
MAJOR INDUSTRIAL HAZARDS

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Introduction

Chemical industries are growing very fast. Major installations such as Gas processing complexes, Petroleum Refineries, Fertilizers Industries are processing thousands of tons of hazardous chemicals everyday. Need for a large inventory of flammable and /or toxic material arises to meet the manufacturing demand.

This rapid growth in the use of hazardous chemicals in industry and trade has brought about a very significant increase in the number of people, both workers and members of the general public, whose life could be endangered at any one time by an accident involving these chemicals.

The release of hazardous chemicals is inevitable irrespective of many safety precautions taken during design, construction, commissioning and normal operation of any chemical processing unit. It is therefore important, particularly for industries involving the storage and use of hazardous chemicals, to address both on-site and off-site safety when deciding on the safety measures to be taken.

Types of Major Industrial Hazards

Major industrial hazards are generally associated with the potential for fire, explosion or dispersion of toxic chemicals and usually involve the accidentally release of material from containment. Accidents involving major hazards could include:

- Leakage of flammable material, mixing of material with air, formation of flammable vapor cloud to a source of ignition, leading to a fire or an explosion affecting the site and possibly a populated area.
- Leakage of toxic material, formation of a toxic vapor cloud and drifting the cloud, affecting directly the site and possibly populated area.

Depending upon the state of released chemical, cause and on its consequences, the major hazards in chemical process industry are classified as:

- **Fire**
- **Explosion**

- **Toxic release**

Fire

The Fire is a process of burning that produces heat, light and often smokes and flames. The effect of fire on the people takes the form of skin burn due to the exposure to thermal radiation. The severity of the burns depends upon the intensity of the heat and exposure time. In general terms the skin withstands heat energy of 10kw/m^2 for approximately 5 seconds and that of 30kw/m^2 for 0.4 seconds before pain is felt. The effect of various heat radiation levels is given in table-I.

Radiation Level (kW/m²)	Observed Effect
37.5	Sufficient to cause damage to process equipment
25	Minimum energy required to ignite wood at indefinitely long exposures (non-piloted)
12.5	Minimum energy required for piloted ignition of wood, melting of plastic tubing
9.5	Pain threshold reached after 8s; second degree burns after 20s
4	Sufficient to cause pain to personnel if unable to reach cover within 20s; however blistering of the skin (second degree burns) is likely; 0: lethality
1.6	Will cause no discomfort for long exposure

Table-I: Effects of Radiation (World Bank) -Recommended Design Flare Radiation Levels (API 521)

Fire can take several different forms i.e.

- **Flash Fire**
- **Jet fire**
- **Pool Fire**
- **Secondary fire**

Flash Fire

A flash fire occurs when a cloud of flammable gas and air is ignited. The speed of burning is function of the concentration of the flammable component in the cloud and also the wind speed. Within a few second of ignition the flame spreads both upwind and downwind of the ignition source. Initially the flame is contained with in the cloud due to premixed

burning of the regions within the flammable limits. Subsequently the flame extends in the form of a fire plume above the cloud. The downwind edge of the flame starts to move towards the spill point after consuming the flammable vapor downwind of the ignition source.

Typical flame propagation speeds are the order of 4m/s The flame velocity and dispersion increases with wind speed. The duration of this fire is very short and the damage is caused by thermal radiation and oxygen depletion.

Jet Fire

A jet fire occurs when a flammable liquid or gas is ignited after its release from a pressurized, punctured vessel or pipe. The pressure of release generates a long flame, which is stable under most conditions. A flash flame may take the form of jet flame on reaching the spill point.

The duration of the jet fire is determined by the release rate and the capacity of the source. Flame length increases directly with flow rate. Typically a pressurized release of 8kg/s would have a length of 35m. The cross winds also affects the flame length. An increase in the crosswind velocity increases the flame length.

Pool fire

A pool fire occurs on ignition of an accumulation of liquid as a pool on the ground or on water or other liquid. A steadily burning fire is rapidly achieved as the flame vapor to sustain the fire is provided by evaporation of liquid by heat from the flames.

The maximum burning rate is function of the net heat of combustion and heat required for its vaporization. Generally heat radiation dominates the burning rate for flame greater than 1m diameters.

Combustion of flammable materials those are not directly concerned with the process, and some time present unnecessarily. For example:

- Stored raw material and products, including packaging materials.
- Combustible insulation of vessels and pipelines and electrical cables.
- Combustible building construction and linings.

Protection is by elimination or segregation of combustible materials, use of incombustible materials of construction and insulation, and control of ignition sources. Careless or deliberate actions may defeat in-built precautions.

Fire Hazards To Plant

Fire damage occurs more frequently than losses by explosion but the damage is generally less extensive. Pool fires are less dangerous to human life than flash fires but their longer durations results in greater structural damages. The jet fires mainly affect the mechanical properties of the structures. Material of construction loses mechanical strengths when exposed to high temperatures.

Heat radiations emitted by the fires cause damage outside the fire. Human body may suffer the skin burns after its exposure to these thermal radiations. Other lethal effect that must be considered in case of fire is the depletion of oxygen by the consumption of oxygen in the combustion process generally in the vicinity of the fire. Of the importance also are the health effects arising from the exposure to the fumes generated as a result of fire. These fumes may include toxic gases, such as sulfur dioxide, nitrous oxides, oxides of carbon etc.

Explosion

An explosion is the process involving the production of a pressure discontinuity or blast wave resulting from a rapid release of energy. A pressure disturbance is generated in to the surrounding medium. Air becomes heated due to its compressibility and this leads to an increase in the velocity of sound, causing the front of disturbance to steepen as it travels through the air.

The loading and hence the damage to the nearby targets are governed by the magnitude of and duration of pressure wave. Missiles may be generated by an explosion and are capable of causing severe damage to adjacent plant structures and people.

The explosion mainly occurs due to the rapid combustion of a flammable material but can be brought about the chemical reactions other than combustion, provided they release large amount of energy (heat). Examples of these chemical reactions are Polymerizations, the decomposition of unstable substances and exothermic interactions of many kinds.

Classification of Explosions

- **Chemical Explosions**
- **Physical Explosions**
- **Vapor Cloud explosions**

Chemical Explosion

Chemical explosions in plant or in vessel can arise due to exothermic reaction occurring internally. Such reaction may involve decomposition of unstable substances, polymerization of monomers, or combustion of fuel oxidant mixtures. Heating and increase of molecular number can result in a rise in pressure to the bursting point of the vessel, and explosives decompose so quickly that confinement and the development of pressure are self-imposed.

Physical Explosion

It occurs simply due to over pressure as in the case of steam boiler and air receiver explosions. Fire is not necessarily a consequence. But fire involving stock, buildings and plant ancillaries can cause physical explosions due to overheating followed by the overpressure in vessels and also the fireballs if contents are flammable. One such case is termed as Boiling Liquid Expanding Vapor Explosion (BLEVE).

Boiling Liquid Expanding Vapor Explosion (BLEVE)

An American, Wilbur Walls, adopted the term “Boiling Liquid Expanding vapor Explosion (BLEVE)” some 40 years ago. Between 1950 and 1970, 18 incidents involving LPG were tackling the road and rail tanker fires lost lives due to sheer ignorance of dealing with BLEVE situation. Those 18 fires resulted deaths of two fire fighters and 20 civilians and serious injury to 318 firefighters and civilians. In the next five years from 1970, there was sharp rise in casualty figure claiming lives of 18 fire fighters and causing serious bur injury to over 300 people. The risk of a large loss of life from BLEVE is obviously far greater in a highly populated area. Tankers carrying flammable liquid use roads and rails through highly populated areas thus producing Hazards, which ought to be self-evident.

MEXICO CITY

The incident, which occurred in Mexico City, claimed many lives. It occurred at 5.42 am on Monday, November 19, 1984 at an LPG storage complex in a North Western district of Mexico. The disastrous effect of BLEVE can be gauged through the following lines.

- A road Tankers being loaded burst into flame first. Followed by at least 12 explosions as LPG tanks BLEVE'd and setup a firestorm.
- Fires had leveled 66 acres of land. Troops sealed off an area of 2.40 km. around the complex.
- Fire was brought down under control after 36 hours and at times the brilliant red flames reached height of 500 meters.
- The actual diameter of a fireball was estimated from photograph to be about 200 to 300 m.
- 554 persons were killed, more than 350,000 people were evacuated and 10,000 were left homeless. Over 600 children were known to have lost their parents.

Assessment of damage to the site and surrounding area revealed that the cost of replacing physical plant and equipment was relatively low. However, the scale of the loss of life and personal injuries in Mexico City has made this an incident on which it is impossible to put an overall price tag.

BLEVE AND SUBSEQUENT FIRES

In order for a BLEVE to take place, the following four conditions must be present.

1. There must be a substance in liquid form. Most of the destructive BLEVE's that have occurred have involved flammable liquids and liquefied flammable gases. BLEVE can occur with any liquid, even water. The only difference is that with non-flammable liquids there is no fireball. However, there will still be damaging effect including the propagating of cracks in the structure of the container together with possibility of subsequent failure and propulsion.
2. The liquid must be in a container like sphere, bullet, and road/rail tanker.
3. The contained liquid must be at a temperature above its normal boiling point at atmospheric pressure at the time container allows the

pressure inside to build up above atmospheric pressure, the fluid, in the container is able to remain in the liquid state, even though its temperature is above its normal boiling point. This increase in pressure raises the Boiling point of the contained liquid above its boiling point.

An example of this is a steam boiler, where water is kept at a temperature above its normal 100°C boiling point and called superheated water.

4. There must be a failure of the container in order to have BLEVE. This container failure can be due to following causes:
 - Flame impingement.
 - Internal structural weakness of the container
 - Failure of improperly designed SRV
 - Impact from a mechanical cause such as a road accident, tanker derailment allowing flammable liquid to flow out.

The physical force that causes the BLEVE is because of the large liquid to vapor expansion of the liquid in the container. LPG will expand 250 times its volume when changing from liquid to vapor and water will expand 1700 times its original volume. It is this expansion process that provides the energy for propulsion of the container and the rapid mixing of vapor from the container with air, resulting in the characteristic fireball when flammable liquids are involved. In most BLEVEs caused by exposure to fire, the container failure originates in the metal area of the vapor space because it is extremely difficult to heat the container metal significantly where it is in contact with liquid. The liquid conducts the heat away from the metal and acts as a heat absorber. Therefore, the metal around the vapor space can be heated to the point of failure.

Points for Guidance

- The application of water must be at the point of flame contact. The tank's vapor spaces (the area above liquid level) are the most critical and are the high priority area for cooling. (It is, however, not always possible to identify the exact level of the liquid).
- For effective cooling 2,000 liters per each point of flame contact is the minimum amount of water that should be used (Priority should be given to the uppermost portions of the tank).

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- A large and sustained supply of water is required for both cooling and personal protection. There must be an available water supply to sustain an attack for periods of several hours or longer.
 - Ensuring accurate direction of water is of major importance. This is often impossible in a transportation incident, due to the weak / lack of visibility.
 - It should be carefully noted that any personnel positioning ground monitors or using hand lines would be exposed to extreme danger, therefore, if a decision is made to approach the fire only personnel essential for the operation should be put to the task.
 - Personnel must be given clear instructions on the tactics to be employed. The entire operation must be highly coordinated.
 - Entry to attempt to extinguish fire by shutting valves or plugging hole should only be attempted after establishing effective cooling streams on the tank shell at the points of flame contact. This only is to be carried out when absolutely essential.
 - The approach to a tank should be made from its side whenever possible.
 - Pre-fire planning for this type of an incident should arrange for maximum support. Safe area must be established to ensure protection, proper control and development.

The Hazards of BLEVE

A BLEVE poses the following hazards:

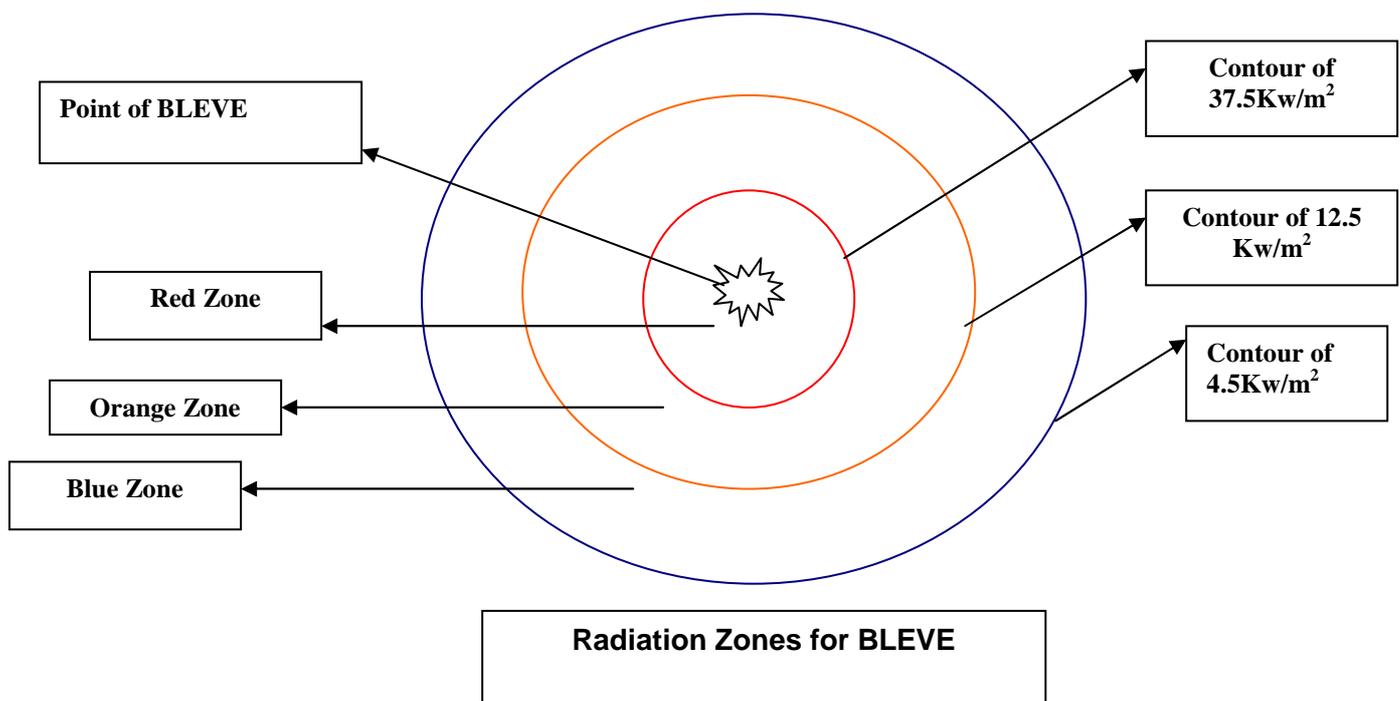
- Fireball with thermal radiation with some rainout forming pool fires.
- Missiles and Major fragmentation
- Rocketing vessel parts
- Overpressure from minor shock waves

The past experience has shown that whenever there is BLEVE; it is only the heat radiation of the fireball and the over pressure, which do the offsite damages. The effects of both can be well understood by the following zones of the heat and over pressure generated by the BLEVE.

Radiation Zones

The very first zone for the heat effects of BEVE is the “Red Zone”. It stretches from the release point to the contour representing radiation level of 37.5Kw/m^2 . In this zone the radiation level varies from maximum (At the point of BLEVE) to the radiation level of 37.5Kw/m^2 . In this zone complete burning of human body is likely to be occurred. The buildings and the industries may undergo the secondary fires. This radiation level of this zone can also damage the process equipment.

The second zone is the “Orange zone”. It spans from the contour representing radiation level of 37.5Kw/m^2 to the contour of radiation level of 12.5Kw/m^2 . In this zone human body may suffer third degree burn injury. The buildings or the industries near to the point of BLEVE may suffer the local fire in celluloid materials like wood, paper, cotton and plastic etc.



The third zone that is considered to be safer than the red and orange zone is the “Blue Zone”. It extends from the contour with radiation level of 12.5Kw/m^2 to the contour with radiation level of 4.5Kw/m^2 . In this zone the human body may suffer the 2nd degree burn injuries if unable to reach in cover with in 20 seconds. The buildings and the industries may suffer the local fires due to liquid rainout.

Vapor Cloud Explosion (VCE)

An accidental escape of flammable material leads to subsequent rapid combustion on encountering a source of ignition and may result in to fireball on immediate ignition. But if there is delay in the ignition it may result in to either flash fire or in to "Vapor Cloud Explosion" if turbulence-inducing features are present. A VCE is an extremely damaging outcome from the release of flammable material. A large amount of flammable material can accumulate in the cloud form and subsequently release its energy on encountering some local ignition source in the form of over pressure (Explosion).

A VCE to take place, the following conditions are required:

- The release should be greater than one tone of flammable hydrocarbon.
- The cloud must be above its lower flammability limit (LFL).
- The cloud must mix and find ignition source and this generally implies late ignition.
- The vapor-air mixture will be denser than the surrounding air either due to its molecular weight or because of cooling.
- Turbulence and non-uniform mixing conditions must be present; obstacles such as buildings pipe work and vessels usually provide these conditions.

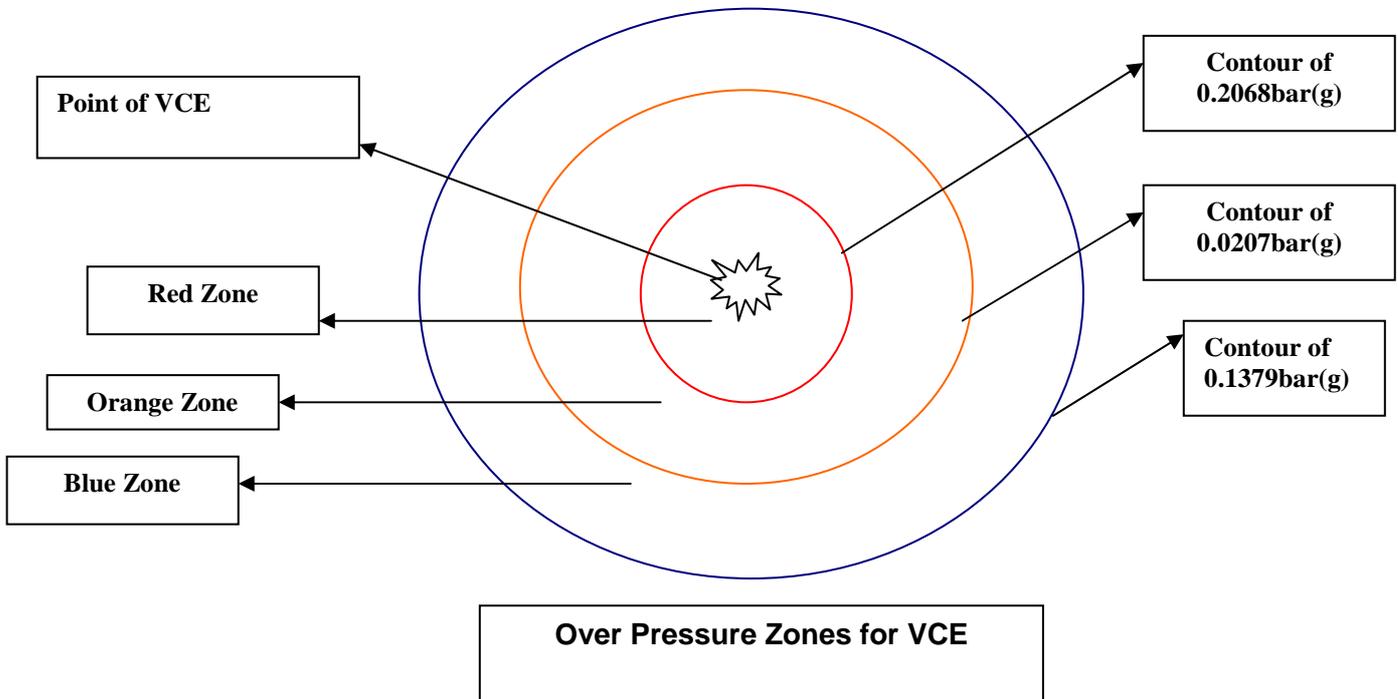
Hazards of VCE

- Over pressure due to Blast wave.
- Heat Effects generating fire.

The explosion effects of VCE are predominating damaging outcomes. The explosions can disturb essential services especially fire fighting services, so that the secondary fires which are often follow the initial blast can not readily be controlled.

The pressure effects of VCE can be well understood by the following zones of different over pressure levels.

Over Pressure Zones



Like BLEVE, the very first zone is the "Red Zone". In this the pressure level varies from maximum (at ignition point) to the 0.2068 bar (g). Thus it stretches from the point of ignition to contour representing the pressure level of 0.2068 bar (g). The pressure level of this zone is sufficient to cause collapse of buildings; steel frame buildings can be distorted and can be pulled away from foundations.

Similarly the second zone is called orange zone. It extends from the contour with pressure level of 0.2068 to contour of pressure level 0.0207 bar (g). The pressure levels of this zone are sufficient to cause partial collapse of walls and roofs of houses. A slight distortion of steel frame buildings may also occur in this zone.

The third and the last zone vary from the contour with pressure level 0.0207 bar (g) to the contour with pressure level of 0.1379 bar (g). It is the projectile limit. Breaking of small windows under strain may occur.

The human body can bear the pressure levels of all the three zones without any major injury but the injuries can be caused by the collapse of structures and the buildings.

TOXIC HAZARDS

A toxic substance, when introduced into or absorbed by a living organism, can destroy life or injure health. A poison is a common term for a toxic substance. The term toxic release refers to the release of a toxic chemical either from a rupture or through an abnormal opening. There are large numbers of chemicals with which particular care needs to be taken to prevent them from having harmful effects on the population.

A toxic major gas incident occurs when there is,

1. An Accidental Release of the toxic substance
2. The substance fails to disperse after release and accumulates in hollow.

The human body is complex organism. What happens to chemical which enter the body, and hence what effects, depends upon:

- The way the chemical enters the body ;
- The metabolic process in the body;
- The toxicity of the chemical;
- Toxic exposure.

Bodies are designed to take raw materials (food, water, air), process them chemically and/ or biologically, and eliminate waste materials. It is very likely that it will recognize and seek to eliminate a toxic material. Toxic material in the body may enter the body via

- Respiratory system, by inhalation to lungs through nose or mouth;
- Digestive tract, by ingestion to stomach through the nose or mouth;
- Skin when intact or damaged, by absorption to blood circulatory system.

Materials entering via lungs may be absorbed into blood and hence transported around the body. Materials entering via the skin may also enter the blood. Digested material passes via the stomach to the intestines where, again, it may enter the blood. Materials can also enter through the eyes.

The term toxic exposure refers to the amount of a toxic substance to which an individual is exposed. This may represent the amount ingested, absorbed or inhaled, or it may refer to the integral of concentration with time in immediate environment. The exposure limit for the particular chemical which can be dangerous to human health is different for the different chemicals.

For example Chlorine is known to be dangerous to human health at concentration of 10-20 parts per million (ppm) for exposure of 30 minutes. The gas becomes fatal at concentrations of 100-150 ppm with exposure duration of 5-10 minutes. Similarly for ammonia the concentration which is fatal for human is 400-700ppm for 30-min exposure (Source- ILO's Major Hazard Control).

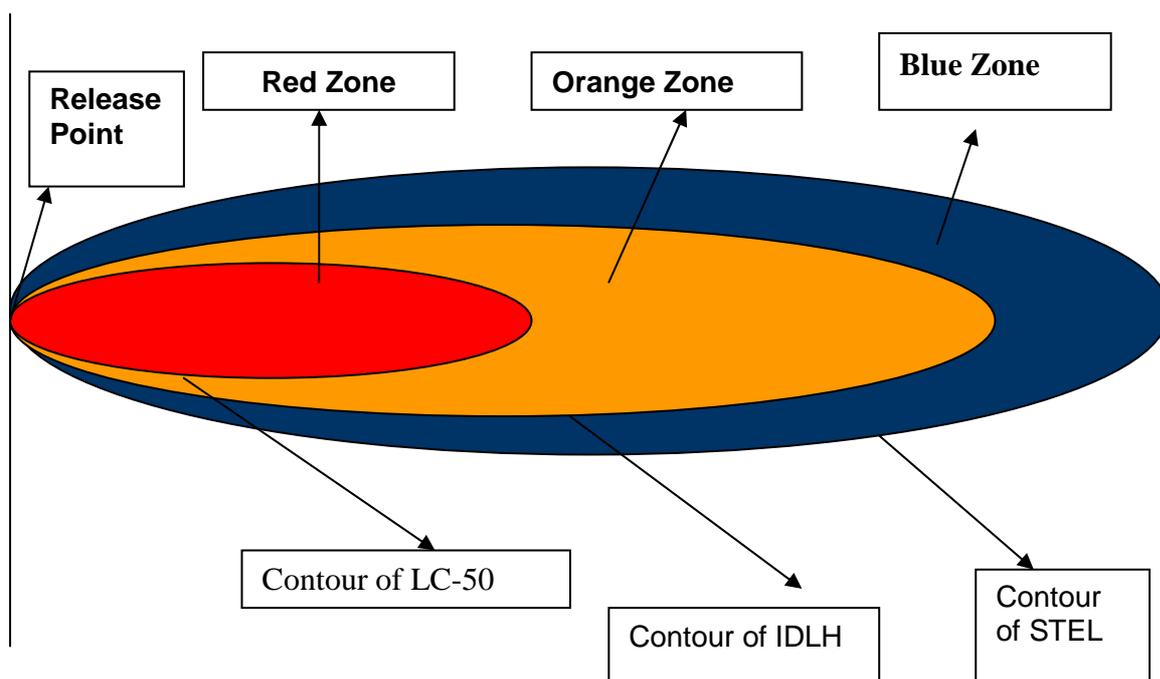
Toxic Zone

To understand exposure limits and their respective effects we can divide the affected area into three zones of various concentration levels. The three zones are Red, Orange & Blue.

Unlike the zones for the VCE & BLEVE the three dimensions express the zones for the toxic release. The length, width and height of a particular zone depend upon the following parameters:

- Molecular Weight of released chemical
- Rate of release
 - Mode of release
 - Fluid conditions
 - Phase of release
- The duration of release
- The quantity and composition of vapor evolved
- Weather Conditions
- Prevailing Wind Speed at the time of release
- Topography near the released point i.e. Flat land, Green Belt, Industrial estate or Village etc.

The prevailing wind speed and the weather conditions play the important role in determining the dimensions of the toxic plume. A stable weather condition with lesser wind speed result in to the formation of large plume. A neutral weather conditions with the moderate wind speed results in to the smaller plume than that of stable conditions. An unstable conditions with high wind speed result in to the smallest plume than that of stable /neutral conditions. The following figure shows the variation of plume dimension with different weather conditions.



Red zone

The span of the zone is shown in fig: toxic zones. The concentration of this zone can be lethal for the 50% of the total exposed population if the exposure last for more than 30minutes.

Orange zone

The area under this zone is the area amid concentration contour of LC-50 and the contour with concentration of IDLH (Immediately Dangerous to Life and Health). The exposure for more than 30 minutes may produces chronic health effects on the body.

Blue Zone

The area under this zone is the area amid concentration contour of IDLH and the contour with concentration of STEL (Short Term Exposure Limit). The exposure for more than 15 minutes may produce acute health effects on the body.
