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162. Study on the Accidental Release of Toxic Gases and its Consequences Using ALOHA Technique

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Abstract

The present study is based on; accidental release of hazardous gases and their consequence along with solutions to deal with the gravity of the situation. When an accident occurs regarding the leakage of toxic gasses, the residents present in the vicinity having major health issues. ALOHA (*Areal locations of hazardous atmospheres*) software is used to study the effects of accidental leaks and to defuse the situation which is the most suitable proactive approach. This study was carried out on two chemical manufacturing plants that using three toxic gas phosgene, chlorine and ammonia in their processes. *Public Exposure Guidelines* (PEGs), ERPG-2 (*Public exposure planning guideline*) and IDLH (*Immediately dangerous to life & health*) were used to compare the result obtained from the study. Indoor concentrations of toxic gasses were calculated, but the major focus of interest on outdoor concentrations. The result obtained from *Gaussian dispersion model* was much lower than the corresponding result of the heavy gas model. This study provides a gateway regarding the consequence evaluation and contingency planning in case of leakage of toxic gases.

Keywords: *Accidental release; toxic gases; Ammonia; Chlorine; Phosgene*

1. Introduction

Industries present in the country and their production show the economy of the country. Chemicals production and their use have environmental effects on human beings and the environment. A massive quantity of toxic substances used in various industries and these require careful handling of process chemicals. Leakage of hazardous chemicals could result in the dispersion of toxins into the adjoining environment that can lead to severe environmental problems and casualties[1, 2].

Like other countries, Industry in Pakistan is growing by leaps and bounds. There is an ever increasing concern regarding the safety of the chemicals used in industry. Hazards are associated with chemicals used at workplace**.** However, safety data sheets of chemicals are helpful to give information about the hazards associated with that particular chemical. Data given in material safety data sheet (MSDS) are widely used in simulation and accidental release of chemicals[3]. Proactive approach of risk assessment, analysis and risk management is used to find the probability of risk and rectify it before it affects the production process. HAZOP (Hazard and Operability Study) and FMEA (Failure modes and effects analysis) are the common techniques used to identify the existing hazards and risks [4].

The risk involved in any accidental establishment is not essential to be always severe. Risk is defined in three categories, acceptable, tolerable and unacceptable. For the risk to be acceptable it should be reasonable and kept as low as reasonably practicable i.e. the ALARP (As Low as Reasonably Practicable) principle. If the risk at hand comes out to be unacceptable and does not fulfil the principle of ALARP then there is a need of further control for reducing the risk to acceptable range. While dealing with a risk, individual risks and social concerns should be taken into account[5] .

A number of simulation software's are available which are used for the applications of safety analysis like EPI code, ALOHA, Phast and Safety etc. Commonly used software's are EPI code and ALOHA (Areal Locations of Hazardous Atmospheres), both estimates the rate of evaporation, evaporation rates from the pool of liquid chemicals spilled and then the subsequent dispersion into the atmosphere but they differ only the algorithm by which these software calculate the results[6-8]. The ALOHA software consisting of various dispersion models like Gaussian and heavy gas dispersion models have been applied for various pollutants i.e. gaseous pollutants [9-11]. This study was carried on three production plants located in a chemical complex in Pakistan with operations involving toxic chemicals without mentioning their names. Software is used to simulate the measure of threat zones and dispersion when chlorine, ammonia and phosgene (these are chosen because of their relatively massive use of these plants and higher concentrations present in the plant environment) are released from their storage tanks.

2. Materials and methods

In present study dispersion of hazardous gases was observed by using ALOHA software, with built-In Gaussian dispersion and heavy gas dispersion models[12]. The research work was carried out by using latest version of ALOHA 5.4.4 [13]. This simulation software was developed by the joint venture of the Emergency Response Division (ERD) of National Oceanic and Atmospheric Administration (NOAA) and Environmental Protection Agency (EPA). Its basic application lies during emergency cases especially during the accidental release of hazardous chemicals to provide emergency response and ultimately give the rough estimate of the danger to locality and Level of Concern (LOC). ALOHA deals with the human health related hazards e.g. effects on respiration system of humans by the exposure of toxic chemical gases and vapors and pressure waves from vapor cloud explosion [14].

Hazardous gases that are selected for this study with their corresponding boiling points and level of toxicity are depicted in table 1. Level of Concern (LOC) can be fully understood if we incorporate the Public Exposure Guidelines. Table 1 shows the public exposure guidelines (PEGs) namely (ERPG-2) Emergency Response Planning Guidelines and (IDLH) immediately dangerous to life and health [15, 16]. These two PEGs were selected because they are widely used by analysts now a day due to the easy availability of their data in the literature. The downwind distance was selected constant and the maximum outdoor and indoor concentrations are calculated at the selected downwind distance.

The data were collected from the industry-I, which produces urea fertilizer and Industry-II, which manufactures refrigeration cooling gases. Industry-I contains the storage tanks for ammonia and chlorine gases which are used in the upstream processes for urea production, whereas Industry-II contains the storage tank for phosgene gas. The concentration and diagrams of storage tanks are given in the Table 2. The accidental release from the storage tanks of the hazardous gases take place through a hole and these gases are in liquid form. It is also important to consider that ammonia should be in anhydrous form in its storage tank.

Overhead space of 10% is allocated to liquid gases for any expansion due to temperature effects. The boiling points (T_b) of these gases are lower than the ambient temperature (T_{amb}) i.e. $T_b < T_{amb}$. The hole is assumed to be taken in the bottom, hence the liquefied gas will flow into the liquid state under the force of gravity with maximum flow rate.

To calculate the effects of the chosen toxic gases in the atmosphere, one parameter is varied and other parameters remained constant. Maximum outdoor and indoor concentrations (ppm) are found by changing various parameters across a fixed downwind distance (D) with the assumption that there is just only the downwind that affects and crosswind effects are taken as zero. The parameters which were investigated and the following major assumptions were taken during the study

- Hole diameter was varied by keeping other parameters constant like wind speed, temperature, humidity and cloud amount or degree of cloud cover. The hole diameter was changed from 0.5cm to 5 cm in the case of ammonia whereas of chlorine and phosgene, it was changed from 0.25cm to 2.5cm.

- The wind speed is changed by keeping the rest of the parameter constant. It was also ensured that the wind speed selected remains constant with the Pasqual Stability Class. It was same for all the gases under study, i.e. from 2 m/s to 12m/s.

- The temperature was changed while the values of other parameters were kept fixed and the effects were observed on the maximum outdoor and indoor concentrations. Temperature values taken were 5 to 50 ^{o}C.

The investigation of parameters was done by using both calculation models present in ALOHA i.e. Gaussian dispersion method and heavy gas dispersion method so that we can compare the results obtained from both the models. The parameters which remained constant throughout the study are given in the Table 3.

3. Results and discussion

This study was based on hazardous gases, equally harmful for both human beings and the environment. Three types of analysis were made at each gas separately and the corresponding results are tabulated in each case. The concentration of these hazardous gases was taken after the release time of 60 minutes. The gases used in this research form only toxic cloud with no fire. Chlorine and phosgene are responsible for greenhouse effect whereas ammonia is not involved in any ozone depletion in stratosphere or any climatic change[17].

The research was focused on two public exposure guidelines, ERPG-2 and IDLH. ERPG-2 is that maximum airborne concentration of the chemical below which all individuals can be exposed to the chemical released for up to one hour and it will not cause or develop any permanent or serious health issue or any symptom that take away an individual’s ability to Figurant against the dangerous situation. The calculation of the impact areas has been made for each substance with reference to the toxic levels of gases in Table. 4. The results of parameters like air temperature, hole diameter and wind speed were analyzed by ALOHA software that can provide help to decision makers to adopt a proactive approach and prevent the number of people living in the vicinity.

3.1 Ammonia

Ammonia flashes into vapours readily and goes to the atmosphere when its temperature is above -33^{o}C which is its boiling point and it can cover distance of several Km in gaseous phase. Some specified models are present in literature to deal with such conditions as commonly used equations and methods are not consistent with the scenario given [18].

The parts of the environment which are mostly affected by the accidental release of ammonia are air, soil and water bodies (Table 4).

3.1.1 Effects of Hole Diameter

With the increase in hole diameter there is always an increase in the maximum outdoor and indoor concentration as shown in Table 5. In this study the hole is located in the bottom of the storage tank so the force of gravity is acting its maximum value. The discharge rate is directly proportional to the hole diameter. In the Gaussian dispersion model, the maximum outdoor concentration crosses the ERPG-2 when the hole diameter is 5 cm but it cannot approach the IDLH value. On the other hand, in heavy gas model, the maximum outdoor concentration approaches ERPG-2. When the hole diameter is merely 1.5cm and crosses the IDLH value when hole diameter is 2.5 cm.

The maximum outdoor and indoor concentrations are taken against the hole diameter by using two models, i.e. Gaussian dispersion and heavy gas model. The values are taken from the graphs obtained from the simulation done in ALOHA and results are shown in Table 5. In Gaussian dispersion model the outdoor concentration starts from 1.8 ppm that further increases by an increase in hole diameter and reaches at 175 ppm (5 cm hole diameter).Whereas in case of heavy gas model outdoor concentrations were in the range of 17.5 –1400 ppm with hole diameter 0.5-5 cm.

3.1.2 Effects of Wind Speed

By changing the wind speed the Pasqual stability classes changes to a suitable value accordingly. When the wind speed is 2 m/s then the Pasqual stability class is “B” which changes to “C” when the wind speed changes to 3 m/s. From a wind speed of 4 m/s to onward the Pasqual stability class remains “D”. The concentration values increase up to the wind speed of 4 m/s and after that its value start decreasing. In Gaussian dispersion model neither ERPG-2 nor IDLH values are reached (Table 6) whereas in the heavy gas model the maximum outdoor and indoor concentrations passes through both ERPG- 2 and IDLH values at 8m/s and 4 m/s respectively.

3.1.3 Effects of Temperature

The effect of an increase in temperature with the change in concentration is not complex, i.e. the maximum outdoor and indoor concentration increases with the rise in temperature (Table 7). Minor increase in concentration is observed in case of Gaussian dispersion model as compared to the heavy gas model. By using a Gaussian dispersion model, initially there is an abrupt change in concentration, then after the increase in concentration continues with a slower pace. In Gaussian dispersion model the concentration never approaches ERPG-2 and IDLH values, whereas in the heavy gas model the concentration is above ERPG-2 during the initial stage and it crosses the IDLH value at the temperature of 30 ^{o}C.

3.2 Chlorine

The major effected parts in an environment in the case of chlorine release are air and water as given in Table 4. When chlorine is exposed to soil, it might react with the components of soil to form chlorides.

3.2.1 Effects of Hole Diameter

The effect of hole diameter is same as discussed in the case of ammonia. The maximum outdoor and indoor concentration increases with the increase of hole diameter (Table 8). The maximum outdoor concentration crosses ERPG-2 on the diameter value of 1.25cm and IDLH on 2.25 respectively. On the other hand, in the heavy gas model, the ERPG-2 and IDLH values are crossed at the hole diameter value of 0.5 cm and 0.75 cm respectively.

3.1.2 Effects of Wind Speed

The effect of wind speed does not remain similar. Initially, it increases up to a certain level then it decreases progressively. It is clear from the table 9 that initially in Gaussian dispersion model the maximum outdoor concentration is above the ERPG-2 value and at the wind speed of 3 m/s it crosses the IDLH value. The concentration value increases up to wind speed of 4 m/s and then it start decreasing as shown in Table 9. Maximum outdoor concentration in the heavy gas model is initially far greater than the ERPG-2 and IDLH values.

A similar trend was observed just like the Gaussian dispersion model as after 4 m/s the value of concentration start decreasing, but the ultimate value of concentration obtained at a wind speed of 12 m/s was still much greater than IDLH value shown in Table 9.

3.1.3 Effects of Temperature

The maximum outdoor concentration increases with the increase in temperature as shown in Table 10. In Gaussian dispersion model, the concentration value reaches the ERPG-2 value of the temperature of 15^{o}C but never reaches its IDLH value even at 50^{o}C. On the other hand, the trend remains similar to the heavy gas model, but the initial value of concentration is too higher than the IDLH value.

3.3 Phosgene

Phosgene gas has wide industrial applications. It is used to make plastics, pesticides and as a refrigeration gas. The major parts of environment affected by accidental release of this gas are air and water bodies. There are minor effects on soil if the accidental release of phosgene gas takes place, but if the soil is wet, then there are chances that soil might get polluted (Table 4).

3.3.1 Effects of Hole Diameter

As usual, maximum outdoor concentration increases with increase in diameter. In Gaussian dispersion model, ERPG-2 and IDLH values were obtained at the hole diameter of 1 cm and 1.75 cm respectively. In the heavy gas model, the maximum outdoor concentration crosses its ERPG-2 and IDLH values at the diameter of 0.5 cm and 0.75 cm respectively. The concentration approaches 38 ppm when the hole diameter reaches its ultimate value, i.e. 2.5 cm (Table 11).

3.3.2 Effects of Wind Speed

With the increase in wind speed the initial concentration increases up to the wind speed of 4 m/s and then it falls down. In the Gaussian dispersion model (Table 12) the initial concentration at 2m/s is above the ERPG-2 and IDLH values i.e. 2.7 ppm as. On the other hand, in the heavy gas model, the initial concentration at the wind speed of 2 m/s is much above the ERPG-2 and IDLH value i.e. 25 ppm as shown in table 12.

3.3.3 Effects of Temperature

The increase in temperature results in increase of maximum outdoor concentration (Table 13). In Gaussian dispersion model, the concentration is higher than the ERPG-2 at the temperature of 5ºC i.e. 1.12 ppm, which then crosses the IDLH value at the temperature of 15ºC and reaches the concentration value of 2.1 ppm. On the other hand, in the heavy gas model, the initial concentration value is above the both ERPG-2 and IDLH value at the temperature of 5ºC i.e. 11 ppm. The concentrations at other values of temperature are shown in Table 13.

4. Conclusions

The results obtained from the heavy gas model were much higher than the corresponding Gaussian dispersion model results. This study emphasizes on the requirement of a thorough contingency plan in case of leakage:

- Emergency alarm specifically for accidental release should be activated. It must be taken into account that the people in the workplace and in the close proximity should be aware of the specific alarm.
- People should start evacuation the affected area immediately after the leakage is observed.
- When the concentration reaches ERPG-2 value people should be removed from the workplace at least.
- The rescue team should evacuate the entire area which is under the threat of hazardous gas and the specialist team dealing with such kind of disaster should be sent to mitigate the effects of the release.
- Finally, the industries which are dealing with dangerous gases should incorporate ALOHA in their safety program with the necessary safety precautions to be taken during the situation of accidental release.

Table 1: Selected hazardous gases with their respective boiling point and toxicity

Chemicals Selected	Tb (ºC)	Molecular Mass (Kg/Kgmol)	ERPG- 2 (ppm)	IDLH (ppm)
Ammonia	-33	17.03	150	300
Chlorine	-34	68.91	3	10
Phosgene	8.3	98.92	0.5	2

Table 2: Configuration of storage tanks and their specifications

Hazardous Gases	Shape of Storage Tanks	Diameter (m)	Length n)	Actual Volume (m^3)	Volume Used (m^3)
Ammonia	Spherical	8	-	268	241
Chlorine	Cylindrical	4	9	113	102
Phosgene	Cylindrical	4	9	113	102

Table 3: Parameters with values remained constant throughout Study

Parameters	Value
Wind Direction	ESE
Ground Roughness	Urban or Forest
Cloud Cover	Partial
Inversion Height	No
Humidity	Medium
Liquefied Gas Volume	90% of Tank Volume
Leakage Position	Bottom of the Tank
Downwind Distance (D)	1000 m
Crosswind Distance (W)	0 m

Table 4: Environmental compartments affected by evaluated substa

Dangerous Substances	Environmental Compartments		
	Air	Water	Soil
Ammonia	+	+	-
Chlorine	+	+	-
Phosgene	+	+	-
LPG	+	-	-
Gasoline	+	+	+

Table 5: Effects of hole diameter on maximum outdoor and Indoor concentrations (ppm)

	Gaussian Dispersion Model Results		Heavy Gas Model Results	
Hole Diameter (cm)	Max. Outdoor Conc. (ppm)	Max. Indoor Conc. (ppm)	Max. Outdoor Conc. (ppm)	Max. Indoor Conc. (ppm)
0.5	1.8	1.4	17.5	13
1	7	5.5	65	53
1.5	16	13	150	120
2	29	21	280	225
2.5	42	32	420	340
3	63	50	600	490
3.5	86	70	800	640
4	120	80	1000	770
4.5	145	100	1200	900
5	175	140	1400	1000

Table 6: Effects of wind speed on the maximum outdoor and indoor concentrations (ppm)

	Gaussian Dispersion Model Results		Heavy Gas Model Results	
Wind Speed (m/s)	Max. Outdoor Conc. (ppm)	Max. Indoor Conc. (ppm)	Max. Outdoor Conc. (ppm)	Max. Indoor Conc. (ppm)
2	28	23	270	205
3	45	38	280	210
4	76	62	300	225
5	62	52	240	185
6	51	43	205	175
7	45	37	180	155
8	40	32	160	130
9	34	27	147	110
10	32	26	130	100
11	28	24	120	90
12	26	22	110	80

Table 7: Effects of temperature on the maximum outdoor and indoor concentrations (ppm)

	Gaussian Dispersion Model Results		Heavy Gas Model Results	
Temperature (ºC)	Max. Outdoor Conc. (ppm)	Max. Indoor Conc. (ppm)	Max. Outdoor Conc. (ppm)	Max. Indoor Conc. (ppm)
5	18	14	180	150
10	22	17	200	165
15	24	18	220	190
20	26	20	250	205
25	29	23	280	220
30	31	25	300	250
35	34	27	320	280
40	38	29	345	300
45	41	31	380	310
50	44	33	410	330

Table 8: Effects of hole diameter on the maximum outdoor and indoor concentrations (ppm)

	Gaussian Dispersion Model Results		Heavy Gas Model Results	
Hole Diameter (cm)	**Max. Outdoor Conc. (ppm)**	**Max. Indoor Conc. (ppm)**	**Max. Outdoor Conc. (ppm)**	**Max. Indoor Conc. (ppm)**
0.25	0.15	0.12	1.3	1.1
0.5	0.6	0.42	4.2	4.2
0.75	1.35	1.1	10	10
1	2.3	1.8	17	17
1.25	3.8	3	26	26
1.5	5.3	4.2	35	35
1.75	7.2	5.8	48	48
2	9.5	7.8	65	65
2.25	13	10	80	80
2.5	15	12	95	95

Table 9: Effects of wind speed on the maximum outdoor and indoor concentrations

	Gaussian Dispersion Model Results		Heavy Gas Model Results	
Wind Speed (m/s)	**Max. Outdoor Conc. (ppm)**	**Max. Indoor Conc. (ppm)**	**Max. Outdoor Conc. (ppm)**	**Max. Indoor Conc. (ppm)**
2	9.5	7.3	85	65
3	16	13	90	67
4	25	21	95	70
5	21	18	80	60
6	17.5	14	68	55
7	15	12	6o	48
8	13	11	55	40
9	12	10	48	39
10	11	9	43	37
11	9	7.8	41	33
12	8.5	7	37	3o

Table 10: Effects of Temperature on the maximum outdoor and indoor concentrations (ppm)

	Gaussian Dispersion Model Results		Heavy Gas Model Results	
Temperature (ºC)	**Max. Outdoor Conc. (ppm)**	**Max. Indoor Conc. (ppm)**	**Max. Outdoor Conc. (ppm)**	**Max. Indoor Conc. (ppm)**
5	2.5	1.8	24	17
10	2.8	2.1	26	19
15	3	2.3	28	21
20	3.3	2.8	31	23
25	3.5	3	34	26
30	3.9	3.2	36	27
35	4.1	3.3	39	28
40	4.5	3.5	41	31
45	4.9	3.7	44	34
50	5.2	4.2	48	37

Table 11: Effects of hole diameter on the maximum outdoor and indoor concentrations (ppm)

	Gaussian Dispersion Model Results		Heavy Gas Model Results	
Hole Diameter (cm)	**Max. Outdoor Conc. (ppm)**	**Max. Indoor Conc. (ppm)**	**Max. Outdoor Conc. (ppm)**	**Max. Indoor Conc. (ppm)**
0.25	0.042	0.032	0.4	0.3
0.5	0.18	0.13	1.6	1.3
0.75	0.39	0.31	3.5	2.7
1	0.68	0.57	6.1	4.2
1.25	1.1	0.8	10	7.7
1.5	1.51	1.3	17	12
1.75	2.1	1.8	18.5	14
2	2.8	2.2	25	17
2.25	3.4	2.8	31	25
2.5	4.2	3.7	38	29