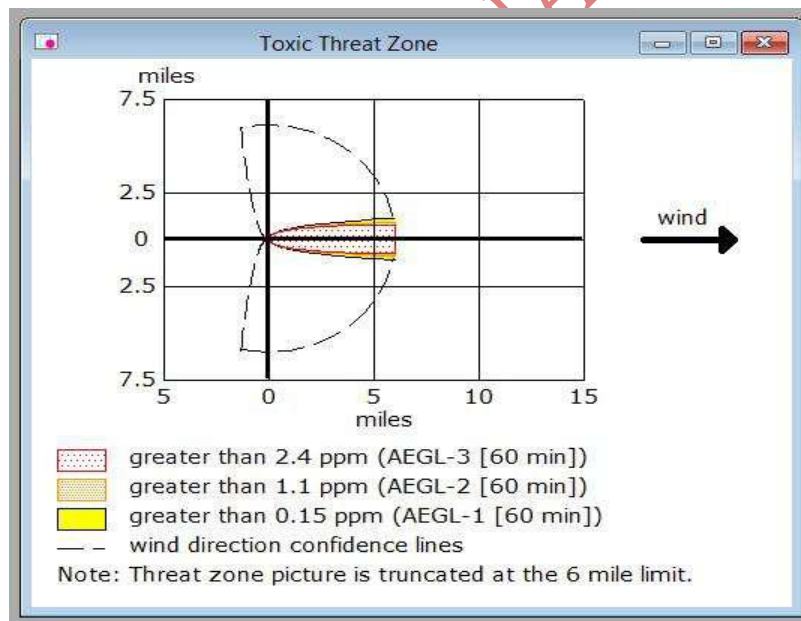


Fig.5 Release of Chlorine dioxide from the storage tank during night time.

From these results, there are some flaws found out in simulation. It does not show the each threat zone distance accurately which is very important for calculating threat zone to evacuate people and safe zones for evacuees. This is due to the AEGL values given for the ALOHA to simulate the dispersion but in which the ALOHA dispersion is limited to 6 miles so it simply shows the results are greater than 6 miles for all threat zones according to AEGL. There is a alternate method available to predict the results by using the same ALOHA software but using the different AEGL or ERPG level as said by AIHA based on the hierarchy of alternate concentration guidelines. By this, the modified guideline levels are ERPG 3 as LC 50, ERPG 2 as IDLH and

ERPG 1 as concentration which cause irritation to Respiratory systems which leads some problem to people when inhaled. By the above new guideline levels, the ALOHA simulate the same scenario.

5.1 Results of ALOHA Simulation with alternate data:

The result from ALOHA showed that the ClO₂ release duration is 1 hour and then release rate of ClO₂ chemical is estimated around 1560 kgs/min. The ALOHA result showed that all three threat zones are as 3.6 kms (ERPG 3 (RED) = 32ppm), 7.5 kms (ERPG 2 (ORANGE) = 10 ppm) and 11 kms (ERPG 1 (YELLOW) = 5 ppm) for day time which is shown in the figure No.: 10.4 in graphical representation.. And 3.6 kms (ERPG 3 (RED) = 32ppm), 6.9 kms (ERPG 2 (ORANGE) = 10 ppm), 9.9 kms (ERPG 1 (YELLOW) = 5 ppm) for night time which is shown in the below figure no: 10.5 in graphical representation. Persons in red zone will probably die due to pulmonary edema, persons in orange zone will probably have respiratory tract problem such as higher concentrations can cause inflammation in the upper respiratory tract, bronchial spasms and difficulty in breathing and leads to pulmonary edema when there is longer exposure and persons in yellow zone will probably have respiratory tract problems such as irritates the nose, throat, trachea and bronchi at very low concentrations (5ppm) resulting in breathlessness, wheezing and coughing because of the effects of ClO₂ release[15].

Table No: 1 Modified data used for the ALOHA simulation and the result.

Chlorine Di Oxide	Scenario 1	Scenario 2
TLV = 0.1 PPM	Release of ClO ₂ from storage tank during day-time. (fig 4.4)	Release of ClO ₂ from storage tank during night-time. (fig 4.5)
IDLH = 10PPM		
ATMOSPHERIC DATA :		
1. Wind Speed	3.5 m/s	2.5 m/s
2. Wind direction	NE	NE
3. Cloud cover	3	3
4. Air temperature	32 °C	28 °C
5. Stability Class	E	F
6. Relative Humidity	57%	61%
SOURCE STRENGTH :		
1. Leak type	Hole	Hole
2. Tank Diameter	4m	4m
3. Tank Length	11.9 m	11.9 m
4. Tank Volume	150 m ³	150 m ³
5. Internal Temperature	18.3 °C	18.3 °C
6. Chemical Mass in tank	80 %	80 %

7. Hole Diameter	50mm	50mm
8. Hole at a height in tank	10%	10%
9. Ground type	Concrete	Concrete
RESULT :		
1. Release Rate	1560 kgs/min	1560 kgs/min
FOR TOXIC :		
1. Red :	3.6 kms (ERPG 3= 32 PPM)	3.6 kms (ERPG 3= 32 PPM)
2. Orange	7.5 kms (ERPG 2= 10 PPM)	7.5 kms (ERPG 2= 10 PPM)
3. Yellow	11 kms (ERPG 1= 5 PPM)	11 kms (ERPG 1= 5 PPM)

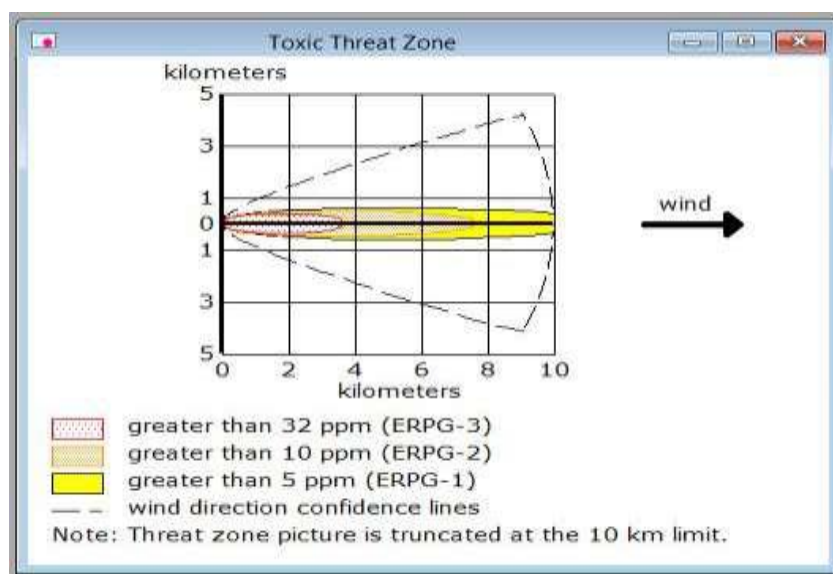


Fig.6 Release of Chlorine dioxide from the storage tank during day time with modified data.

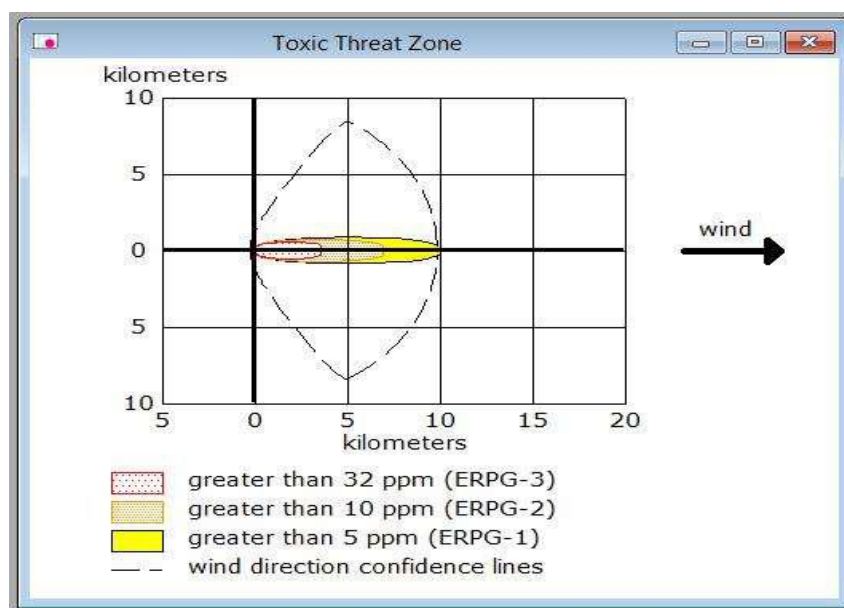


Fig. 7 Release of Chlorine dioxide from the storage tank during night time with modified data.

5.2 LOSS CALCULATION

After the calculation of threat zones distance from ALOHA software, the human health and safety loss should be calculated. Hosted and Stair suggested six categories of consequence values under four hazard/threat categories. They recommended a total of 11 loss categories. These are loss of life in major accidents, loss of life in other accidents, acute personal injury, chronic disease, reduced functionality, acute pollution on external environment, continuous pollution on external environment, material damage, and loss of production (could include deferred and damaged production), loss of data/information/knowledge, and loss of reputation as shown in fig no:6 . Out of the 11 loss categories, the first 9 categories relate to four targets namely, human, environment, material, and production and are contributing the major share of potential losses as reported globally. The remaining losses such as loss of data information and loss of reputation are difficult to quantify and not available in most of the cases. Finally, the losses can be broadly categorized into production loss, assets loss, human health and safety loss and environmental loss. In this project, only human health and safety loss is taken into account.

5.3 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 6 For toxic release calculations, the below three should be considered, which are

- 1. 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.
- 2. 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.
- 3. 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.

The human health and safety loss (HHSL) due to accident scenarios such as toxic release, explosion, and fire are estimated using the following relation,

$$\text{HHSL Toxic} = \{(\text{Cost of death 1 of } N1 \in \text{DA1}) + (\text{Cost of injury 2 of } N2 \in \text{DA2}) + (\text{Cost of injury 3 of } N3 \in \text{DA3})\}$$

Where,

DA1= damage radius of ERPG-3 concentration, DA2= damage radius of ERPG-2 concentration and DA3= damage radius of ERPG-1 concentration.

For the calculation of HHSL Toxic, the inputs needed are damage radius, cost of life, major injuries and minor injuries and population density.

6. 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 Di oxide (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 so 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. Spray barrier 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. Even though use of corrosion resistant Fiber 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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