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GUIDELINES FOR RISK ASSESSMENT AND MANAGEMENT IN PETROCHEMICAL PLANTS

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C O N T E N T

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RISK ASSESSMENT AND MANAGEMENT IN PETROCHEMICAL COMPLEXES

.J.M. Dave

1. Introduction

Rapid growth of industries, using chemical technologies to produce consumer goods and fertilizers, pesticides etc. for food production to improve quality of life in developing countries, has increased the potential of risk to human health and the environment through the release of harmful chemicals. The incidences of Seveso (1976), Bhopal (1984) and Basel (1986) have caused unacceptable loss of life and damage to property and the environment. This has brought forth the importance and need of proper risk assessment and management in chemical industries to minimise the potential of release of hazardous substances and the damages.

Petrochemical Complexes can be classified as high risk industries as they use variety of processes and chemical substances, some of which can be extremely hazardous. Therefore risk assessment and management and emergency preparedness should form the basic approach to safety in these plants.

As UNIDO Consultant in Brazil and as a Consultant in India to the Petrochemical and Chemical Complexes, programmes for risk assessment and management were prepared by the author and are presented here as guidelines for industrial safety in similar plants.

2. The Petrochemical Complexes and the hazardous chemicals

Petrochemical Complexes can have large number of products and processes using hazardous chemicals and have few basic similarities of hydrocarbon processing followed by down stream products based units, which may vary significantly. The data presented here are based on complexes which had following products or processes.

1. Gas and Oil Cracker Units
2. Olefine Plants
3. Aromatics Plants
4. Acrylo Nitrile
5. Acrylic Fibre
6. Linear Alkyl Benzene
7. Ethylene Glycols (Mono-di-Tri and Poly)
8. Vinyl Chloride Monomer (VCM)
9. Polyvinyl Chloride (PVC)
10. High Density Polyethylene (MDPE)
11. Low Density Polyethylene (LDPE)
12. Poly Butane Rubber (PBR)
13. Poly Propylene (PP)
14. Poly Urethene Foam (PUF)
15. Caustic Soda and Chloride
16. Hydro Chloric Acid Plant (HCL)
17. Polystyrene
18. Styrene Butadiene Rubber (SBB)
19. Power Plants Oil/Gas Based

20. Xylene Plants
21. Purified Terepthalic Acid (PTA)
22. Polyester Fibre Plants

These plants used the following chemicals :-

1. Acetone
2. Acetylene
3. Acrylic Acid
4. Acrylonitrile
5. Acetonitrile
6. Acetic Acid
7. Ammonia
8. Benzene
9. n-Butane
10. Butylene
11. Butyl Acrylate
12. Butyl Alcohol
13. 1-3 Butadien
14. Carbon disulfide
15. Carbon monoxide
16. Diethyl Ether
17. Dimethyl sulfide
18. Ethane
19. Ethylene
20. Ethylene Oxide
21. Ethylene Glycol
22. Ethyl Alcohol
23. Ethyl Acrylate
24. 2-Ethyl Hexyl Acrylate
25. Gasoline
26. n-Heptane
27. Hexylene
28. Heptylene
29. Hydrogen
30. Hydrogen Cyanide
31. Kerosene
32. Linear Alkyl Benzene
33. Linseed Oil
34. Methane
35. Methanol
36. Ethyle Ethylene
37. Methyl Acrylate
38. Methyl Alcohol
39. Naphtha
40. Octane
41. O-xylene
42. Propane
43. Propylene
44. n-Pentane
45. Tolune
46. Monoethyl Glycol
47. Di-ethyl Glyco_
48. Tri-ethyl Glycol
49. Poly-ethyl Glycol
50. Raffinate
51. Fuel Oil
52. Liquified Petroleum Gas
53. Liquified Natural Gas

Most of the chemicals used as inputs and products were stored on the complexes in tank-farms or specially designed storage tanks or units. The quantities stored varied from few thousand litres to millions of litres. There were also facilities for loading road tankers and rail road tanker wagons with products, and unloading of inputs like LNG, LPG, Naptha, etc.

The processing units were located adjoining each other and interconnected with pipe lines sharing common utilities like power, steam, water and waste water treatment and workshop facilities.

The staff employed consisted of highly qualified professional chemical engineers, middle level supervisors and low level operators and workers.

These complexes had minor mishaps with no serious damages to staff or environment, but had very high potential risk to workers and the people living in the vicinity.

3. Risk Assessment

In Petrochemical Complex Operation, the risk of damage to human health and the environment are of two types:

i. Release of chemical substances in routine operation procedures to air, water and soil with potential of damage over a long time.

ii. Accidental massive release or explosion with or without fire.

Both these cases need to be examined scientifically to asses risk to the health of the people and the environment, in order to develop suitable control and management plans. The first one normally accepted as "pollution" may pose a serious threat and risk over a long period while accidental massive releases can cause instantaneous catastrophe.

3.1 Routine Operational Releases

These can be divided into:

Process Releases:- Such as process vents and off gases, safety valves, etc. controlled and uncontrolled unwanted process wastes, liquid, gaseous or solids released with or without treatment

Non process releases like storage vents, leakages from pipelines, valves, spillages in plants and during loading and unloading operations

These are generally accepted as inevitable pollution and the real risk is often not visualised, but in the long term it may cause irreversible damage to human health and the environment and should be evaluated

to minimise risks.

The effects of inevitable pollutant released routinely can be on:

- Human health directly or indirectly through foodchains
- Wild life - Terrestrial and aquatic
- Ecological damage by changes in chemistry of air, water, soil, etc.

Many times routine pollution effects are cumulative and may take years or decades before they are visible or measurable and possibly with irreversible damage.

The assessment of effect of low level discharge on long term basis is complex and difficult due to very limited availability of data on cause-effect relationship at low concentrations. Mostly statistical approaches are used. Predictive models have very limited applications. Therefore the basic approach is to use available effect criteria with reasonable factor of safety. The factor used can be any where between 2 to 100 depending on the characteristics of the substance, local situation - specific to the site.

This may inlcude:

i. Vulnerability of the local population

ii. Sensitivity of local species of plants, animals etc.

- Geographical, topographical and metereological conditions governing the behaviour and the fate of the pollutants released.

3.2 Accidental Massive Release

This can occur from many sources, such as

- Breakage of pipes, valves or leakages from process reactors, units, etc.
- Release from storage containers or reactors due to temporary changes in pressure, or temperature, mostly in limited quantities through pressure relief valves, discs, or overflow devices.
- Violent release in massive quantity, by bursting of a container, ~~strange~~ tank, or pipe breakage due to abnormal situation of pressure, or temperature.
- Violent release from a process unit due to run away reaction in the reactors - may be in limited or massive quantity.
- Human error or accidental mixing of substances causing explosive reaction in storage tanks, reactors, transmission or transfer lines of the chemicals.
- Failure of control equipment for routine discharges like flares, scrubbers, neutralisers, or reactors for gases or liquid, releasing massive quantities.

Effects of Massive Release

The second aspect of the risk assessment is the consequences of the release. Depending on its characteristics it will cause effects which can be broadly classified into four categories:

- Fire and/or explosion
- Health
- Reactive
- Ecological

3.2.1. Fire and Explosion

The degree of damage will depend on the characteristics of the chemical and its behavior when it catches fire. It may range from highly explosive conflagration to just combustible. The assessment of the risk is done using:-

i. Pressure wave impacts
ii. Missile action damage
iii. Boiling liquid expanding explosions
iv. Thermal radiation burn injury criteria
vi Combustion by product toxicities

These can be estimated by ready made models in "ARCHIE" or similar codes and the potential of damage of various distances are assessed for protective measures.

3.2.2 Health

Chemicals can enter the human system through inhalation, ingestion or by contact through skin. The effects depend on concentration and duration of exposure. The effects can be irritation, asphyxiation, anasthetic or narcotic, carcinogenic, or mutagenic. The toxicity can affect the liver, kidney, brain, lungs or other organs. For risk assessment concentration limits are prescribed such as:

- TLV Threshold limit by American Conference of Government Industrial Hygienists (ACGIH).
- PEL Permissible Exposure Limits by Occupational Safety and Health Administration.
- WEEL Work Place Environment Exposure Limit by American Industrial Hygiene Association (AIHA).
- IDLH Immediately Dangerous to Life and Health (30 min) by National Institute of Occupational Safety and Health (NIOSH).
- EEGL Emergency Exposure Guidance Levels by National Academy of Science - National Research Committee (NAS/NRC).
- SPEGL Short-term Public Emergency Guidance Limits NAC/RAC.
- ERPG Emergency Response Planning Guidelines published by AIMA.

(All by U.S. Administration non-governmental Organisations)

These are all useful in evaluating the potential effect of the substances released on the health of the worker and the surrounding population.

The concentration of the substance released is estimated using the ARCHIE model. It covers the single puff or continuous discharges at various heights and different metereological conditions and gives the concentrations at different points and time intervals after release and their durations.

These values are then used to assess the potential risk to the health of all concerned, and to plan protective measures.

3.2.3. Reactivity

Many chemicals are self-reactive with air, water or soil, under certain conditions. They may also react with other chemicals resulting in fire, explosion, or violent rise in temperature with or without by products. There are various types of reactivities and those of special concern in risk assessment are:-

- i. Reactivity with water, air and soil
- ii. Reactivity with organic substances - oxidation
- iii. Exothermic polymerisation
- iv. Exothermic decomposition
- v. Corrosive action

These characteristics are mostly specific to the chemical and should be throughly investigated in each case for a correct assessment of the risks involved for planning proper management.

3.2.4. Ecological

The release of chemicals routinely or accidentally in large quantities can be of serious ecological conseuqence endangering the well being of man. It can affect climate, terrestrial and aquatic ecology. The most accepted impacts are:

i. Damage to vegetation, forests, agricultural crops, etc.

ii. Aquatic ecology, plants and all other life forms in water

iii. Soil biota and its chemical balance

iv. Wild life-directly or indirectly through affected food chain

v. Global climate due to CO_2, gases emission of CH_4, NO_x, and CFC, their contribution to the atmosphere, green house effect.

To assess the risk to the ecology, behaviour and the fate of the chemicals in rivers, lakes, estuaries and coastal and deep oceans or in the atmosphere and soil should be studied in each case to develop a strategy for its management.

Table No. 1

IDENTIFICATION OF FIRE HAZARDS

HEALTH	FLAMMABILITY	REACTIVITY	ECOLOGICAL
Identification of Health Hazard Color Code : BLUE	Identification of Flammability Color Code : RED	Identification of Reactivity (Stability) Color Code : YELLOW	Damage to Vegetation or other ! Life.
Type of Possible Injury	Susceptibility of Masterials to Burning	Susceptibility to Release of Energy	
Signal	Signal	Signal	Signal
4. Materials which on very short exposure could cause death or major residual injury even though prompt medical treatment is given	4. Materials which will rapidly or completely vaporize at atmospheric pressure and normal ambient temperature or which are readily dispersed in air and which will burn readily	4. Materials which in themselves are readily capable of detonation or of explosive decomposition or reaction at normal temperatures and pressures.	4. Permanent damage even in low concentration and short time-
Materials which on short exposure could cause serious temporary or residual I injury even though prompt medical treatment is given	Liquids and soilds that can be ignited under almost all ambient temperature conditions	Materials which in themselves are selves are capable of detonation or explosive or explosive reaction but require a strong initiating source or which must be heated under confinement before initiation or which react explosively with water	Temporary damage in low in short time

Table No. 1 continued

2. Materials which on intense or continued exposure could cause temporary incapacitation or possible residual injury unless prompt medical treatment is given.	2. Materials that must be moderately heated or exposed to relatively high ambient temperatures before ignition can occur	2. Materials which in themselves are normally unstable and readily undergo violent chemical change but do not detonate. Also materials which may react violently with water or which may form potentially explosive mixtures with water	2. Permanent damage in low constitution in long time.
1. Materials which on exposure would cause irritation but only minor residual injury even if no treatment is given-	1. Materials that must be preheated before ignition can occur	1. Materials which in themselves are normally stable, but which can become unstable at elevated temperatures and pressures or which may react with water with some release of energy but not violently.	1. Temporary damage on high constitution in long time.
0 Materials which on exposure under fire conditions would offer no hazard beyond that of ordinary combustible material.	0 Materials that will not burn.	0. Materials which in themselves themselves are normally stable, even under fire exposure conditions and which are not reactive with water.	0. No damage on high contribution on long time.

In order to simplify the risk assessment all the four types of risk are categorised in five levels, zero to four as recommended by the National Fire Prevention Association (1984). has been adopted. It is precise and provides a practicable approach to facilitate the classification and categorisation for the purpose of risk assessment and is used here with a modification of adding a fourth column for the ecological impact as given in table No. 1 (A-B)

Brief summary of the risk assessment of a Petrochemical Complex is given in the Annexure I. as illustration.

4.0 Risk Management

All the sources like routine unwanted by products as wastes - polluting air, water and soil, operational releases due to spills, leakages, vents, relief valves, etc. and the massive violent release due to accidents are threat to human health and the environment. For petrochemical complexes using large number of chemicals and products and by products, these sources pose serious risk with high potential of damage and need careful evaluation as discussed earlier.

Once the risk potentials are identified for the substances and the process used, the logical approach would be to plan actions to prevent or minimise them.

In petrochemical complexes, this can be done in two areas:

i. In plant and on site actions

ii. Outside and off site actions

4.1. In Plant and On Site Management

Can be divided into following steps

4.1.1. Siting or Location of the Plant

Based on estimated potential, extent of damage and area likely to be affected, the first consideration should be to avoid a site which can affect population or environment seriously. For this following parameters should be examined critically:

a. Meteorological conditions, like wind pattern, temperature inversion conditions, etc. on annual basis

b. Topographical and land form features to avoid accumulation in valleys or discharges into water bodies like lakes, estuaries, backwaters etc.

c. Proximity of population concentration, conservative or ecologically important area, or a sensitive place

or of human heritage

of natural beauty, national monuments, etc. If any of these onsiderations justify, then the selection of the site of the complex should be changed to an alternative safer one at the planning and the design stage itself.

4.1.2. Design Review for Plant and Equipment

Risk identification is done by asking questions "What happens if - ?" for all the operations at the plants and the processes and system as a whole, at the drawing board stage. Each of the processes and equipment is reviewed. The basic approach is:

a. Use of alternative chemicals and processes to use clean technologies where possible.

b. Provide appropriate "Backups" for vital instruments and controls in critical processes with automatic shut off or interlocks to restrict undesirable pressure or temperature in reactors to prevent "Run away Reactions".

c. Provide pressure sensors in important pipe lines and storages for detecting major leakages, or breakages and they should activate alarms and automatic shut-offs where applicable.

d. Proper isolation of the reactive chemicals in system storage and handling to avoid violent reactions.

e. Sound design of pipelines and valves to minimise probability of breakage or leakage and with isolation valves

f. Location and spacing of units to provide adequate safety with operational ease to prevent cascade events

g. Provision dykes, fire walls etc. for confinement of chemicals and prevent spread of fire.

h. Providing safety zones and green belts around, wherever possible, to reduce impact on the people and the environment.

4.1.0. Safety Measures - Fire

Safety measures are provided in addition to the design reviews as they may not be a applicable at many points. These are provision of equipments, systems to contain or combat the chemicals released in the plant by accident such as:

a. Fire Control with built in water or foam spray systems on storage tanks, pipes, valves and potentially fire prone areas, provision of fire walls fire extinguishers of required type at all the critical locations.

b. Centralised fire alarm and control set up with alarms, loud phones. The system should have sufficient alarm activators at all the critical points in all the plants. These alarms should be break the glass or push button type and should be with food accessibility under emergency conditions.

c. Central fire control of the complex should have direct communication facilities with the city and county fire stations for immediate contact and help.

d. Well designed fire fighting system with adequate water supply, piping, storage, pumping capacity with fire hydrants at ground and upper levels with good accessibility. The system should specify pressures sustainable for long duration if required.

Typical Fire - Safety measures for a petrochemical plant is given in Annexure - II

4.1.4 Toxic or Hazard ous Chemical Control

This is most difficult to provide safety measures because of their variable characteristics and even small quanties may be highly dangerous if released. Normally following basic approach is used:

a. Built in sprays of neutralising chemicals at all critical points and along pipelines spray maneuverable with hose and nozzle should be located at all critical areas (large presence of persons).

b. Air supply masks with compressed air cylinder and or piped supply with good lengths near the points of likely release, canister masks of suitable type at peripheral areas with good accessibility.

c. Detectors and sensors for the toxic substances with alarm - visuals and audibles, actuated automatically at predetermined concentrations.

d. Central display system with lined net work to sensors in all plants similar to fire which will sound alarm also in main control room when sensors actuate local alarm, indicating location the emergency point and the substance released. (if not for all chemicals it should be atleast for selected few)

4.1.5. Operational Release Controls

Operational releases are generally small in quantities or low concentration in large volumes either continuous or intermittent. They may endanger human health and the environment when continued over long period of time with comulative effect and can beome a serious risk. Therefore these have to be inlcuded in the risk assessment of the Petrochemical Complexes.

There are two types of discharge sources:-

a. In plant vents, stroage tank breakers, relief valves, rupture disk, minor leakages, spillages during handling and loading unloading operations.

b. Waste discharges from the plant of unwanted by products into air, water, or soil, either continuously or intermittently.

a. Inplant

i. Vents, storage tank breakers, exhaust system from process rooms all should be evaluated and steps should be taken to control them by directing them through existing control systems or providing individual control at each outlets. If required neutralising cartridges or columns should be incorporated at the design signes for strangers and processes.

ii. Leakages, spillages will need special care by both design and training of the personnel for safety practices.

b. Waste discharges should be controlled by:

i. Use of clean technology to eleminate the generation of wastes. This may inform of substitution of the raw materials, or change of process which donot produce wastes, for example.

ii. Recycling the waste into the process or into another process. This may be liquid, gaseous or solids

iii. Providing the treatment of the wastes to change the harmful characteristics and recycle it

4.2.0 Administrative Measures and Enforcing Safety Code of Practices

Human factor is of vital importance in risk assessment and management. Best of the system design and safety measures have to be operated and maintained by operators and helpers, the consequences of their failure can be equally serious. The risk of human failure can be equally serious. The risk management should be never minimised. The control approach should be of :-

4.2.1 Enforce Safety Codes and Safety Practices

These are:

a. Color coding of pipes lines valves storages as per the National Fire Protection Association

b. Placarding boldly (minimum size 300 mm x 300mm) each critical equipment operation panels, valves safety valves, rapture discs, pipe line or its accessories appurtenances, specially isolation valves etc.

c. Prominently displaying safety cards giving information types of damage potential of the chemical, effects, counter measures and first aid information. These should be attached to walls, or displays placed in plants at all critical points and should be written in local languages.

d. Prepare a safety order for the plant and indoctrinate habit of strict adherence by all the workers and the supervisors. (Typical safety order is given in Annexure III)

4.2.2 Skill Development in the Staff

a. The workers, operators and supervisors be trained for correct operation and precautions to avoid any lapse to cause a mishap and maintain equipment strictly as specified. As a rule skill requirements for each category of staff should be specified with training certificate as prerequisite for holding such positions in the plants.

b. Provide appropriate safety information to the staff in a fromat and language they can understand, regularly updating it to help them maintain and enhance their competence.

c. Recognise cultural and personal attitudes of the workers towards safety and help them to overcome them by special programmes.

4.3.0 Emergency Response - Plans of Actions

4.3.1 In Plant, Plan of Action

Plan of action as emergency response is essential responsibility of management to minimise impact on community such as damage to human health, property and the environment. The basic elements of emergency response plans in the plant are creation of coordinating committee or group its organisational structure and the responsibilities of individuals in case of mishao these should be inlcuded.

a. Risk evaluation of the complex and the area including neighbouring units or population centres, using ARCHIE or other suitable models

b. Notification and communication system for immediate intimation of accident, by automatic alarms, central control room with identification of accident site and notification to the management, local authorities, neighbouring industries medical aid and to the neighbouring population with public alarm system.

c. Emergency equipment and facilities readiness for fire containment of toxic chemicals, medical supplies, masks, protective clothings, and communication mobility and other facilites.

d. Information and data on "Emergency Procedures" for each process units for shut down procedures, isolation valves, and safety measure-activities, methods, location of control panels, etc.

e. Training, drills and mock exercises for plant staff, equipments and to test the effectiveness of setup.

f. Detailed information on characteristic of chemical released and its damage potential toxic, reactive, fire, etc.

4.3.2 Offsite - Plan of Action

As discussed in onsite assessment the sources of releases for off site or outside the plants will be same ones and the chemical will have impacts on surrounding population and environments as described earlier.

The overall goal of off-site management should be to prevent loss of life, property and to protect environment from damages as far as possible from such a release. The risk management approach has to be based on:

a. Assuming the potential of damage to be maximum (To be assessed by using standard procedures discussed in section 3)

b. Physical planning to reduce the impact on population and the enfironment, by proper land use.

c. Developing an "Emergency Response" for immediate action by all concerned in a coordinated manner to mitigate the impacts.

Worst Scenario

For an off site management worst possible scenario from violent release should be assumed to provide maximum efforts for precautions and safety. The potential of damage with respect to type extent and area to be affected should be calculated using ARCHIE or equivalent model based on data such as characteristic of the chemical, volume of storage and nature of violent release expected. Prepare quantitative and qualitative estimates of damage around the complex and plot it on maps to assess the population and the environment likely to be affected for planning the abatement measures

b. Physical Planning

Once the potential of damage and area likely to be effected is determined efforts should be made to reduce these impacts by taking steps like:-

i. Providing safety zone by using surrounding lands for any purpose other than residential. This should be 1000 to 1500 meter wide and can be used for small scale or non hazardous industries with few employees or workers who can be evacuated rapidly

ii. Use of green belts 800 to 1000 meter wide with mix of local trees like ever greens to attenuate the impact of the released substances (Specially effective in many reactive and the inflamable chemicals.

c. **Emergency Response Plan**

This is the most crucial off site risk management activity as once an accident has occurred, only a well prepared emergency plan is of any help.

The emergency response action for a Petrochemical Complex should have following basic elements

i. It has to be site specific to suit the complex, location - urban, rural or in an isolated large industrial complexes away from population centres.

ii. Should involve all local agencies such as
- Municipal and local administrative authorities
- Fire department
- Police, and local law and order agencies
- Civil defence units
- Health department and emergency medical care units, hospitals, ambulance units etc
- Environment protection agencies local, state and federal
- Municipal and local administrative authorities

- Red Cross, voluntary health agencies
- Community Organisations - representatives prominent leaders, elected public bodies officials (major, sherif, etc.)
- Trade and industry organisation
- Labour unions - representatives
- Neighbouring industries and their management (if located in large industrial complexes)
- Non-governmental voluntary organisations - environmentalists, social service or those who can offer voluntary help.

iii. Organise emergency response coordinating committee or group from the involved local agencies with a leader.

iv. Prepare action plans for

- Information progagation and create awarness in the population about potential nature of hazards from the chemical it released by accident
- Educate public on how to protect themselves in case of public alarm and actions to be taken (close the doors and windows, cover face with wet towels, etc.
- Evacuation plan and organisation of transport vehicles - public and private, identification of routes and organised system to keep them open.
- Arrangement of shelters, foods, etc. for evacuees.
- Post emergency procedures

v. Points of contact and information for the public, publication of telephone numbers, the name location and address of the contact person.