7.1 HAZARD ANALYSIS AND RISK ASSESSMENT

Introduction:

Industrial plants deal with materials, which are generally hazardous in nature by virtue of their intrinsic chemical properties or their operating temperatures or pressures or a combination of these. Fire, explosion, toxic release or combinations of these are the hazards associated with industrial plants using hazardous chemicals. More comprehensive, systematic and sophisticated methods of **Safety Engineering,** such as, **Hazard Analysis** and **Quantitative Risk Assessment** have now been developed to improve upon the integrity, reliability and safety of industrial plants. The primary emphasis in safety engineering is to reduce risk to human life, property and environment. Some of the more important methods used to achieve this are:

Quantitative Risk Analysis: Provides a relative measure of the likelihood and severity of various possible hazardous events by critically examining the plant process and design.

Work Safety Analysis: The technique discerns whether the plant layout and operating procedures in practice have any inherent infirmities.

Safety Audit: Takes a careful look at plant operating conditions, work practices and work environments to detect unsafe conditions. Together, these three broad tools attempt to minimize the chances of accidents occurring. Yet, there always exists, no matter how remote, probability of occurrence of a major accident. If the accident involves highly hazardous chemicals in sufficiently large quantities, the consequences may be serious to the plant, to surrounding areas and the populations residing therein.

M/s Popular Chemical Manufactures & Supplies (Karnataka) proposes project for manufacturing technical grade Pesticides at Survey No. 380, Karagada village, Belur Tehsil, Hassan District (Karnataka)

Key issues in Risk Assessment (RA) of the proposed project are discussed in this chapter. The RA is a document and need to be updated whenever there are changes in operations, equipment or procedures.

Key Definitions:

The terminologies used in this Risk Assessment (RA) study are defined below.

A. Consequence: A result of a particular action or situation, often one that is bad or not convenient. Also called Magnitude or size of damage or loss. In terms of health and safety, it is the degree of harm that could be caused to the people exposed to hazard, the potential severity of injuries or ill health, and/or the number of people who could be potentially affected. Consequence of hazard involved the human safety criteria as well as financial loss due to production, incurred costs due to repairs/replacement, environmental impacts and public outrage.

B. Disaster: A catastrophic consequence of a major emergency/accident that leads to not only extensive damage to life and property, but also disrupts all normal human activity for a significant period of time and requires a major national and/or international effort for rescue and rehabilitation of those affected.

C. Emergency: A serious, unexpected, and often dangerous situation requiring immediate action. An emergency is a situation that poses an immediate risk to health, life, property, or environment. Most emergencies require urgent intervention to prevent a worsening of the situation, although in some situations, mitigation may not be possible, and agencies may only be able to offer palliative care for the aftermath.

D. Hazard: A hazard is a situation that poses a level of threat to life, health, property, or environment. Most hazards are dormant or potential, with only a theoretical risk of harm; however, once a hazard becomes "active", it can create an emergency. A hazardous situation that has come to pass is called an incident. Hazard and possibility interact together to create risk.

E. Immediately Dangerous to life and health (IDLH): It represents the maximum concentration of a chemical from which, in the event of respiratory failure, one could escape within 30 minutes without a respirator and without experiencing any escape/ impairing (e.g. severe irritation) or irreversible health effects.

F. Lethal Concentration Low (LCLo): It is the lowest concentration of a material in air, other that LC50, which has been reported to cause death in human or animals.

G. Risk: It is a Combination of the likelihood of a specific unwanted event and the potential consequences, if it occurs. Generally, risk is a product of frequency of the likely hood of the unwanted event and the consequence (degree of damage) due to the event.

H. Risk Assessment: A process that involves estimation and measurement of risk to determine priorities and to enable identification of appropriate level of risk treatment (used also to describe the overall process of risk management).

I. Risk Control: Risk control is the method by which firms evaluate potential losses and take action to reduce or eliminate such threats. Risk control is a technique that utilizes findings from risk assessments, and implementing changes to reduce risk in the industries.

J. Risk Management: Overall description of the steps taken to manage risk, by identifying hazards and implementing controls in the workplace. There are T's of risk management.

- **Tolerate** – low level of risk which can be live with.
- **Treat –** Take measure to reduce the risk to make it tolerable e.g. Use of PPE.
- **Transfer –** Change the location or transfer the process to some other who can take a risk and carry out the activity**.** E.g. Many advanced countries are getting the operations executed which is banned in their country by law**.**
- **Terminate-** Drop the operation or do not carry the activity where very high risk is involved . E. g. Online repairs on high voltage line.

K. Risk Rating: The category, level, or risk assigned following risk assessment (e.g. High, Medium, or Low).

L. Threshold Limit Value (TLV): it is the permitted level of exposure for a given period on a weighted average basis (usually 8 hrs for 5 days in a week).

M. Short Time Exposure Limit (STEL): it is the permitted short-term exposure limit usually for a 15 minutes exposure.

N. Toxic Concentration Low (TCLo): It is the lowest concentration of a material in air, to which humans or animals have been exposed for any given period of time that has produced a toxic effect in humans or produced carcinogenic, neoplastigenic or tetratogenic effect in humans or animals.

7.3 METHODOLOGY FOR RISK ASSESSMENT:

The scope of work includes site inspection, hazard identification, selection of potential loss scenarios, and simulation of release source model on DNV's PHAST Professional consequence analysis and plotting of Damage contour on site map in order to take strategic decision to

mitigate/minimize the level of risk to the facility and to the community. The steps undertaken to carry out Risk Assessment for the proposed increased capacity are described in subsequent sections.

7.3.1 CAS Development Procedure

As a first step towards risk assessment it is required to identify the selected scenarios based on available information about Scenario development for potential Maximum Credible Loss Scenarios (MCLS). MCLS' selected are based on the findings of the HAZOP and HAZID study.

7.3.2 Introduction:

Toxic Gas Scenarios

These include: Bursting of a toxic gas container under pressure causing a puff of toxic gas. Leak from a major pipeline of gas leading to a plume scenario of toxic gas.

7.3.3 Toxic Liquid Scenario :

These include Flash vaporization scenarios for toxic liquids stored above their atmospheric boiling point, causing a puff dispersion scenario.Formation and spill pool evaporation scenarios due to substrate heat conduction including first minute rapid evaporation, followed by steady state pool evaporation.

7.3.4 Flammable Gas Scenarios:

These include: Bursting of a flammable gas container under pressure causing a gas puff. Leak from a major pipeline of gas leading to a plume scenario of flammable gas.

7.3.5 Flammable Liquid Scenarios:

These include: Flash vaporization scenarios for flammable liquids stored above their atmospheric boiling point (BP) causing a puff scenario.

Pool formation and spill pool evaporation scenarios due to substrate heat conduction including first minute rapid evaporation, followed by steady state pool evaporation.

7.3.6 Secondary Scenarios for Flammable Liquids & Gases:

These may include (after containment loss of the liquid / gas): No ignition of puff, leading to puff dispersion. No ignition, causing dispersion of pool evaporation.

Immediate ignition of puff, causing fire ball scenario. Ignition of spill pool, causing pool fire. Delayed ignition of the puff, causing a VCE (Vapor Cloud Explosion), flash back fire ('flash fire') and pool fire.

7.3.7 BLEVE Scenarios:

These include: Boiling Liquid Evaporating Vapor Explosion (BLEVE) scenarios for flammable liquid storages getting engulfed by fire, getting over pressurized, vessel bursting and flash vaporization and explosion. The scope of work includes hazard identification, risk assessment and ranking, resulting in treatment controls and action plans.

7.4 RISK ASSESSMENT APPROACH

The risk assessment levels are generally consistent with the practices encountered through various assignments for medium and large chemical complexes. The brief outline approach is given below:

7.4.1 Level 1: Hazard Identification - Hazard identification includes:

Study of Safety Issues Pertaining to the Project

- Study of process and engineering, operational information including safety concepts used in design of equipment and storages.
- Listing of hazardous inventory and identification of key hazardous substances to be used.
- Preliminary identification of hazardous sections of the plant and that of storage with recourse to fire and explosion index for these units.
- Analysis of major inventories in process and storage for identification of major hazardous locations of the plant with recourse to "Manufacture, Storage and Import of Hazardous Chemicals Rules, 1989".
- Consultation with the personnel, who carry out or are likely to carry out the jobs.
- Delineation of the vulnerable operations.
- Maximum Credible Accident (MCA) Analysis for construction and operation and maintenance hazards.
- Past history of accidents and near misses, at an industry level.
- The expected outcome of this study will be identification of hazard prone operations and estimation of maximum damages, distances based on probable accident/release scenarios.

Identification of Hazard Scenarios

Identification of scenarios that can cause damage to life and property within the plant premises as well as in surrounding areas.

7.4.2 Level 2: Risk Assessment and Evaluation:

Risk Assessment

As defined in foregoing paragraph, the risk is a function of likelihood and consequence.

Likelihood is the chance that the hazard might occur. Since the risk of any hazard is dependent upon the chance that it will occur (likelihood), and the impact of an occurrence (consequence).

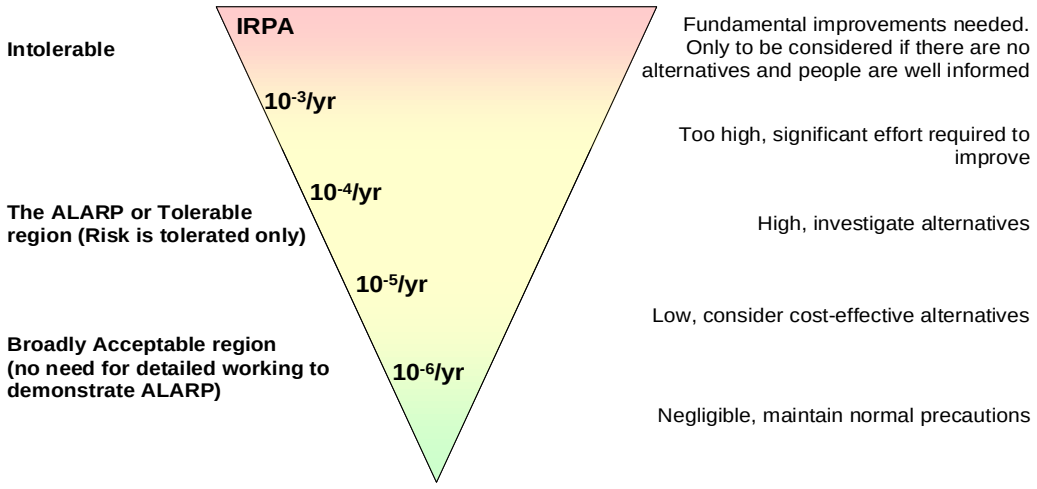
Risk Score = Likelihood x Consequence

In some cases personnel are only exposed to the hazard for part of the time. Hence, a more detailed analysis of the risk ranking can be carried out, by taking exposure (% time personnel are present) and probability (chance that they will be harmed) into consideration. Thus:

Risk Score = (Probability x Exposure) x Consequence

The values used for likelihood, consequence, exposure or probability need to be agreed to by the risk assessment team, and there is an element of professional judgment in exercising these choices.

IRPA (Individual Risk per Annum)



Note: A risk of 10 per million per year, or 10-5/Year, effectively means that any person standing at a point of this level of risk would have a 1 in 100 000 chance of being fatally injured per year.

(ALARP – As low as Reasonably practicable/possible)

7.4.3 Level 3: Treatment Controls and Action Plans

Treatment Controls

After examining the high priority risks, a prime consideration is given to the potential to reduce or eliminate the risk by using the hierarchy of controls. This assists in establishing methods to reduce risk. From experience, the effectiveness of each method is given as a percentage after each of the control descriptions. The desirability of control plans (with reducing effectiveness) is as follows

- Elimination: Remove step to eliminate the hazard completely.
- Substitution: Replace with less hazardous material, substance or process.
- Separation: Isolate hazard from person by guarding, space or time separation.
- Administration: Adjusting the time or conditions of risk exposures.

Training: Increasing awareness, improving skills and making tasks less hazardous to persons involved.

Personal protective equipment: Used as the last resort, appropriately designed and properly fitted equipment, where other controls are not practicable.

Control measures can reduce either the likelihood or consequence of the event or both.

Depending on the level of reduction of the hazard, there could still be a residual risk that needs to be monitored so that a secondary prevention process can be initiated when trigger points are reached.

Action Plans

The team should develop an action plan recommending actions, responsibilities and when it should be completed. The proposed action plan is required to be put forward to the decision making authority and reviewed, if necessary, before taking a final decision to proceed.

7.4.4 Level 4: Development of Disaster Management Plan

The suggested DMP is organized in a Plan, Do, Check, Review (PDCR) cycle to enable its effective implementation.

7.5 PHYSICAL & TOXICOLOGICAL PROPERTIES OF CHEMICALS:

11 chemicals (raw material) will be used in proposed project manufacturing of technical grade pesticides at plot No. 546/A, B elure industrial area Dharwad, Karnataka. The details of physical and toxicological properties are given in ***Table 7.1***

Table 7.2: Physical and Toxicological Properties of Chemicals

Sr. No.	Chemical Name	Quantity Cons. /Prod. (MT/ month)	Physical Properties				Toxicity					Lower Limit (LEL) & Upper Limit (UEL)	Toxic category as per NFPA	Hazardous according to MSIHC Rules, 2000
			Physical State	Flash Point	Auto ignition Temp.	Boiling/ Melting Point	Oral LD50 (mg/kg)	Dermal LD50 (mg/kg)	Inhalation LC50 (mg/m^3)	TWA (mg/m^3)	TLV mg/m^3			
	Physical & Toxicological Properties of the products													
1.	Aluminum Phosphide	500 MTA	Solid	NA	> 620^0C	**B.P: NA** **M.P:** > 1000º C	25 mg/kg (Rat)	1852.83 mg/kg (rat)	38.945 ppm (rat)	The product liberates Phosphine gas and its TWA is 0.3 PPM & STEL is 1 ppm.		**LEL**: 1.8%	2 Phosphine gas 4.	Schedule I, part II, Item No. 24
2.	Zinc Phosphide	250 MTA	Solid Black powder / Granul	NA	NA	**B.P: 1100**°C **M.P:** 420 °C	910 mg/kg	>2000 mg/kg	NA	0.3 mg/m^3	NA	NA	4	NA

			es											
3.	Phosphoric acid 85% as a byproduct	150 MTA	Viscous liquid	NA	NA	**BP –** 158 °C **MP** – 21 °C	1530 mg/kg Acute	2740 mg/kg Acute	850 mg/litre	1 mg/m^3	3 mg/m^3 STEL	NA	3	Schedule-1 Part II item No 497
	Physical & Toxicological Properties of the raw materials													
4.	Aluminum Powder	35	Powder	Powder is highly flammable	400^0 C	**B.P:** >999^0 C **M.P:** 660^0 C	2000 mg/kg (rat)	NA	>888 mg/l (rat)	It can burn skin *TWA & TLV: NA*		Aluminium dust is explosive.	1	Schedule I, part II, Item No. 19
5.	White phosphorus	50.25	solid	NA	30^0 C	**B.P:** 281^{0}C **M.P:** 44^0 C	3.03 mg/kg (Rat)	100 mg/kg (Rat)	4.3 mg/L (1 hr-Rat)	0.1 mg/m^3	NA	NA	4, extremely toxic as LD50 is 3.03	Schedule I, part I Item No.

													mg/kg	503
6.	Paraffin wax	2.9	Solid	**C.C:** 199° C **O.C:** 235° C	245°C	**B.P:** NA **M.P:** 47^{0} C	5000 mg/kg (Rat)	> 3600 mg/kg (Rabbit)	NA	2 mg/m^{3}	NA	NA	NA	No
7.	Urea	4.20	Solid	NA	NA	**B.P:** Decomposes 133^{0} C **M.P:**131-135^{0} C	8471 mg/kg (rat)	NA	NA	10 mg/m^{3}	NA	NA	2	NO
8.	Ammonium Carbamate	19.50	Divided Solid	NA	NA	**B.P: NA** **M.P: 140^{0}** C, sublimes	681 to 1470 mg/kg (Rat)	> 2000 mg/kg (Rat)	10 mg/m^{3}	10 mg/m^{3}	NA	UEL - 25% LEL - 16%	2	Schedule I, part II, Item No. 31

9.	Zinc Stearate	4.5	Solid	>100 °C	>371°C	**B.P:** NA **M.P:** NA	>5000 mg/kg [Rat].	> 2000 mg/kg (Rabbit)	NA	15 mg/m^3	10 mg/m^3	LEL - 30%	2	No
10.	Graphite Powder	5.80	Solid	NA	730 °C	**B.P:** NA **M.P:** 2820^0 C	NA	NA	NA	2 mg/m^3	NA	NA	2	NO
11.	Zinc Dust	39.90	Solid	NA	460^0 C	**B.P:** 908^0 C **M.P:** 419.5^0 C	It can cause skin and eye irritation. It can cause gastrointestinal irritation with nausea, vomiting and diarrhea. By inhalation it can cause fever, cough, and chest pain. Repeated Inhalation can cause chronic bronchitis					NA	2	No

RISK ASSESSMENT FOR STORAGE AND HANDLING OF HAZARDOUS CHEMICALS/SOLVENTS (HAZOP STUDY). ACTION PLAN FOR HANDLING & SAFETY SYSTEM TO BE INCORPORATED.

7.14.1 Introduction

There is a risk of toxic exposure in the pesticide industry, as the product as well as many of the raw materials are highly toxic. The toxicity hazard level of the chemicals being handled can be 3 or 4, which indicates a low lethal dose of exposure. Hence it is necessary to carry out the risk assessment for toxic exposure. If the risk level is high, then we have to suggest mitigation measures to lower the risk to an acceptable level.

7.14.2 Risk assessment: - Risk is the combination of the severity of hazard and probability of the occurrence of the incident. Risk assessment is the process of evaluating the potential risks that may be involved in the activity or project. There are several methods for evaluation of risks; here we give numerical values to the severity of the hazard and the probability or likely frequency of occurrence hazardous event. Then to evaluate the risk by assigning a number to a level of Hazard and also to the Probability or frequency of occurrence of the hazardous event as given in the rating scale. The product (combination) of the two will give us an idea about the risk level as given below

7.14.3 Rating scale

1. **Level of Hazard -** Negligible - 1, Low - 2, Moderate – 3, High - 4 Excessive - 5
2. **Probability Frequency-** Once in more than five years, Rare - 1 , Once in a year, Low - 2 , Once in a Month, Moderate – 3, Once in a week, High – 4, Very Frequently, Very High - 5
3. **Rating Score Scale -** 1 to 5 - low risk, 6 to 10 – Medium risk, 10 and above – High risk.

7.14.4 Managing the risk: - In order to manage the risk, it is necessary to know the potential hazards and the probability of occurrence of the hazardous event. Then you determine the risk level by combination (multiplication) of the above. This will give you if the risk is low, medium or high. Then manage the risk as follows

1. You live with the low risk activities.
2. Manage the medium risk activities, by suitable control and mitigation measures which are describe below after the risk assessment. This make the medium risk activities, to a low risk level. Which is called ALARP – As low as reasonably practicable.
3. Avoid or eliminate high risk activities.

7.14.5 Risk Assessment: - Risk assessment of the hazards involved in various activities in operation phase is given in the table below. The mitigation and control measures are given in para 5, after risk assessment. After the control measures the risks become tolerable. Hence it is a requirement for the project proponent that all the actions and measures are required to be taken to make the risk tolerable and manageable. This will ensure accident free operation with good work conditions for years together.

Table No. 7.6- Risk assessment –operation phase

Sr. No.	Process/Activity	Hazard involved	Risk	Level	Probability/ Frequency	Risk rating
1	Transportation of raw material and chemicals	Spillage of material during transportation.	Exposure of the liquid chemical can cause injuries, burn and due to inhalation it can causes health problems. Especially chemicals like zinc phosphide, white phosphorous etc. The liquid material/chemical spillage can cause water pollution, air pollution due to spread of vapours of the chemicals.	Low – minor leakage 2	Once or twice in a year 3	6
				High – Heavy leakage 5	Rare less than once in five years 1	5
2	Unloading of material from road tanker/truck	Leakages of liquid material during transfer – unloading using hose. Risk of fire.	Exposure to toxic vapours and fumes as highly hazardous materials like Ammonium Carbamate, Aluminium powder, white phosphorous is handled. Health risk to workers.	High 4	Once in five year or rare 1	4

Sr. No.	Process/Activity	Hazard involved	Risk	Level	Probability/ Frequency	Risk rating
3	Storage of raw material and finished product	Spillage of material during handling. The material may catch fire as chemical like white phosphorous is flammable Health risks in case of contact with material.	Exposure to toxic vapours and fumes. Health risk to workers.	Moderate to high 4	Once or twice in a year 3	12
			Risk of catching fire	Very high 5	Rare, less than once in five years 1	5
4	Use of electrically operated machines and pumps	Hazards due to electrical shock	Electrical shock can result in serious injury or can be fatal. There can be risk of fire due to short circuit	Moderate to high 4	Low less than one in a year 2	8
5	Degradation or contaminated by incompatible material. Uncontrolled reaction.	Possibility of runaway reaction Possibility of deterioration of product quality and generation of process waste	Risk of fire, injury and health problems to workers.	High to excessive 5	Rare with the control measures 1	5

Sr. No.	Process/Activity	Hazard involved	Risk	Level	Probability/ Frequency	Risk rating
		(Hazardous)				
6	Disposal of solid and hazardous waste like packing material and used chemical drums.	Exposure to toxic remains of material. Injury while handling solid and hazardous waste drums.	Health effect and minor injury	Moderate 3	Once or twice in a year, moderate 3	9
7	Reactor operation	Overheating of material may cause runaway reaction and generation of hazardous waste due to bad quality of material.	Health risks to workers.	Moderate 3	Once in more than five years, Rare 1	3
		Spillage of material while transferring and charging the material to reactor. Generation of vapours, fumes while Hazardous Chemicals like bromine to	Health risk due to inhalation of toxic vapours while charging the material in the reactor	High 4	High, very frequent 4	16

Sr. No.	Process/Activity	Hazard involved	Risk	Level	Probability/ Frequency	Risk rating
		reactor.				
8	Storage and handling of finished goods.	Chances of spillage while transferring from reactor to storage drum or container. Chances of accident while transporting the goods.	Injury to workers. Health risks are also involved.	Very Low 1	Low 2	2
10	Operation of DG set and rotating machines	Generation of noise due to rotating machines/DG set.	Impairment of hearing	Moderate 3	Once or twice in a week 4	12

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Sr. No.	Process/Activity	Hazard involved	Risk	Level	Probability/ Frequency	Risk rating
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5	Degradation or contaminated by incompatible material. Uncontrolled reaction.	Possibility of runaway reaction Possibility of deterioration of product quality and generation of process waste	Risk of fire, injury and health problems to workers.	High to excessive 5	Rare with the control measures 1	5

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