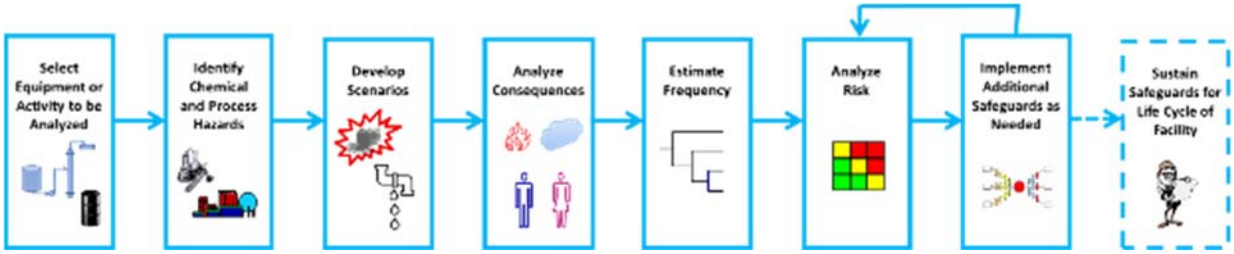
Chemical Hazards Engineering Fundamentals (CHEF)

CHEF Manual



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DOCUMENT INFORMATION

Purpose

This document, the CHEF manual, provides an overview of conceptual methods and mathematical techniques used within the Risk Analysis Screening Tool (RAST). RAST is intended to fill the gap between qualitative and detailed quantitative methods. This manual is available on the CCPS RAST/CHEF website [1].

Feedback Request:

Please provide feedback or comments on the content of this document to the RAST Committee, via the CCPS RAST/CHEF website [1].

Revision History:

This manual's history is located at the end of this document.

Disclaimer

It is sincerely hoped that the information presented in this document will lead to an even better safety record for the entire industry; however, neither the American Institute of Chemical Engineers, its consultants, CCPS Technical Steering Committee and Subcommittee members, their employers, their employers officers and directors, nor The Dow Chemical Company, and its employees warrant or represent, expressly or by implication, the correctness or accuracy of the content of the information presented in this document. As between (1) American Institute of Chemical Engineers, its consultants, CCPS Technical Steering Committee and Subcommittee members, their employers, their employer's officers and directors, and The Dow Chemical Company, and its employees, and (2) the user of this document, the user accepts any legal liability or responsibility whatsoever for the consequence of its use or misuse.

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1. INTRODUCTION

Intended Audience

The intended audience for the Chemical Hazard Engineering Fundamentals (CHEF) manual is personnel performing screening level or risk analyses (including Hazards Identification and Risk Analysis {HIRA} and Layers of Protection Analysis {LOPA}) for existing and future manufacturing facilities including:

- Manufacturing personnel
- Improvement engineers
- Process engineers
- Other process safety roles

The overall Learning Objectives for Chemical Hazard Engineering Fundamentals are:

- Develop familiarity with concepts and simple methods such that Hazard Evaluation Teams with the help of Facilitators, Technology Experts, and Process Safety Specialists should be able to perform screening level Hazard Identification and Risk Analysis studies.
- Demonstrate the models used in the CHEF Calculation Aid workbook.
- Document the methods utilized in the Risk Analysis Screening Tools (RAST) workbook.
- Understand the limitations of the methodologies and when to utilize more advanced methods or to engage a Subject Matter Expert.

Sections

There are 14 sections included in this Chemical Hazard Engineering Fundamental manual including:

1. Introduction (this section)
2. Flammability
3. Toxicity
4. Reactivity
5. Other Hazards
6. Hazard Screening
7. Hazard Evaluation
8. Introduction to Consequence and Risk Analysis
9. Source Models
10. Vapor Dispersions
11. Explosions
12. Impact Assessment
13. Likelihood Evaluation
14. Layer of Protection Analysis

Risk-Based Process Safety

Hazard Identification and Risk Analysis (HIRA) is part of an overall Process Safety program to protect people, property and the environment. The study team should be very familiar with their company's Process Safety Management Systems (such as Operating Procedures, Safe Work Practices, Asset Integrity and Reliability) to aid in developing the scope of an HIRA study. It may be that some hazards are adequately addressed by these management systems such that further consideration through HIRA may not be needed. It may also be that management systems adequately address lower risk situations but that higher risk portions of the chemical operations should be included in the HIRA. An example management system is the CCPS Risk Based Process Safety approach shown in Figure 1.1 [2] [3]. The HIRA is highlighted in Figure 1.1 as one of the RBPS Elements.

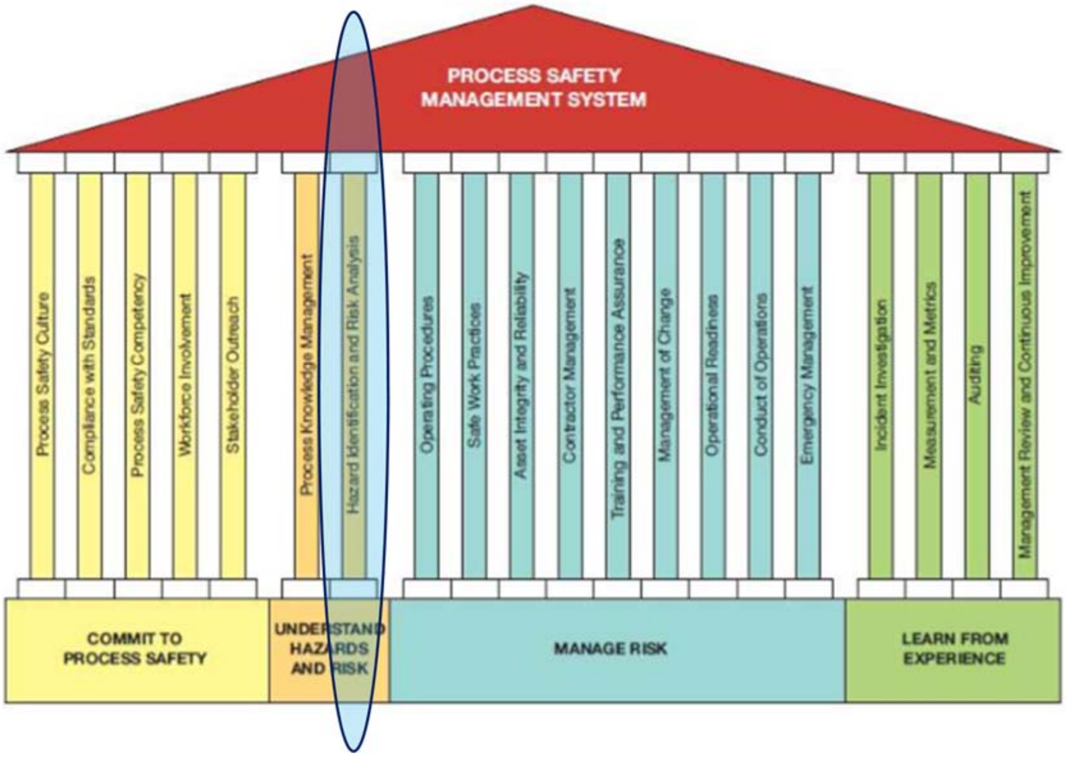


Figure 1.1 Four Building Blocks and 20 Elements of Process Safety in the CCPS RPBS Approach

General Approach to Hazard Identification and Risk Analysis

There are many methods and techniques commonly utilized within a Hazard Identification and Risk Analysis (HIRA) study. Only a few are described in this manual. Those described are generally simple methods often employing empirical correlations. The intent is to provide a reasonable result with minimal time and input information required. For complex evaluations, or when a more accurate result is warranted, more rigorous methods than described here may be needed.

Process Risk Management

Process Risk is a measure of human injury, environmental damage, or economic loss resulting from an incident in terms of both likelihood and magnitude of the loss or injury. Risk Management is the systematic application of management policies and procedures in analyzing, assessing, and controlling risk. It utilizes both *Risk Analysis* and *Risk Assessment.* Process Risk management is intended to continuously improve safety, health, and environmental performance of plants over the long term by addressing risk to people, property, and the environment. A simplified risk management flowchart is depicted in Figure 1.2.

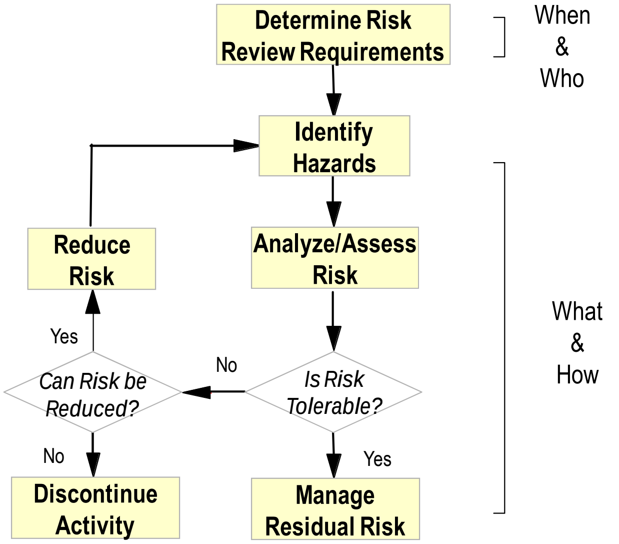


Figure 1.2 Simplified Risk Management Flowchart

Risk Analysis

Risk Analysis involves qualitative and quantitative Hazard Evaluation methods. Qualitative Hazard Evaluation techniques are commonly used to pinpoint weaknesses in process design and facility operation that could lead to incidents with potential safety consequences or impacts. Quantitative methods are typically used to determine the magnitude of an incident and estimate the likelihood of occurrence for a specific sequence of events leading to an Incident.

Risk Assessment

Risk Assessment in one form or another is inherent in all decision making. If the risk exceeds predefined and agreed upon criteria:

- Methods of reducing the risk must be implemented, or
- The activity creating the risk must be reviewed with corporate management to agree upon appropriate actions, or
- The activity creating the risk must be discontinued.

Hazard Identification and Risk Analysis

Hazard Evaluation and Risk Analysis is a collective term that encompasses all activities involved in identifying hazards and evaluating risk at facilities, throughout their life cycle, to make certain that risks to employees, the public, or the environment are consistently controlled within the organization's risk tolerance [4]. The Risk Analysis Screening Tool (RAST) is based on a suggested HIRA work process (Figure 1.3) to answer basic questions involving:

- What are the Hazards?
- What can go wrong?
- How Bad can it be?
- How Often might it happen?
- Is the Risk Tolerable?

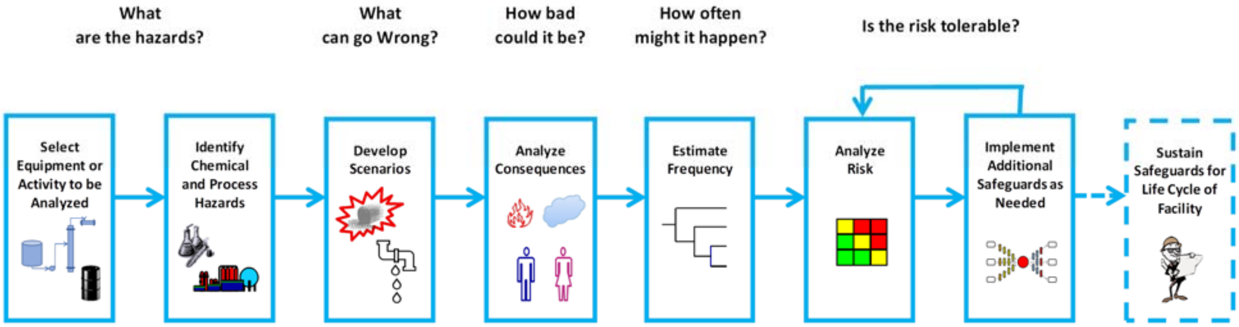


Figure 1.3 Overall Work Process Steps for Hazard Evaluation and Risk Analysis

The structure of the sections in the Chemical Hazards Engineering Fundamentals (CHEF) manual is based on performing each Hazard Identification and Risk Analysis (HIRA) task in a specific order. The order of task execution is based on an overall work flow such that results of a specific estimate (such as a source model) being available as input for the subsequent task (such as vapor dispersion). The overall Work Process for a HIRA includes:

Identify the Equipment or Activity for the analysis. For example, the operation of a storage tank, a reactor, a piping network, etc.

Identify Chemical and Process Hazards or “inherent chemical or physical characteristics that have the potential for causing damage to people, property, or the environment” [4]. Both Chemical and Operational related hazards are considered. Chemical Hazards include flammability, toxicity, corrosivity, and reactivity (stored chemical energy). Operational Hazards include stored pressure-volume energy, high or low temperature (potential for thermal burns) and, to some extent, electrical conductivity (potential for static discharge).

Development of Scenarios involves “a detailed description of an unplanned event or incident sequence that results in a loss event and its associated impacts, including the success or failure of safeguards involved in the incident sequence” [4]. Identification and development of scenarios through a Process Hazards Analysis (PHA) Team often involve qualitative techniques such as Brainstorming, What-IF Checklists, and Hazard and Operability Analysis (HAZOP) [5].

Consequence Analysis may be qualitative (based on judgment of the study team), simplified quantitative, or detailed quantitative. A simplified quantitative approach is described in the manual that uses various source and effect models from CCPS and other literature sources. Loss events are categorized as related to hole size (vapor, liquid, or two-phase), material balance (such as overfill), heat balance (such as vaporization resulting from fire exposure), rupture (instantaneous release) or equipment damage. Various Incident Outcome may result from a Loss Event such as Flash Fire, Vapor Cloud Explosion, Toxic Release, or Explosion damage. Finally, various effect models are used to estimate (and sometimes quantify) the impact to people, equipment, and the environment.

Scenario Frequency is estimated to provide an expected probability or frequency of occurrence for an event sequence.

Risk Analysis involves the combination of frequency and consequence magnitude for scenarios of concern. Commonly, order-of-magnitude results are utilized in simplified risk analysis. Scenarios of relatively low risk may be screened out from more detail risk analysis based on a company’s risk screening criteria. The screening criteria can be achieved through RAST for prioritizing the PHA Team recommendations.

During risk analysis, the study team may need to **Identify Additional cost-effective Safeguards** in order to manage risk to or below the tolerable risk criteria. Implementation of additional safeguards will typically reduce the frequency or severity of the scenario consequence. There is an option within RAST to use the semi-quantitative Layer of Protection Analysis (LOPA) to help identify any additional safeguards that can be used to lower the risk [6] [7].

Once appropriate safeguards and barriers have been implemented, they must be managed and **Sustained for the life of the facility** [8] [9].

The Risk Assessment process for decisions regarding specific requirements or management systems to appropriately manage or control risk are beyond the scope of CHEF Manual and CHEF's associated training.

Finding Chemical Process Hazard Information

There are several excellent resources to find chemical hazard information in preparation for a Hazard Identification and Risk Analysis study.

Safety Data Sheets (SDS)

Safety Data Sheets (SDS) are a typical source of information for hazards associated with the chemicals. Information for flammability, toxicity and environmental issues are commonly included. The US National Fire Protection Agency (NFPA) has a rating system for Flammability, Health, and Reactivity based on a numerical value from 0 to 4 (with 4 being most hazardous) commonly found on an SDS. The European Dangerous Substances Directive on Classification, Labeling and Packaging of Substances and Mixtures; in addition to the United Nations Globally Harmonized System (GHS) for Classification and Labeling of Chemicals, utilize *Physical Hazard Statements* and *Health Hazard Statements* based on quantitative measures which may be referenced on an SDS.

CAMEO

The CAMEO® software suite is a system of software applications used widely to plan for and respond to chemical emergencies. It is one of the tools developed by EPA and the National Oceanic and Atmospheric Administration (NOAA) to assist front-line chemical emergency planners and responders.

Hazard Classification criteria under NFPA 704

Classification criteria under the US National Fire Protection Agency [10]:

Health

4 – Materials that, under emergency conditions, can be lethal

3 – Materials that, under emergency conditions, can cause serious or permanent injury

2 – Materials that, under emergency conditions, can cause temporary incapacitation or residual injury

1 – Materials that, under emergency conditions, can cause significant irritation

0 – Materials that, under emergency conditions, would offer no hazard beyond that of ordinary combustible materials

Flammability

4 – Materials that will rapidly and completely vaporize at atmospheric pressure and normal ambient temperature or that are readily dispersed in air and will burn readily.

3 – Liquids and solids that can be ignited under almost all ambient temperature conditions.

2 – Materials that must be moderately heated or exposed to relatively high ambient temperatures before ignition can occur

1 – Materials that must be preheated before ignition can occur.

0 – Materials that will not burn under typical fire conditions including intrinsically noncombustible materials as concrete, stone, and sand.

Instability

4 – Materials that in themselves are readily capable of detonation or explosive decomposition or explosive reaction at normal temperatures and pressures

3 – Materials that in themselves are capable of detonation or explosive decomposition or explosive reaction but require a strong initiating source or must be heated under confinement before initiation.

2 – Materials which readily undergo violent chemical change at elevated temperatures and pressures

1 – Materials which can become unstable at elevated temperatures

0 – Materials that are normally stable, even under fire conditions

There may also be additional information associated with the NFPA classification including aquatic toxicity, oxidizing material, not to use water for fire-fighting, etc. The most reliable NFPA hazard ratings are typically found on Safety Data Sheets for the associated chemical supplier.

Hazard Classification criteria under *European Dangerous Substances* Directive or Globally Harmonized System (GHS) [11]

Classification criteria under European Dangerous Substances Directive on Classification, Labeling and Packaging of Substances and Mixtures and Globally Harmonized System for Classification and Labeling of Chemicals includes:

Flammability

<u>*Extremely Flammable*</u> – liquids with a Flash Point below 0°C and a Boiling Point less than 35°C or gaseous substances which are flammable in contact with air at ambient temperature and pressure

<u>*Highly Flammable*</u> – liquids with a Flash Point below 21°C which are not Extremely Flammable, solids or vapors which may readily catch fire in contact with ambient air.

<u>*Flammable*</u> – liquids having a Flash Point between 21°C and 55°C. (Note that the United Nations Globally Harmonized System – GLS - requires labeling liquids have a flash point less than 60°C as flammable.)

Toxicity

<u>*Fatal, Very Toxic*</u> – Oral LD_{50}, rat, < 25 mg/kg (Very Toxic if swallowed); Dermal LD_{50}, rat or rabbit, < 50 mg/kg (Very Toxic in Contact with Skin); Inhalation LC_{50}, rat, < 0.25 mg/liter/4 hr. for aerosols or particulates or < 0.5 mg/liter/4 hr. for gases and vapors (Very Toxic by Inhalation)

Toxic – Oral LD_{50}, rat, between 25 and 200 mg/kg (Toxic if swallowed); Dermal LD_{50}, rat or rabbit, between 50 and 400 mg/kg (Toxic in Contact with Skin); Inhalation LC_{50}, rat, between 0.25 and 1.0 mg/liter/4 hr. for aerosols or particulates –or- between 0.5 and 2.0 mg/liter/4 hr. for gases and vapors (Toxic by Inhalation)

Harmful – Oral LD_{50}, rat, between 200 and 2000 mg/kg (Harmful if swallowed); Dermal LD_{50}, rat or rabbit, between 400 and 2000 mg/kg (Harmful in Contact with Skin); Inhalation LC_{50}, rat, between 1.0 and 5.0 mg/liter/4 hr. for aerosols or particulates –or- between 2.0 and 20 mg/liter/4 hr. for gases and vapors (Harmful by Inhalation)

In addition to these classification criteria, specific risk and safety sentences (R and S sentences) are used that may clarification the hazard information.

Other Sources for Chemical Hazards Information

In addition to these Hazard Ratings found on an SDS, flammability information such as flash point or lower flammable limit, toxicity information such as Emergency Response Planning Guideline (ERPG) concentrations [12], and reactivity information such as heat of reaction may be used. This information may be found in Cameo Chemicals (a downloadable database for emergency responders of hazardous chemicals available through the US National Oceanic and Atmospheric Administration) [13], the Chemical Reactivity Worksheet [14], and other literature sources.

2. FLAMMABILITY

Potential consequences from fires within chemical and hydrocarbon facilities can be significant. Fire related incidents can cause significant business interruption and loss of life.

Section Objectives

The following objectives are covered in this section:

- The definitions for Lower and Upper Flammable Limits (LFL, UFL) and Limiting Oxygen Concentration (LOC).
- Identification of LFL, UFL, and LOC on a flammability diagram.
- Estimation of Flammable Limits for Vapor Mixtures
- The definition of Flash Point
- The definitions for Explosion, Deflagration and Detonation
- Fundamental Burning Velocity and Deflagration Index
- The definition of Combustible Dust
- Phrases related to the concepts of the Dust Explosion Pentagon
- Identification of common ignition sources
- Concepts for managing ignition sources.

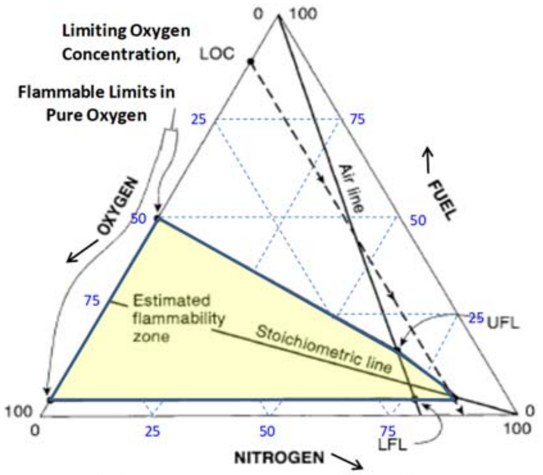
Fire Triangle

The essential elements for combustion are fuel, an oxidizer, and an ignition source. This can be represented by a “fire triangle” with each of the sides of the triangle representing these three elements. Fires (combustion) – occur in the vapor phase: liquids are volatilized and solids decompose into vapor prior to ignition and combustion**.**

Flammability Parameter Definitions

- *Flash Point (FP)* – lowest temperature at which a liquid will give off sufficient vapor to be ignited in air.
- *Lower Flammability Limit (LFL)* – lowest ***vapor*** concentration of a substance in air that will sustain combustion when exposed to sufficient ignition source.
- *Upper Flammability Limit (UFL)* – highest ***vapor*** concentration of a substance in air that will sustain combustion when exposed to sufficient ignition source.
- *Limiting Oxygen Concentration (LOC)* – minimum oxygen concentration required to propagate a flame.
- *Minimum Ignition Energy (MIE)* – minimum amount of energy required to ignite a combustible vapor, gas or dust cloud.
- *Autoignition Temperature (AIT)* – lowest temperature at which a material will spontaneously ignite and continue burning in a normal atmosphere without an external source of ignition, such as a flame or spark.

Several flammability properties can be explained by the use of a triangular flammability diagram (Figure 2.1). Typically, the diagram is defined by the concentration of the chemical of concern, the oxygen concentration and concentration of inert gas present (typically nitrogen). The flammability envelope is pie-shaped and a function of the oxygen concentration. The greater the oxygen content, the wider the flammable concentration.



Note that Flammability Diagrams represent specific conditions of temperature and pressure (often ambient temperature ant atmospheric pressure)

Figure 2.1 Flammability Diagram

Predict Safe Oxygen in Combustible Gases describes a method to construct an approximation of a flammability diagram from limited data [15].

Where to Obtain Flammability Data

Flammability data for common chemicals can often be found in the open literature such as SDSs, NFPA standards, or even internet searches. Example flammability data from the literature is compiled from various resources in Table 2.1.

Table 2.1 Example Flammability Data

Chemical	Boiling Point (C)	Flash Point (C)	Lower Flammability Limit (vol %)	Upper Flammability Limit (vol %)	Autoignition Temperature (C)
acetone	56.1	-17.8	2.6	13	465
ammonia	-33.4	-	15	28	650
i-butane	-11.8	-81.2	1.6	8.4	460
carbon disulfide	46.2	-30	1.3	50	90
carbon monoxide	-191.5	-	12.5	74	609
ethanol	78.3	13	3.3	19	365
ethyl chloride	12.3	-50	3.5	15.8	519
ethylene oxide	10.5	-50	3	100	429
n-hexane	68.7	-22	1.1	7.5	226
hydrogen	-252.8	-	4	75.6	400
methane	-161.5	-187.2	5	15	537
methanol	64.5	11	6.7	36	385
methyl acetate	57	-10	3.1	16	454
n-octane	125.6	13	0.95	6.5	206
propane	-42.1	-102.2	2.1	9.5	450
i-propanol	82.2	12	2.2	12	399
styrene	145.2	31	0.88	6.84	470
toluene	110.6	4	1.08	7.06	480

Estimation of Flammable Limits for Vapor Mixtures

The Lower Flammable Limit (LFL) is the primary parameter for evaluating flammability hazard for vapors and is roughly 45 g/m^3 for many hydrocarbons. As mixtures are common in chemical processing, the mixture LFL is routinely needed and may be estimated from Le Chatelier's equation, Equation 2-1 [16, p. 253]:

$$\mathbf{LFL_{mix} = 1 / \Sigma\ (\ y_i / LFL_i\ )} \qquad \text{Equation 2-1}$$

where y_i is the vapor mole fraction and LFL_i the Lower Flammable Limit for each component i.

The Upper Flammability Limit (UFL) for mixtures may also be estimated from Equation 2-1. The LFL in air generally decreases slightly with increasing temperature and is not dependent on pressure. The UFL generally increases slightly with increasing temperature and increases significantly with increasing pressure. The Le Chatelier equation assumes flammable limits for each component are measured at the same temperature and that combustion kinetics is independent of the presence of other components in the mixture.

Example Estimation of LFL for Vapor Mixtures

As an example; the estimated lower flammable limit for a mixture at ambient temperature in air for 0.5 mole fraction methane (LFL of 5 %) and 0.5 mole fraction carbon disulfide (LFL of 1.1 %) is:

$$LFL_{mix} = 1 / \Sigma\ y_i / LFL_i = 1 / [\ 0.5 / 5 + 0.5 / 1.1\ ] = 1 / 0.5545 = 1.8 \text{ volume } \%.$$

Estimation of Flash Point for Liquid Mixtures

As noted earlier, the Flash Point is the primary parameter for evaluating flammability hazard for liquids. Flash Point *for a liquid mixture* in air may be roughly estimated as the temperature at which the equilibrium *vapor* composition (at atmospheric pressure) is approximately equal to the Lower Flammable Limit (in volume fraction). Experimentally determined values are always recommended, particularly for mixtures containing more the one flammable component.

Liquid Aerosol or Mist

Release of a liquid aerosol or mist (resulting from a high velocity release or condensed vapor) may result in an energetic explosion as the mass of fuel per volume is large relative to vapor. Operations such as splashing, aeration and vigorous agitation where electrostatic charging and atomization may occur should be avoided or maintained within an inert atmosphere. Aerosol below its flash point may be ignited although a strong ignition source may be required, as the liquid must partially vaporize to ignite.

Aerosol with droplet size less than 0.01 mm quickly evaporates and acts similar to flammable vapor with respect to Minimum Ignition Energy, Lower Flammable Limit and Fundamental Burning Velocity[17]. Aerosol with droplet diameter greater than 0.04 mm acts similar to a dust where droplets may burn individually and the Minimum Ignition Energy required increases with increasing droplet size[8]. Aerosol droplets greater than 0.6 mm typically do not support flame propagation [16, pp. 274-275].

Limiting Oxygen Concentration

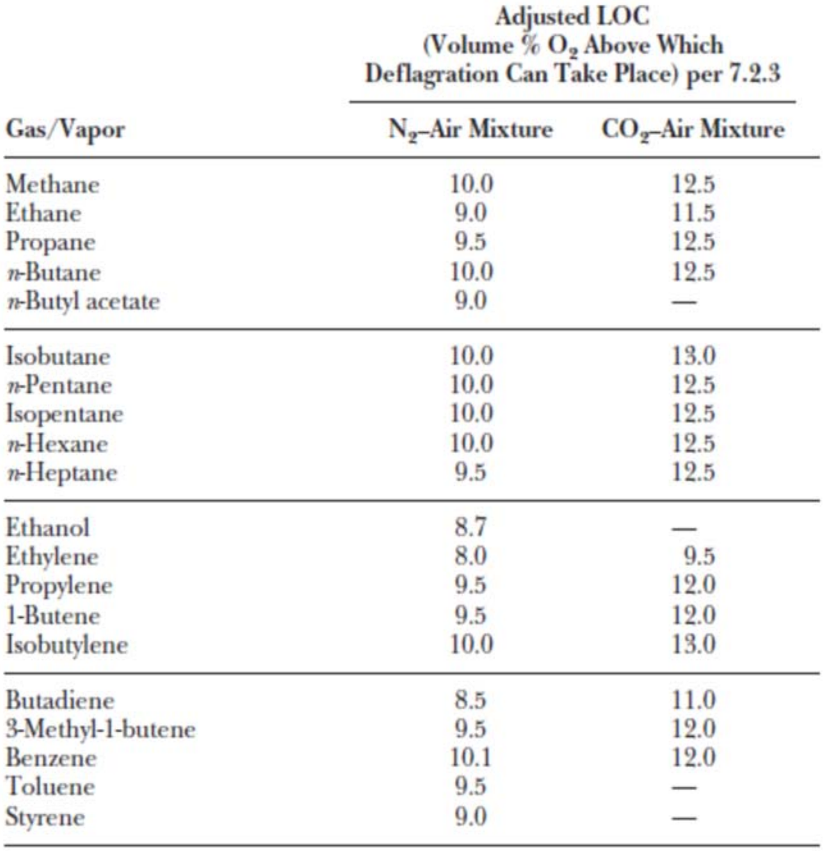
Most organics have a Limiting Oxygen Concentration (LOC) of roughly 9 to 10 volume % if N_2 is the inert (Table 2.2). At less than 9-10% oxygen (e.g. by adding an inert gas to the system), it is not possible to have a flammable atmosphere.

Notable exceptions to the 9-10% Limiting Oxygen Concentration are:

Acetylene	2.5%
Carbon disulfide	1.3%
Carbon monoxide	12%
Ethylene Oxide	3%
Hydrogen	4%
Propylene Oxide	2.3%

Note that less than 5 volume % oxygen is typically considered a “non-ignitable” atmosphere (based on roughly ½ the limiting oxygen content).

Table 2.2 Limiting Oxygen Concentration



	Adjusted LOC (Volume % O_2 Above Which Deflagration Can Take Place) per 7.2.3	
Gas/Vapor	N_2–Air Mixture	CO_2–Air Mixture
Methane	10.0	12.5
Ethane	9.0	11.5
Propane	9.5	12.5
n-Butane	10.0	12.5
n-Butyl acetate	9.0	—
Isobutane	10.0	13.0
n-Pentane	10.0	12.5
Isopentane	10.0	12.5
n-Hexane	10.0	12.5
n-Heptane	9.5	12.5
Ethanol	8.7	—
Ethylene	8.0	9.5
Propylene	9.5	12.0
1-Butene	9.5	12.0
Isobutylene	10.0	13.0
Butadiene	8.5	11.0
3-Methyl-1-butene	9.5	12.0
Benzene	10.1	12.0
Toluene	9.5	—
Styrene	9.0	—

Partial Listing of Limiting Oxygen Concentration per NFPA 69 [17]

Fire and Explosion - Definitions

The major distinction between a Fire and an Explosion is the *combustion rate* of a flammable gas, vapor or dust and *degree of confinement* where combustion is occurring. Explosions can occur within buildings, equipment, or in potentially congested outdoor areas. The definitions are as follows [4]:

- ***Explosion:*** A release of energy that causes a pressure discontinuity or blast wave. An explosion typically requires some level of confinement (such as within a vessel, piping, or building) or a process area of high equipment or structure congestion.

- *Deflagration:* Propagation of a combustion or reaction zone at a speed that is less than the speed of sound in the un-reacted medium.
- *Detonation:* Propagation of a combustion or reaction zone at a velocity that is greater than the speed of sound in the un-reacted medium:

Fundamental Burning Velocity

The Fundamental Burning Velocity (or flame speed) in air is indication of combustion rate and potential explosion energy for *vapors*. Fuels with fundamental burning velocity less than 45 cm/sec (such as ammonia and methane) are considered “low fuel reactivity” while fuels with fundamental burning velocity greater than 75 cm/sec (such as acetylene, ethylene oxide, and hydrogen) are considered “high fuel reactivity” resulting in more energetic explosion. Most organic materials exhibit a fundamental burning velocity between 45 and 75 cm/sec and are considered “medium reactivity fuels” (Table 2.3).

Table 2.3 Fundamental Burning Velocities (adapted from **[18, p. Annex C]**)

Fundamental Burning Velocities for Selected Flammable Gases in Air
(NFPA 68 Annex C)

	(cm/sec)
Acetone	**54**
Acetylene	**166**
Benzene	**48**
n-Butane	**45**
Carbon Disulfide	**58**
Carbon Monoxide	**46**
Ethylene	**80**
Ethylene Oxide	**108**
Hydrogen	**312**
Isopropyl Amine	**31**
Methane	**40**
Methanol	**56**
Propane	**46**
Toluene	**41**

Combustible Dusts

A *Combustible Dust* is any finely divided solid material, 420 microns [19] (0.42 mm, 1 mm per some European standards) or smaller in diameter (passing U.S. No. 40 Standard Sieve) which presents a fire or explosion hazard when dispersed and ignited in air. *Particle size* is extremely important in characterizing combustible dusts. The smaller the particle, the easier to suspend in air and ignite. The influence of particle size on the combustion rate is shown in Figure 2.2. In addition, the Explosible Range of dust concentration is very broad [16, p. 287] typically from 20 to 6000 g/m^3.

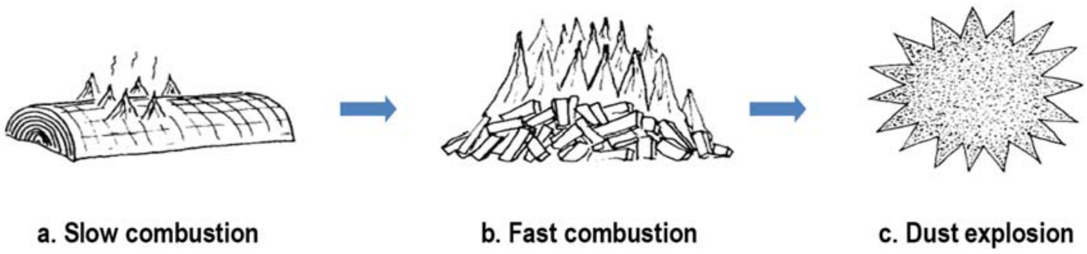


Figure 2.2 Influence of Particle Size on Combustion Rate

Dust Explosion Pentagon

The typical fire triangle does not adequately represent the combustion of dusts. In addition to confinement (which also applies to vapor systems), dusts require suspension or aeration to form an explosive cloud. The dust pentagon is used to represent the conditions for a dust explosion (Figure 2.3). Note that if the confinement element is removed, there is still the potential for a flash fire with combustible dusts.

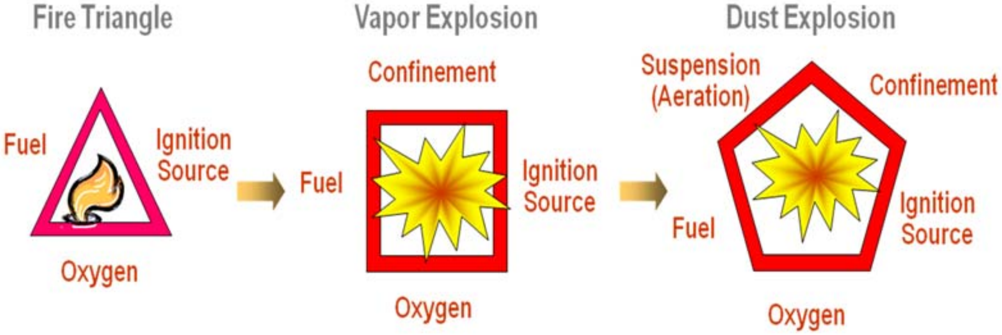


Figure 2.3 the Dust Pentagon

Suspended dust burns more rapidly, and confinement allows for pressure buildup. Removal of either the suspension or the confinement prevents an explosion, although a flash fire may still occur and harm personnel in the fire zone.

Secondary Dust Explosion

An initial explosion or process upset creates a pressure wave that dislodges accumulated dust from the structure (Figure 2.4). Ignition of this suspended dust may lead to a devastating *secondary explosion* that may result is greater damage than the initial incident.

- Good Housekeeping is critical for managing the potential for Secondary Dust Explosions.
- In addition, areas requiring special electrical equipment classification due to the presence (or potential presence) of combustible dust should be identified.

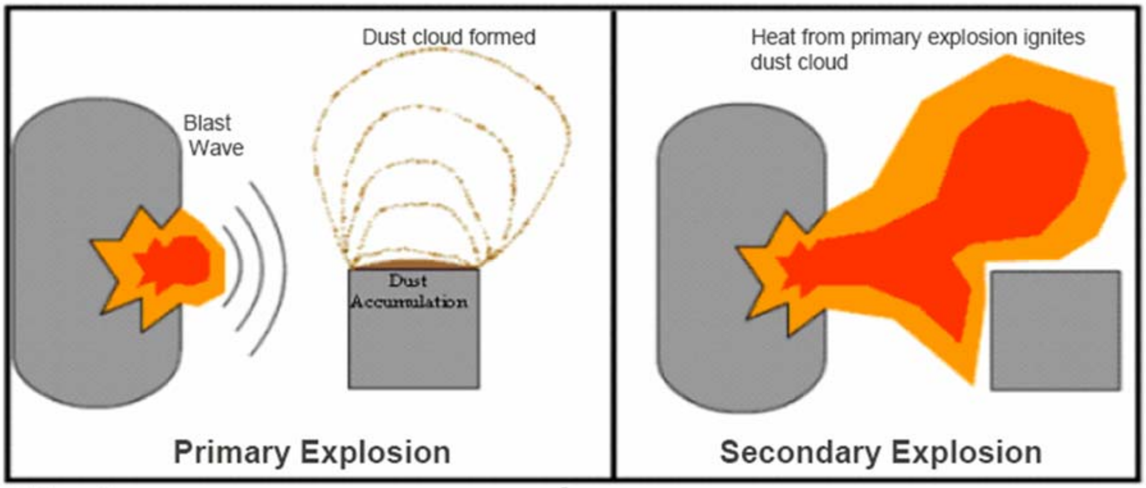


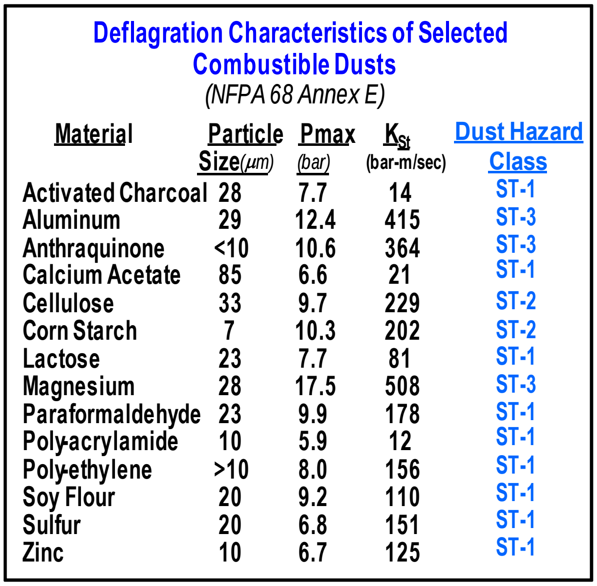
Figure 2

Figure 2.4 Secondary Explosion Mechanism [20]

Deflagration Index

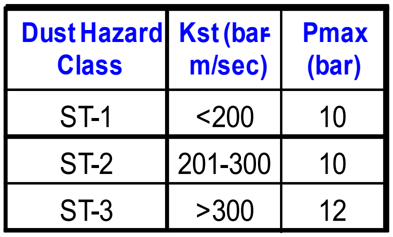
Deflagration Index (K_{St}) is the maximum rate of pressure rise *normalized* to the volume of the vessel in which the explosion occurs. For a given chemical and vessel geometry, it is reasonably constant over a broad volume. The Deflagration Index typically increases with increasing initial temperature and, in the case of dusts, decreasing particle size (Table 2.4). The Deflagration Index for dusts is categorized into three classes with Class "ST-3" (or Class 3) being the most energetic.

Table 2.4 Dust Deflagration Characteristics and Deflagration Index (adapted from [18])



Deflagration Characteristics of Selected Combustible Dusts
(NFPA 68 Annex E)

Material	Particle Size (μm)	Pmax (bar)	K_{St} (bar-m/sec)	Dust Hazard Class
Activated Charcoal	28	7.7	14	ST-1
Aluminum	29	12.4	415	ST-3
Anthraquinone	<10	10.6	364	ST-3
Calcium Acetate	85	6.6	21	ST-1
Cellulose	33	9.7	229	ST-2
Corn Starch	7	10.3	202	ST-2
Lactose	23	7.7	81	ST-1
Magnesium	28	17.5	508	ST-3
Paraformaldehyde	23	9.9	178	ST-1
Polyacrylamide	10	5.9	12	ST-1
Polyethylene	>10	8.0	156	ST-1
Soy Flour	20	9.2	110	ST-1
Sulfur	20	6.8	151	ST-1
Zinc	10	6.7	125	ST-1



Dust Hazard Class	Kst (bar-m/sec)	Pmax (bar)
ST-1	<200	10
ST-2	201-300	10
ST-3	>300	12

Maximum Explosion Pressure

The maximum explosion pressure for organic materials (gas, vapor, or dust) with air ranges from 6 to 12 atmospheres starting from atmospheric pressure. A maximum pressure of 10 atmospheres for deflagration within equipment is commonly used in Hazard Evaluation [21, p. 219].

Minimum Ignition Energy

The Minimum Ignition Energy (MIE) for most flammable vapors is very low compared to ignition sources. Human electrostatic discharge (initiated by walking across carpet) is roughly 20 mJ and much higher than the MIE for nearly all vapors (except ammonia).

The MIE for dust is generally much higher than for flammable vapors and highly dependent on particle size (with smaller particle size resulting in a lower MIE, Figure 2.5). Moisture content is also important with dry material generally having a lower MIE. *Minimum Ignition Energy and Particle Size are the primary parameters for evaluating flammability hazard for dusts.* Be aware of locations where fine dust can accumulate (such as a dust collector or overhead beams / rafters).

The hazard properties of combustible dusts *cannot* be determined theoretically, it is necessary to have test data on specific materials at the operating conditions of concern.

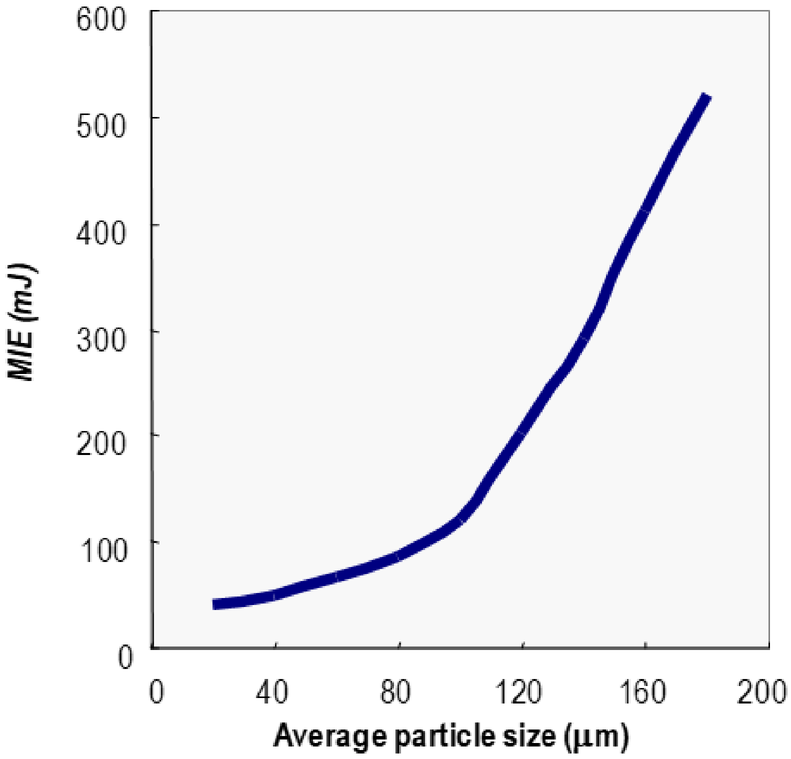


Figure 2.5 Impact of Particle Size on Minimum Ignition Energy for Typical Agricultural Dust (adapted from [18])

Hybrid Mixtures of Dusts and Flammable Liquids generally exhibit a Minimum Ignition Energy of the flammable liquid (which is typically much lower than that of the dust).

Managing Ignition Sources

The sources of ignition are numerous and often difficult to identify and eliminate [22] [23]. Common ignition sources include:

- Hot surfaces (such as heaters, dryers, and hot bearings)
- Open flames (such as a fired heater or boiler)
- Nearby Combustion Engines (such as cars, trucks, or machinery)
- Hot work (from welding, cutting, grinding, or other spark producing activity)
- Smoldering (such as combustion within dust piles or insulation)
- Electrical and Static discharges (from switches, relays, loose connections, etc.)

Adiabatic Compression

There have been significant incidents caused by flammable vapors being drawn into a compressor and heated to a temperature exceeding the Autoignition Temperature, resulting in ignition. The final temperature in a compressor can be determined with Equation 2-2:

$$\mathbf{T_f = T_0 \left(P_f / P_0\right)^{(\gamma-1)/\gamma}} \qquad \text{Equation 2-2}$$

where: T_0 and P_0 are the initial absolute temperature and pressure, T_f is the final temperature. (Note that γ for air is 1.4 such that the exponent above is roughly 0.29)

A compressor is particularly susceptible to reaching autoignition temperatures if it has a fouled after-cooler. A compression ratio, P_f / P_0, of 10 to 20 can heat vapor from ambient temperature to greater than 400 C for many vapors.

Static Electricity

One of the most elusive ignition sources within chemical plants is sparks resulting from static charge build-up and sudden discharge [16, p. 333]. In order to have an electrostatic scenario for ignition of a fire or explosion, there must be Separation and Accumulation of electrostatic charges, sudden Discharge, and an Ignitable Atmosphere.

Charges may be separated as fluids are pumped, mixed, stirred or otherwise transported. Significant charge separation can also occur when there is movement between two phases (gas with solids, two liquid phases, liquid with solid particles or gas bubbles), particularly if the continuous phase is non-conductive (or an insulator). At the same time there is a competing mechanism of charge relation. When charge separation exceeds relaxation or dissipation, accumulation occurs. Accumulation may occur at an ungrounded conductor, the surface of an insulator, or within an insulator.

Sudden discharge occurs between a charged surface (such as a bag, pipe, wall, aerosol or mist, dust cloud, or bulk powder) and a grounded conductor (such as tools, vessel protrusions, instruments, or a person's finger) or between two isolated conductive objects (one of which is charged to a higher potential than the other). The discharge energy commonly associated with *ungrounded* equipment is typically much higher than that required for ignition of flammable vapors. Note: nonconductive materials of construction or non-conductive linings (examples: fiberglass, glass) used with flammable liquids have a high ignition risk associated with charged surfaces.

Managing Electrostatic Discharge from Liquids and Solids

Relaxation is a reduction in stream velocity to provide time for electrostatic charge to dissipate. For liquid flow rate into a vessel, velocity times pipe diameter of less than 0.5 m^2/sec be used for filling of tank trucks to minimize static build-up of nonconductive liquids [24].

Bonding and Grounding reduces the voltage difference of all electrically connected components while grounding reduces the voltage of the entire system to zero. Use of conductive Dip Pipes extending below the liquid surface may also reduce the electrical charge that accumulates when liquid is allowed to free fall.

Increasing Fluid Conductivity with Additives may sometimes be used to minimize charge build-up between solid particles or liquid phases.

Inertion of the equipment atmosphere below the Limiting Oxygen Concentration may be needed if electrostatic discharges cannot be adequately managed.

3. TOXICITY

A potential toxic vapor release into a public area represents one the greatest risks for any facility.

Section Objectives

The following objectives are covered in this section:

- Response to Toxic Dose
- The definition of LC_{50} and LD_{50}.
- Understand the definition of Emergency Response Planning Guideline (ERPG) concentration
- Be able to estimate the equivalent ER value for a vapor mixture.
- Understand the relationship for Inhalation Toxic Dose with exposure duration.
- Be able to determine what concentration of non-toxic vapor represents an asphyxiation hazard.
- Recognize liquid exposure hazards of dermal toxicity, thermal and chemical burns.

How Toxicants Enter Biological Organisms

Toxic hazard is the likelihood of damage to biological organisms based on exposure resulting from transport and other physical factors of usage. Toxicants enter biological organisms by the following routes:

- ingestion: through the mouth into the stomach,
- inhalation: through the mouth or nose into the lungs,
- injection: through cuts into the skin,
- dermal absorption: through skin membrane.

Inhalation and dermal routes are the most significant routes for Process Safety. However, Ingestion Toxicity is important to understand potential environmental impacts of releases.

Toxicological Studies

Acute toxicity is the effect of a single exposure or a series of exposures close together in a short time period. Process Safety considers primarily Acute rather than Chronic toxicity.

- For most toxicological studies, animals are used with the expectation that results be extrapolated to humans.
- The test animal depends on the effects to be measured, cost and availability.
- Dose measurement depends on the methods of delivery.
  - Ingestion and injection are typically milligrams of agent per kg of body weight.
  - Inhalation is typically concentration in air (ppm or mg/m^3) for a test period.
- Initiating of new animal studies is expensive and a "last resort" in obtaining data

Response to Toxic Dose

There are many modes of action and some chemicals may have more than one mode, disrupting more than one biological system in the body. Some chemicals attack the respiratory system (such as acid gases), induce narcosis (a stupor, drowsiness, or unconsciousness), the central nervous system or other specific organs.

Within a biological species, organisms respond differently to the same dose of a toxicant. These differences are a result of age, weight, diet, general health, and other factors. The typical toxic-dose response rate is depicted in Figure 3.1.

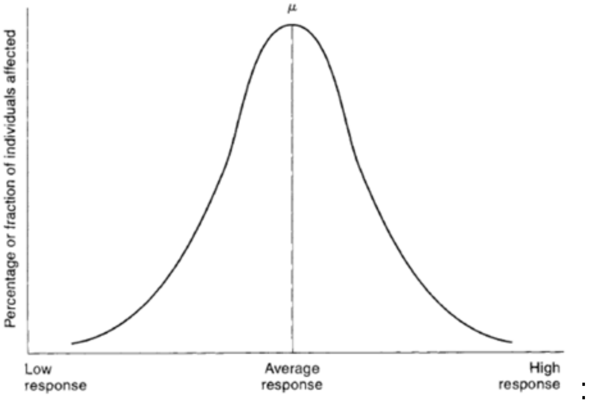


Figure 3.1 Typical Toxic Dose-Response Curve [21, p. 245]

Lethal Concentration and Lethal Dose

<u>*LC*</u> is “Lethal Concentration “. For inhalation experiments, the concentration of the chemical in air that kills 50% of the test animals in a given time (usually four hours) is the LC_{50} value. The LC_{10} value is the concentration which kills 10% of the test animals in a given exposure time.

<u>*LD*</u> is “Lethal Dose”. LD_{50} is the amount of a material, given all at once, which causes the death of 50% (one half) of a group of test animals. The LD_{50} is one way to measure the short-term poisoning potential (acute toxicity) of a material.

LC_{50} is used in the comparison of toxicities. For inhalation, LC_{50} is measured in micrograms (or milligrams) of the material per liter or cubic meter, or in parts per million (ppm) by volume. The lower the concentration, the more toxic the material. Note that LC_{50} values cannot be directly extrapolated from one specie to another or to humans.

Toxic Criteria for Risk Screening

A simple approach for screening of toxic risk is to specify a concentration criterion above which it is assumed that individuals exposed to this value will be in danger.

There are many criteria issued by government agencies and private associations including (references are provided when data from these sources is noted in the following sections):

- Emergency Response Planning Guidelines (ERPGs) for air contaminants issued by the American Industrial Hygiene Association (AIHA)
- Immediately Dangerous to Life and Health levels (IDLH) established by NIOSH
- Emergency Exposure Guidance Levels (EEGLs) and Short-term Public Emergency Guidance Levels (SPEGLs) issued by the National Academy of Sciences/National Research Council
- Acute Exposure Guideline Level (AEGL) – a toxic endpoint issued by the US EPA as part of the Risk Management Process (RMP)
- Protective Action Criteria (PAC) – a database published by the US Department of Energy containing ERPG, AEGL and Temporary Emergency Explosion Guideline (TEEL) values for hazardous chemicals

Emergency Response Planning Guidelines (ERPG)

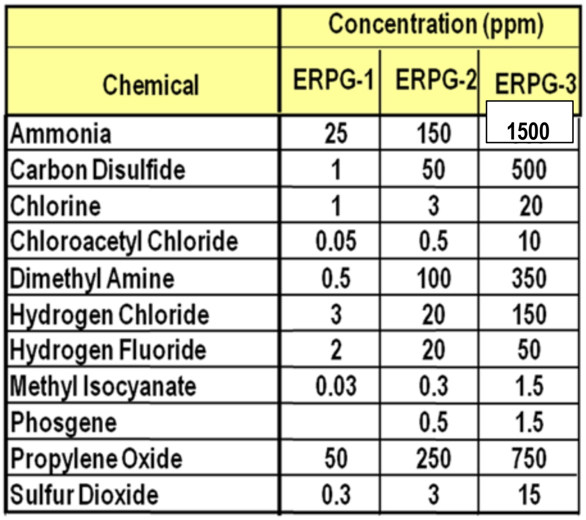
Emergency Response Planning Guideline (ERPG) concentration values (Table 3.1) are published by the American Industrial Hygiene Association and undergo comprehensive peer review [25]. The list of values has expended in recent years such that ERPGs have become broadly acceptable within industry and government.

ERPG-1: the maximum airborne concentration below which nearly all individuals could be exposed for up to one hour without experience effects other than mild transient adverse health effects or perceiving an objectionable odor.

ERPG-2: the maximum airborne concentration below which nearly all individuals could be exposed for up to one hour without developing serious health effects that could impair their ability to take protective action.

ERPG-3: the maximum airborne concentration below which nearly all individuals could be exposed for up to one hour without developing life threatening health effects.

Table 3.1 Example ERPG Values (adapted from [25]**)**



	Concentration (ppm)		
Chemical	ERPG-1	ERPG-2	ERPG-3
Ammonia	25	150	1500
Carbon Disulfide	1	50	500
Chlorine	1	3	20
Chloroacetyl Chloride	0.05	0.5	10
Dimethyl Amine	0.5	100	350
Hydrogen Chloride	3	20	150
Hydrogen Fluoride	2	20	50
Methyl Isocyanate	0.03	0.3	1.5
Phosgene		0.5	1.5
Propylene Oxide	50	250	750
Sulfur Dioxide	0.3	3	15

Inhalation Toxic Dose

Dose is complex as it involves both *concentration and duration*. The potential for adverse health consequences from a toxic vapor is related to concentration and duration of exposure by Equation 3-1.

$$\textbf{Toxic Dose} = C^n t \qquad \text{Equation 3-1}$$

For time varying concentration, dose is commonly evaluated by summation of time increments, as shown with Equation 3-2 [21, p. 260]:

$$\textbf{Toxic Dose} = \Sigma C_i^n \Delta t_i \qquad \text{Equation 3-2}$$

Where:

C is concentration
n an exponent specific to the chemical evaluated
Δt is exposure time increment

For inhalation, values of n ranges from 0.5 to 3 with most chemicals between 1 and 2. A value of 2 if often used if there is not sufficient data at different test durations for estimation of "time scaled" ER values to exposure duration less than one hour. If extrapolation of the “time scaled” ER to greater than one-hour exposure is needed (rare situation), an “n” of 1 is often used.

Estimation of an equivalent toxic dose becomes based on exposure duration divided by test duration raised to the 1/n exponent. The concentration providing a one-hour equivalent dose to a 4-hour test would be twice the test concentration for an exponent of 2.

Inhalation Toxic Mixtures

The ER values for toxic chemicals may be orders of magnitude different from each other.

- Assuming the entire mixture at a toxicity equivalent to the “worst component” may be grossly conservative.
- Assuming the toxicity of each chemical is independent of other toxic materials in the mixture may underestimate the hazard

The US Department of Energy and others have recommended an “additive” approach (which is similar to Le Chatelier’s rule), as is shown in Equation 3-3 [26]:

$$\mathbf{ERPG_{Mixture} = 1 / \Sigma\ (y_i / ERPG_i)} \qquad \text{Equation 3-3}$$

This additive approach is also used for classifying the acute toxicity of mixtures under the United Nations Globally Harmonized System (GHS).

Example Estimation of Equivalent ERPG-3 for Vapor Mixtures

As an example; the estimated ERPG-3 for a mixture of 0.5 mole fraction sulfur dioxide (ERPG-3 of 15 ppm) and 0.5 mole fraction carbon disulfide (ERPG-3 of 500 ppm) is:

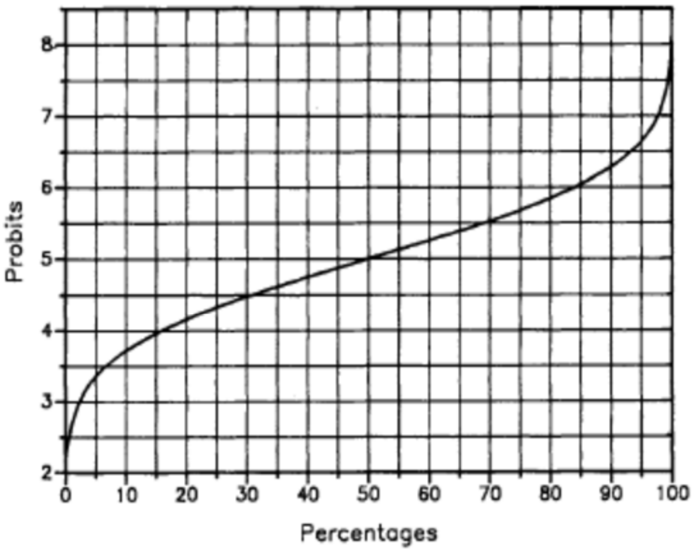
$$\text{ERPG-3}_{mix} = 1 / \Sigma\ y_i / \text{ERPG-3}_i = 1 / [\ 0.5 / 15 + 0.5 / 500\ ] = 1 / 0.034 = 29 \text{ ppm}$$

Lethality Models

The response versus dose curve shown in Figure 3.1 is not particularly convenient approach for analysis of toxic effects. For single exposures, the probit (probability unit) method provides transformation of the dose-response curve to a straight line. The Probit Model relates log (Dose) with a “Probit Value” as:

$$\text{Probit} = a + b \ln(\text{Dose}) = a + b \ln(C^n\ t)$$

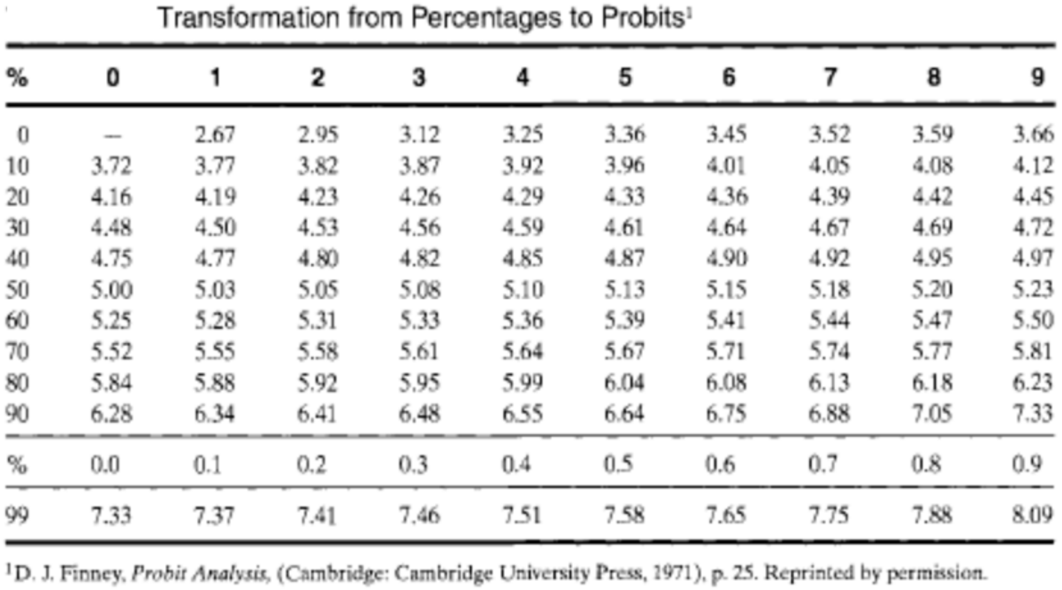
The probit value is then related to percent probability using the graph (Figure 3.2) or table (Table 3.2). As examples, the probit for 1% likelihood is 2.67 while that for 50% likelihood is 5.0.



The relationship between percentages and probits. (Source: D. J. Finney, *Probit Analysis*, 3d ed. (Cambridge: Cambridge University Press, 1971), p. 23. Reprinted by permission.

Figure 3.2 Probits versus Percentages [21, p. 247]

Table 3.2 Table of Percentage to Probits [21, p. 247]



Transformation from Percentages to Probits[1]

%	0	1	2	3	4	5	6	7	8	9
0	—	2.67	2.95	3.12	3.25	3.36	3.45	3.52	3.59	3.66
10	3.72	3.77	3.82	3.87	3.92	3.96	4.01	4.05	4.08	4.12
20	4.16	4.19	4.23	4.26	4.29	4.33	4.36	4.39	4.42	4.45
30	4.48	4.50	4.53	4.56	4.59	4.61	4.64	4.67	4.69	4.72
40	4.75	4.77	4.80	4.82	4.85	4.87	4.90	4.92	4.95	4.97
50	5.00	5.03	5.05	5.08	5.10	5.13	5.15	5.18	5.20	5.23
60	5.25	5.28	5.31	5.33	5.36	5.39	5.41	5.44	5.47	5.50
70	5.52	5.55	5.58	5.61	5.64	5.67	5.71	5.74	5.77	5.81
80	5.84	5.88	5.92	5.95	5.99	6.04	6.08	6.13	6.18	6.23
90	6.28	6.34	6.41	6.48	6.55	6.64	6.75	6.88	7.05	7.33
%	0.0	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9
99	7.33	7.37	7.41	7.46	7.51	7.58	7.65	7.75	7.88	8.09

[1] D. J. Finney, *Probit Analysis*, (Cambridge: Cambridge University Press, 1971), p. 25. Reprinted by permission.

Example Estimation of Lethality Using a Probit Model

As an example, the probit model, Probit = a + b ln(Cn t), for chlorine based on a US Coast Guard study have been summarized in as [21]:

$a = -8.29$
$b = 0.92$
$n = 2$

Estimate the 1% lethal concentration for a one-hour exposure to chlorine vapor. Note these constants use concentration in ppmv and time in minutes.

Probit at 1% = 2.67 = -8.29 + 0.92 ln [C2 (60 minutes)]
$e^{11.913}$ = 149200 = C2 (60 minutes)
$C^2 = 2487$,
C = 49.9 ppmv

Relationship of Lethality to a Multiple of ERPG-3

- Probit models offer the best relationship for risk analysis, but these models are only available for a limited number of chemicals
- When probit models are unavailable, a short-duration exposure criteria associated with 10% fatality rate might be used for risk analysis screening (e. g., multiple times ERPG-3 for less than 10 minutes)

Dose-response models are available in the open literature. There is significant variability among models as effects are typically extrapolated from animal studies, may be based on a variety of safety factors, and represent assumptions of the portion of highly sensitive people, etc. A conservative "fit" of published probability models versus multiples of ERPG-3 provides a rough estimate of vulnerability to personnel (Figure 3.3). A one-hour exposure to ERPG-3 concentration conservatively represents 1% vulnerability, while a one-hour exposure to 2 times ERPG-3 conservatively represents 10 to 15% vulnerability.

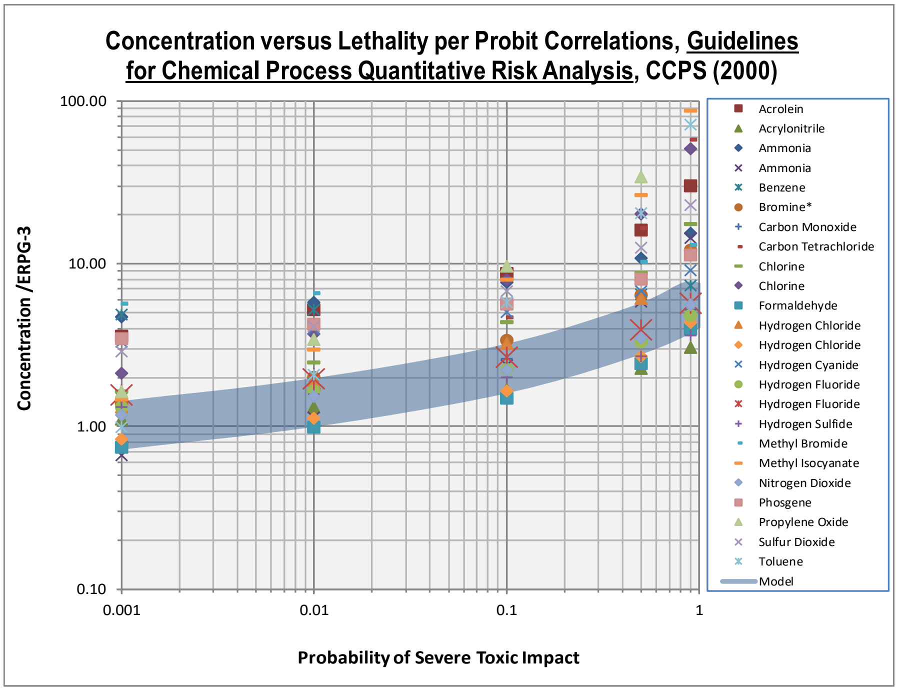


Figure 3.3 Multiple of ERPG-3 Concentration Vs Lethality for 60-minute Exposure

(adapted from [21, p. 259])

People in Occupied Buildings

A simple Effect Zone approach is not effective for Occupied Buildings as not all personnel within a building are typically impacted to the same extent. In these cases, the fraction of people impacted or "vulnerability" is estimated from inhalation of toxic chemicals or level of explosion damage.

Asphyxiation

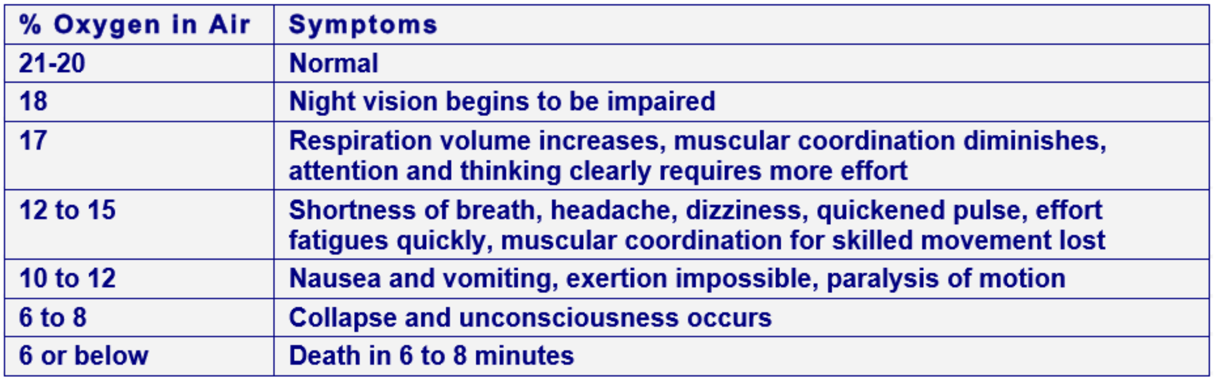
Hazards with gas or vapor inhalation also includes asphyxiation (Table 3.3). Relatively non-toxic chemicals may pose an asphyxiation hazard, particularly for release within an enclosed process area. The oxygen content may be estimated using Equation 3-4:

$$\text{Average Percent Oxygen} = 21\,(1 - C_{\text{Indoor}}/\ 1000000) \qquad \text{Equation 3-4}$$

where C_{Indoor} is the concentration of released material within an enclosed area in ppm.

- Faulty judgment and disorientation occurs at 12-16% oxygen which may be a reasonable level to consider as severe impact in Risk Analysis.
- Less than 19.5 percent oxygen represents the level at which supplied breathing air is required by OSHA.

Table 3.3 Effects of Oxygen Deficiency [27, p. 15]



% Oxygen in Air	Symptoms
21-20	Normal
18	Night vision begins to be impaired
17	Respiration volume increases, muscular coordination diminishes, attention and thinking clearly requires more effort
12 to 15	Shortness of breath, headache, dizziness, quickened pulse, effort fatigues quickly, muscular coordination for skilled movement lost
10 to 12	Nausea and vomiting, exertion impossible, paralysis of motion
6 to 8	Collapse and unconsciousness occurs
6 or below	Death in 6 to 8 minutes

Dermal Toxicity

Dermal Toxicity is a key parameter for evaluation of exposure to *<u>liquids</u>*. It depends on the toxicity of the material, rate of absorption, and body area exposed. It is difficult to quantify dermal exposure as the rate of toxicant absorbed through the skin is not easily estimated. Most chemicals are not readily absorbed unless the skin is damaged from thermal or chemical burns. There are some exceptions, Phenol, for example, requires only a small area of skin to be exposed for a sufficient quantity to be absorbed resulting in death. Exposure to hydrofluoric acid to an area the size of a hand can cause death.

The European Dangerous Substances Directive for Classification and Labeling of Chemicals provides a relative measure for Dermal Toxicity based on data.

- *Fatal, Very Toxic* – Dermal LD_{50}, < 200 mg/kg (Fatal in Contact with Skin, Very Toxic in Contact with Skin) with Category 1 as Dermal LD_{50} < 50 mg/kg.
- *Toxic* – Dermal LD_{50}, between 200 and 1000 mg/kg (Toxic in Contact with Skin)
- *Harmful* – Dermal LD_{50} between 1000 and 2000 mg/kg (Harmful I in Contact with Skin)

Such a relative measure (very toxic, toxic, or harmful) is sufficient in simple Risk Analysis to qualitatively estimate the impact from dermal exposure. Wearing protective clothing is very important in managing dermal toxicity issues.

As a point of reference, “fatal” or “very toxic” (200 mg/kg) would correlate to 10 to 20 grams (or 0.05 to 0.1 cup of liquid) absorbed through the skin for 50% lethality.

Thermal/ Chemical Burns

For Thermal or Chemical Burns, response depends upon the fraction of body area damaged – roughly 10% lethality at 25% and 50% at 50% of body area receiving 2nd or 3rd degree burns (Figure 3.4).

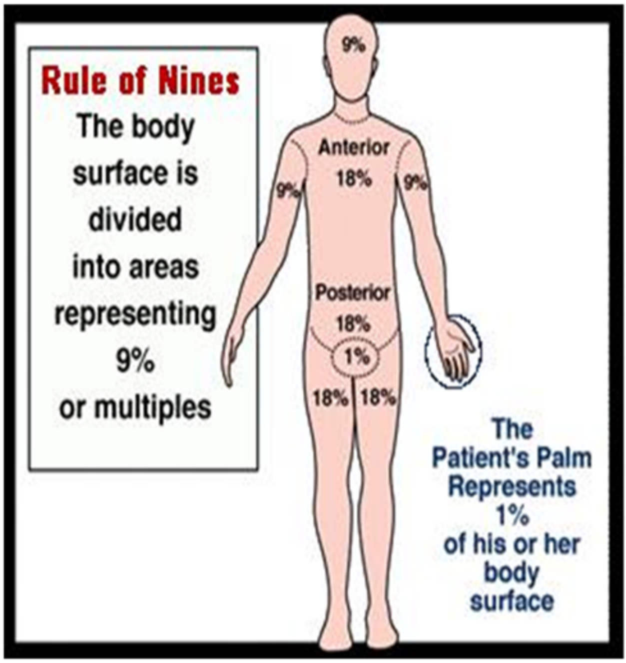


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Figure 3.4 Estimation of Percent Body Surface (adapted from [28])

Environmental Toxicity

Risk Analysis for the possible effects of a substance entering the environment which may harm people should consider exposures through all potential environmental routes (Figure 3.5) in order to determine the total exposure and then the possible effect. Risk increases with increasing release quantity and increasing toxicity.

- It is difficult to quantify environmental toxicity other than by the quantity and relative toxicity of chemical released.
- Chemicals toxic to humans by Ingestion could contaminate the food chain or drinking water.
- Chemicals toxic to aquatic organisms also need to be considered in Risk Analysis.

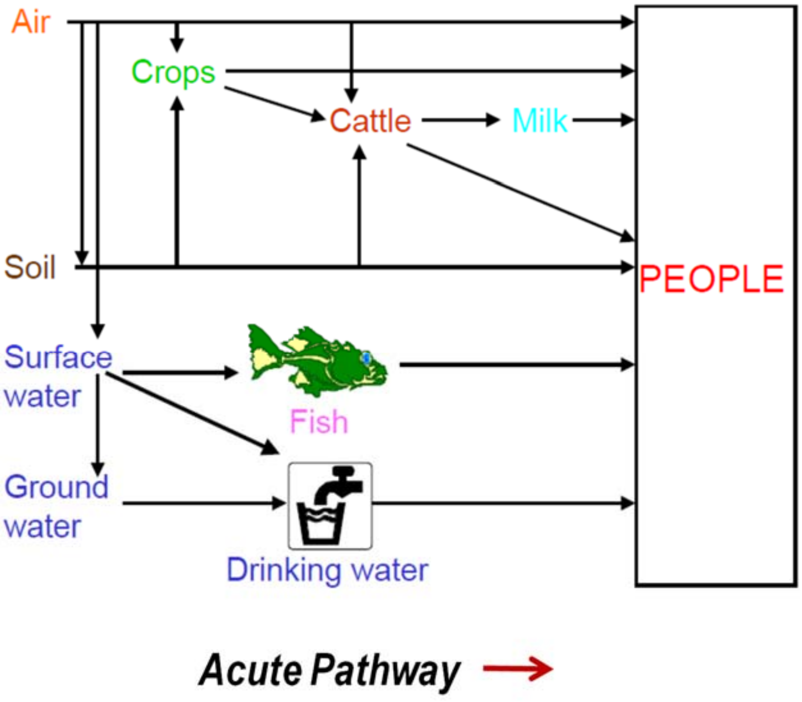


Figure 3.5 Environmental Toxicity Acute Pathways

- Classification and Labeling for Dangerous Substances (United Nations Globally Harmonized System – GHS or European Dangerous Substances Directive) provides relative toxicity categories [11, p. Annex VI].

Ingestion Toxicity

  - *Fatal, Very Toxic* – Oral LD_{50} < 50 mg/kg (Fatal if swallowed, Very Toxic if swallowed) with Category 1 as Oral LD_{50} < 5 mg/kg
  - *Toxic* – Oral LD_{50} between 50 and 300 mg/kg (Toxic if swallowed)
  - *Harmful* – Oral LD_{50} between 300 and 2000 mg/kg (Harmful if swallowed)

Aquatic Toxicity

  - *Very Toxic* – 96 hr. LC_{50} fish < 1 mg/liter, or 48 hr. LC_{50} Daphnia < 1 mg/liter, or 72 hr. LC_{50} algae < 1 mg/liter (Very Toxic to Aquatic Organisms)
  - *Toxic* – 96 hr. LC_{50} fish between 1 and 10 mg/liter, or 48 hr. LC_{50} Daphnia between 1 and For
  - *Harmful* – 96 hr. LC_{50} fish between 10 and 100 mg/liter, or 48 hr. LC_{50} Daphnia between 10 and 100 mg/liter, or 72 hr. LC_{50} algae between 10 and 100 mg/liter (Harmful to Aquatic Organisms)

Additional information on toxic impacts to humans may be found in other resources ([27] [29] [30]).

4. REACTIVITY

Evaluation of reactivity hazards often involves interpretation of reactive chemicals test data. Endothermic reactions represent a potential hazard if gaseous or highly volatile products are generated. Exothermic reactions have the potential for a runaway reaction leading to a dramatic increase in temperature, pressure (if the reaction is contained) and reaction rate.

Section Objectives

The following objectives are covered in this section:

- To identify where unintended reactions may occur in a chemical process.
- To recognize Reactive Chemicals test methods and where to obtain data.
- To recognize an Inter-Reactivity Chart.
- The concept of Heat of Reaction and be able to estimate Maximum Reaction Temperature and Pressure.
- Guidance criteria for when additional Reactive Chemicals Testing is appropriate.
- The concept of simple kinetic modeling to evaluate the Temperature of No Return, Time to Maximum Rate, and potential for Autocatalytic Behavior.
- Recognize common process upsets that impact reactivity hazards.

Reactivity Hazards Evaluation

The US Chemical Safety and Hazard Investigation Board analyzed 167 serious incidents in the US involving Reactive Chemicals from 1980 through 2001. 48 of these incidents resulted in 108 fatalities. They concluded that Reactive Chemicals incidents represent a significant safety problem and recommended that awareness of reactivity hazards be improved.

Regular reviews of process reactive hazards are needed for existing processes, new processes and whenever key personnel or a process is changed, as well as a thorough review of laboratory or pilot plant data prior to scale-up.

Appendix A presents a Reactive Chemicals checklist that was developed by members of the CCPS.

The Search for Reactivity Hazards

Raw materials, process streams, products and waste of any process must be reviewed and evaluated to determine if any potential reactive chemical hazards are involved (Figure 4.1). *Endothermic* reactions represent a potential hazard if gaseous or highly volatile products are generated. *Exothermic* reactions with all reactants initially present have the potential for a runaway reaction leading to a dramatic increase in temperature, pressure (if the reaction is contained) and reaction rate.

In general, if insufficient data are available, then the materials should be subjected to screening evaluations or tests [31].

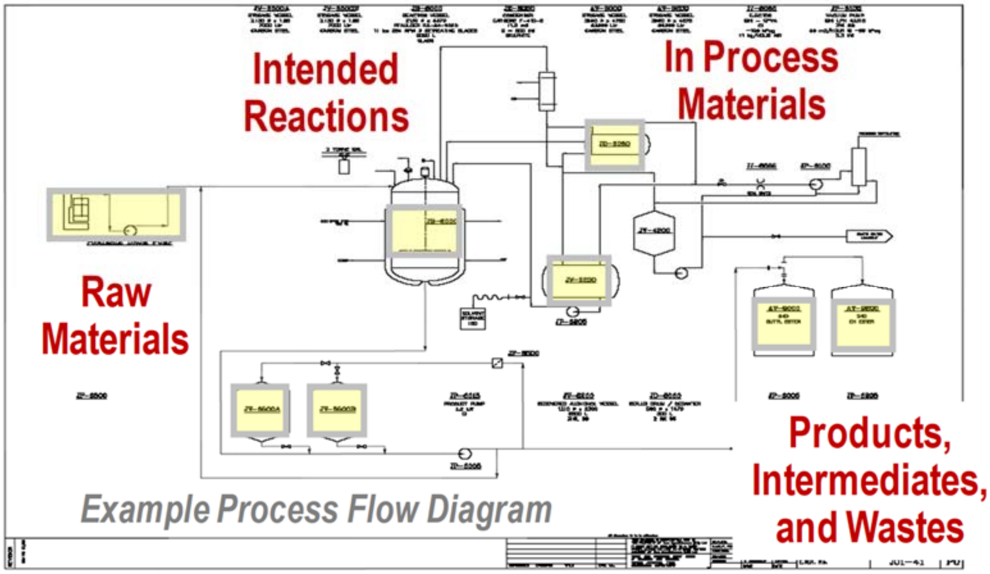


Figure 4.1 Search for Reactivity Hazards

Reactions to consider include *(but are not limited to):*

- Primary or Intended Reactions
- Potential Unintended Reactions (polymerization, decomposition, etc.)
- Reactions resulting from inadvertent mixing of incompatible materials (including waste streams)

Information for the primary or intended reaction is typically available from initial design or operational history. Reactions may be batch, in which all reactants are added and the reaction started, or continuous, with control commonly achieved through addition of a limiting reactant, catalyst or inhibitor, removal of products, ebullient cooling, or other means of heat or material transfer. Of particular concern are reaction characteristics under abnormal conditions or process upsets such as loss of temperature control, introduction of contaminants or wrong proportion of reactants when a significant quantity of reactants is present.

Key Steps in Reactivity Hazard Evaluation

The Key Steps in performing a Reactivity Hazard Evaluation include:

- Compile Available Reactivity Information
- Complete Initial Reactive Chemicals Screening; Heat of Reaction, Maximum Reaction Temperature/Pressure, Detected Onset Temperature, and Limiting Heat Rate (if continuous or semi-batch)
- Assessment of Potential Hazards to decide if additional Testing is warranted.
- Evaluation of Process Upsets and Safe Operating Conditions using Rate Information and Simple Kinetic Modeling as needed.
- Review of Hazards and Lines of Defense with multi-disciplined group as part of the overall Risk Management program for projects and facilities

These steps are intended to minimize the overall time and cost for Reactivity Hazard Evaluation. An effective Reactivity Hazard Evaluation should be a collaborative effort of Plant Personnel, Technology Experts, and Reactive Chemicals Experts.

Reactive Chemicals Screening

There are several sources of Reactive Chemicals information. The heat of reaction for known or proposed chemistry may be found in the open literature or estimated from the difference between heats of formation and thermodynamic properties of products and reactants. The following is a list of common information sources from least to most costly:

- Reactive Chemicals Databases
- Literature
- Estimation from Heats of Formation
- Calorimetry
    - Mixing Calorimetry (2-Drop)
    - Differential Scanning Calorimetry (DSC)
    - Accelerating Rate Calorimetry (ARC)
    - Reactive System Screening Tool (RSST)
    - Vent Sizing Package (VSP)
    - Others
- Development of complete Kinetic Models

Key Reactivity Hazard Screening Information

Key Reactivity Hazard Screening information includes:

- Heat of Reaction per Mass
- Estimate of Maximum Reaction Temperature and Pressure
- Detected Onset Temperature
- Chemicals containing highly energetic functional groups (such as nitro, epoxides, peroxides, etc.) that may indicate shock sensitive or "explosive" instability

Initial screening of reactivity by heat of reaction per mass and maximum reaction pressure allows focus on the highest hazards. Those reactions representing significant hazards are candidates for reactive chemicals testing and further evaluation.:

Categorization of Reactivity Hazard from Heat of Reaction per Mass

Low to Medium Energy Release Potential – Less exothermic than –50 J/g (Adiabatic temperature rise typically will be less than 25 C)

High Energy Release Potential – Between -50 and -1000 J/g (In this region, reaction vapor pressure and rate may result in catastrophic failure of process equipment and vessels)

Potentially Explosive – More exothermic than -1000 J/g (Reactions capable of deflagration and detonation)

Estimation of the Maximum Reaction Temperature and Pressure

In addition to reaction energy release potential, excessive pressure may indicate a significant Reactivity Hazard. Key questions are:

- Could the maximum reaction pressure exceed the equipment design such that catastrophic failure or rupture might occur?
- Could the maximum reaction pressure exceed the relief device set pressure resulting is a hazardous chemical release?

The maximum adiabatic reaction temperature for a batch system may be estimated from the Heat of Reaction per Mass and the heat capacity of the reaction mixture using Equation 4-1:

$$\mathbf{T_{max} = T_0 - \Delta H_R / C} \qquad \text{Equation 4-1}$$

Note that heat evolved is a negative value by convention. The corresponding maximum pressure for a liquid phase reaction may be estimated using Equation 4-2:

$$\mathbf{P_{max} = P_{Pad}\,(T_{max}/T_0) + P_{VP@Tmax} + \beta\ R\ T_{max}\,(V_L/V_V)} \qquad \text{Equation 4-2}$$

where:

T_0 is the initial temperature
P_{Pad} is initial pad gas pressure
ΔH_R is heat of reaction per mass
β is mole gas created per liquid volume
C is liquid heat capacity
R is gas law constant

V_L/V_V is ratio of liquid to vapor volume in equipment or vessel

$P_{VP@Tmax}$ is vapor pressure at maximum temperature

Note that the gas generation term in Equation 4-2 is based on an ideal gas with no liquid solubility. For example, if β = 0.1 mole gas created per liter of liquid at a maximum of 300 K in a vessel with liquid fill fraction of 0.8, then the contribution of gas generation to the overall pressure is $\beta\ R\ T_{max}\,(V_L/V_V)$ = 0.1 (0.082 mole/liter-atm-K) 300 K (0.8 fraction liquid / 0.2 fraction vapor) = 9.84 atm.

The maximum temperature for a continuous reaction is typically evaluated from an overall energy balance based on reactant feed rate. The maximum pressure for a vapor phase reaction may be estimated using the ideal gas law and the moles of products minus reactants plus inert materials, equipment or vessel volume, at the maximum reaction temperature.

Example Estimation of Maximum Reaction Temperature and Pressure

The heat evolved from diluting concentrated sulfuric acid to a 50 wt% solution is approximately -180 cal/g H_2SO_4 or -90 cal/g 50% solution. The average liquid heat capacity for this solution over the concentration range is 0.47 cal/g C. The maximum adiabatic temperature starting from 25 C (298 K) is:

$$T_{max} = T_0 - \Delta H_R / C = 25 + 90 / 0.47 = 216.5 \text{ C or } 489.5 \text{ K}$$

Starting initially at atmospheric pressure, the initial pad gas is 0.99 atmosphere (or 1 atmosphere minus the vapor pressure at 25 C). The vapor pressure of 50% sulfuric acid at 216.5 C is 11.4 atmosphere. The corresponding maximum pressure (assuming adiabatic conditions) is:

$$P_{max} = P_{Pad}\,(T_{max} / T_0) + P_{VP@Tmax} = 0.99\ (\ 489.5 / 298\ ) + 11.4 = 13 \text{ atmosphere}$$

Example Estimation of Maximum Reaction Pressure from Gas Generation

A liquid phase endothermic reaction (absorbs heat) generates 0.1 moles of gaseous products per liter of reaction mass. Estimate the maximum pressure at a temperature of 100 C (373 K), a vapor pressure of the non-gaseous mixture of 2.0 atmospheres, and a liquid fill fraction of 0.8. Ignore any initial pad gas. Use a gas law constant, R = 0.082 liter atmosphere/mole K.

$$P_{max} = P_{VP@Tmax} + \beta\ R\ T_{max}\,(V_L/V_V)$$

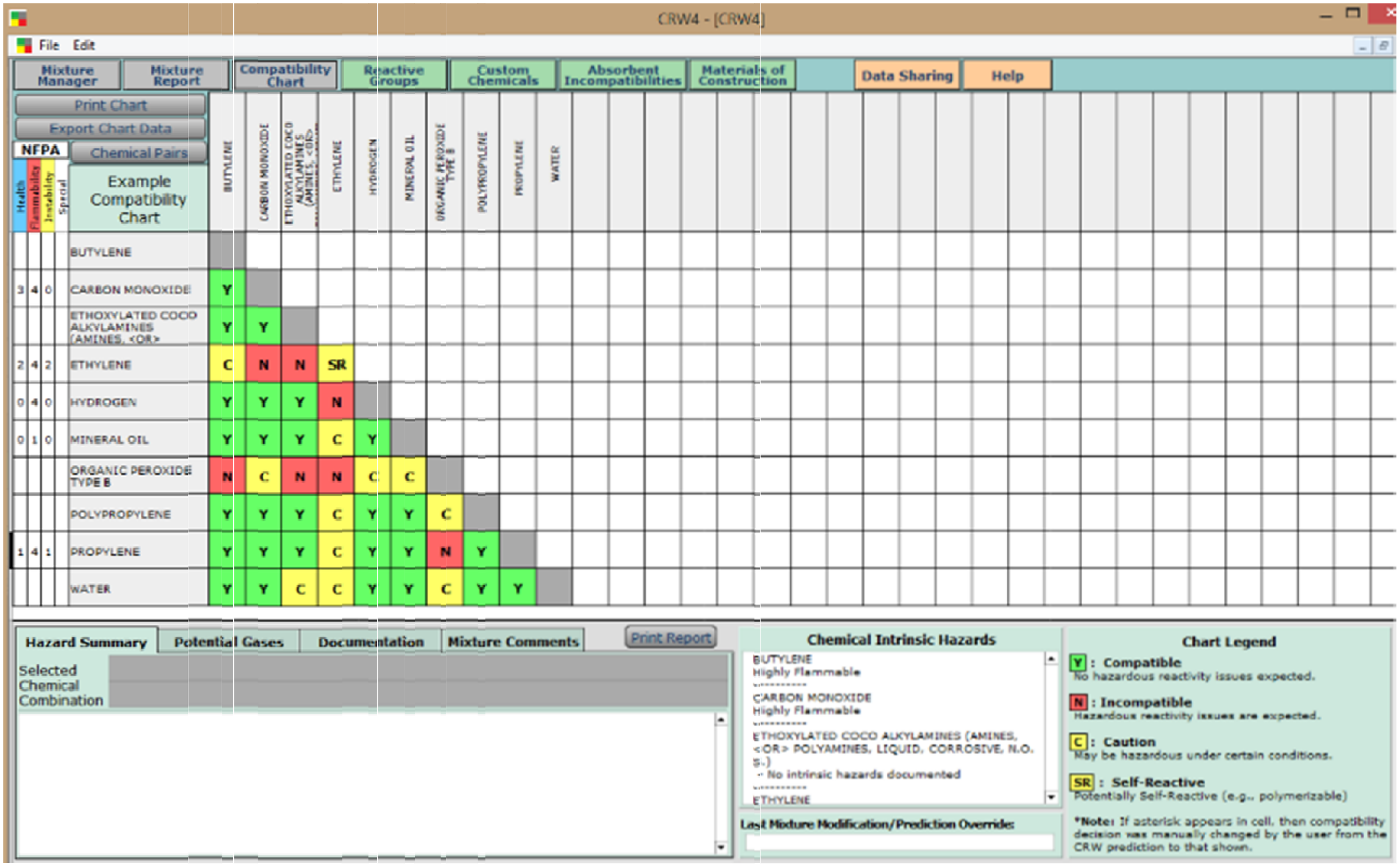
$$= 2 \text{ atmopsheres} + 0.1 \text{ mole/liter } (0.082)\ (373 \text{ K})\ (0.8 \text{ volume liquid } / \ 0.2 \text{ volume vapor})$$

$$= 14.2 \text{ atmospheres}$$

Compatibility *Charts*

Compatibility Charts are commonly used to summarize potential hazards for mixing binary combinations of chemicals within a manufacturing facility. This information in combination with equipment and plant layout information may help to identify specific reaction scenarios for hazard evaluation. Examples include the unintended transfer of material to the wrong tank, spills within production area where multiple chemicals are handled or stored (acids, bases, water, etc.), or reactions with heat transfer fluids or materials of construction**.**

The Chemical Reactivity Worksheet (CRW) is a downloadable software program that can be used evaluate the chemical reactivity of thousands of common hazardous chemicals, compatibility of absorbents, and suitability of materials of construction in chemical processes [14]. Figure 4.2 is an example of a compatibility chart created using CRW.



NFPA Health	Flammability	Instability	Special	Example Compatibility Chart	BUTYLENE	CARBON MONOXIDE	ETHOXYLATED COCO ALKYLAMINES (AMINES, <OR>	ETHYLENE	HYDROGEN	MINERAL OIL	ORGANIC PEROXIDE TYPE B	POLYPROPYLENE	PROPYLENE	WATER
				BUTYLENE										
3	4	0		CARBON MONOXIDE	Y									
				ETHOXYLATED COCO ALKYLAMINES (AMINES, <OR>	Y	Y								
2	4	2		ETHYLENE	C	N	N	SR						
0	4	0		HYDROGEN	Y	Y	Y	N						
0	1	0		MINERAL OIL	Y	Y	Y	C	Y					
				ORGANIC PEROXIDE TYPE B	N	C	N	N	C	C				
				POLYPROPYLENE	Y	Y	Y	C	Y	Y	C			
1	4	1		PROPYLENE	Y	Y	Y	C	Y	Y	N	Y		
				WATER	Y	Y	C	C	Y	Y	C	Y	Y	

Selected Chemical Combination

Chemical Intrinsic Hazards

BUTYLENE
Highly Flammable

CARBON MONOXIDE
Highly Flammable

ETHOXYLATED COCO ALKYLAMINES (AMINES, <OR> POLYAMINES, LIQUID, CORROSIVE, N.O.S.)
- No intrinsic hazards documented

ETHYLENE

Last Mixture Modification/Prediction Override:

Chart Legend

Y : **Compatible**
No hazardous reactivity issues expected.

N : **Incompatible**
Hazardous reactivity issues are expected.

C : **Caution**
May be hazardous under certain conditions.

SR : **Self-Reactive**
Potentially Self-Reactive (e.g., polymerizable)

*Note: If asterisk appears in cell, then compatibility decision was manually changed by the user from the CRW prediction to that shown.

Figure 4.2 Example Inter-Reactivity Chart from CRW

Highly Energetic Reactions

There are several known reactions involving chemical structures of high energy. Examples are shown in the Table 4.1.

Table 4.1 Examples of High Energy Molecular Structures [32, p. 32]

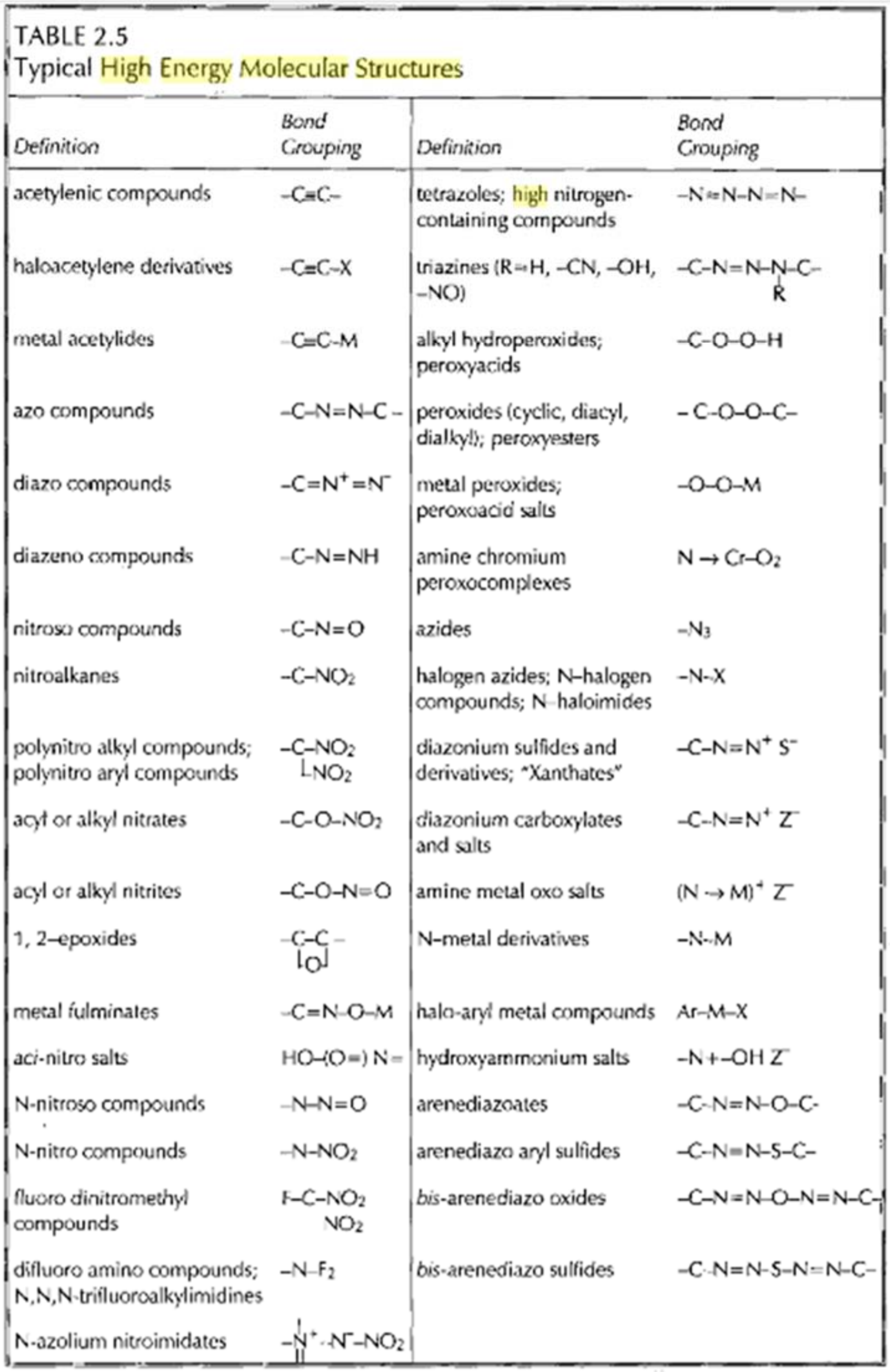


TABLE 2.5
Typical High Energy Molecular Structures

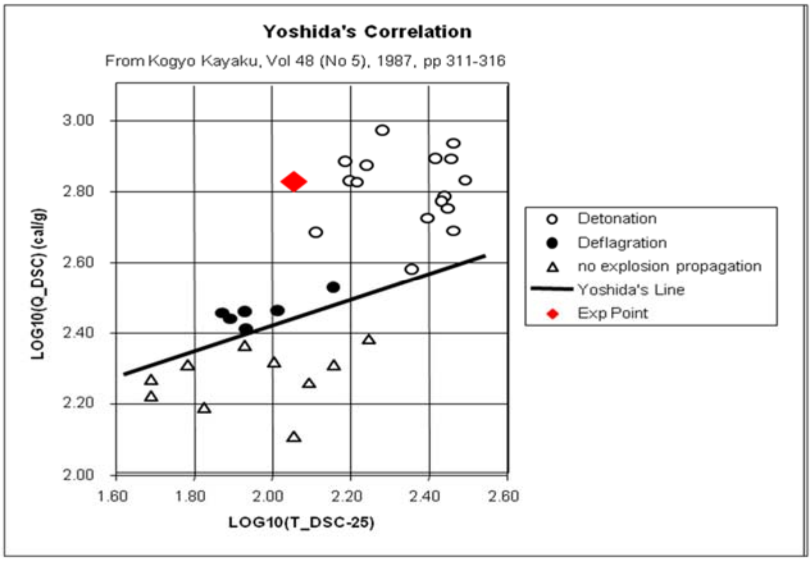
Definition	*Bond Grouping*	*Definition*	*Bond Grouping*
acetylenic compounds	$-C\equiv C-$	tetrazoles; high nitrogen-containing compounds	$-N=N-N=N-$
haloacetylene derivatives	$-C\equiv C-X$	triazines (R=H, –CN, –OH, –NO)	$-C-N=N-\underset{R}{N}-C-$
metal acetylides	$-C\equiv C-M$	alkyl hydroperoxides; peroxyacids	$-C-O-O-H$
azo compounds	$-C-N=N-C-$	peroxides (cyclic, diacyl, dialkyl); peroxyesters	$-C-O-O-C-$
diazo compounds	$-C=N^+=N^-$	metal peroxides; peroxoacid salts	$-O-O-M$
diazeno compounds	$-C-N=NH$	amine chromium peroxocomplexes	$N \rightarrow Cr-O_2$
nitroso compounds	$-C-N=O$	azides	$-N_3$
nitroalkanes	$-C-NO_2$	halogen azides; N–halogen compounds; N–haloimides	$-N-X$
polynitro alkyl compounds; polynitro aryl compounds	$-C-NO_2$ $\llcorner NO_2$	diazonium sulfides and derivatives; "Xanthates"	$-C-N=N^+\ S^-$
acyl or alkyl nitrates	$-C-O-NO_2$	diazonium carboxylates and salts	$-C-N=N^+\ Z^-$
acyl or alkyl nitrites	$-C-O-N=O$	amine metal oxo salts	$(N \rightarrow M)^+\ Z^-$
1, 2–epoxides	$-C-C-$ $\llcorner O \lrcorner$	N–metal derivatives	$-N-M$
metal fulminates	$-C=N-O-M$	halo-aryl metal compounds	$Ar-M-X$
aci-nitro salts	$HO-(O=)N=$	hydroxyammonium salts	$-N+-OH\ Z^-$
N-nitroso compounds	$-N-N=O$	arenediazoates	$-C-N=N-O-C-$
N-nitro compounds	$-N-NO_2$	arenediazo aryl sulfides	$-C-N=N-S-C-$
fluoro dinitromethyl compounds	$F-C-NO_2$ NO_2	*bis*-arenediazo oxides	$-C-N=N-O-N=N-C-$
difluoro amino compounds; N,N,N-trifluoroalkylimidines	$-N-F_2$	*bis*-arenediazo sulfides	$-C-N=N-S-N=N-C-$
N-azolium nitroimidates	$-\overset{\vert}{\underset{\Vert}{N^+}}-N^--NO_2$		

Differential Scanning Calorimetry (DSC)

Calorimetry data is means for assessing Reactivity Hazards associated with intended and unintended reactions. The most common being Differential Scanning Calorimetry (DSC). DSC uses a very small sample and is relatively inexpensive to run. It measures heat evolution (exotherm) and absorption (endotherm) as the sample temperature is increased (a measure of thermal instability). The key disadvantage of DSC testing is the inability to obtain pressure data. In addition, the high temperature scan rate used for Reactive Chemicals Screening (commonly 10 C/min) reduces instrument sensitivity such that the temperature at which reactions are detected may be significantly lower in large-scale equipment under near adiabatic conditions.

Yoshida's Correlation of Highly Energetic Reactions

The Yoshida Correlation[24] is an empirical relationship based on DSC Data. It is very useful for pinpointing potential explosion risk. Data above the correlating represent potential explosive material (capable of Deflagration or Detonation). Below the Yoshida line, explosion did not occur although *pressure sufficient for damage or failure of equipment may be a concern*. (Figure 4.3).


Yoshida's Correlation

From Kogyo Kayaku, Vol 48 (No 5), 1987, pp 311-316

Figure 4.3 Yoshida's Correlation

Detected Reaction Onset Temperature

There is no "start" temperature for reactions. Reaction rate typically increases with increasing temperature such that, at some point, the reaction rate exceeds the detection limit of the calorimeter [33].

There is a "rule of thumb" that a "safe operating temperature limit" of 50 °C below a detected onset temperature by Differential Scanning Calorimetry. It is not very accurate. Estimation of the Temperature of No Return from simple kinetic modeling is a much better means for determining safe operating temperature limits.

When to Consider Additional Reactive Chemicals Testing

Once a reaction is considered hazardous (the estimated maximum pressure exceeds the design limits of the equipment or the reaction is highly energetic), additional evaluation may require calculations of <u>*reaction rate*</u> under normal and process upset conditions. Key considerations include:

- Significant pressure generated
- Highly energetic reaction
- Change in the process or operating conditions
- Change of scale
- Needed for equipment or pressure relief design

The experimental data needed depends on the specific questions to be addressed. Accelerating Rate Calorimetry (ARC) may be appropriate for evaluating process upsets needing confined pressure and temperature rate information. Data from the Vent Sizing Package (VSP) or Reactive System Screening Tool (RSST) may be appropriate if the need is evaluation of emergency pressure relief requirements.

Accelerating Rate Calorimetry (ARC)

Accelerating Rate Calorimetry measures heat evolution (exotherm) and pressure under near adiabatic conditions (Figure 4.4). It uses a larger sample size than DSC and is a more expensive test. Test results provide self heat rate and pressure versus temperature which may be used in the development of simple kinetic models. Mechanical stirring is also available with the ARC such that mixing effects may be evaluated (such as reactants in separate phases – two liquids or solid liquid reactions).

Vent Sizing Package™ (VSP)

The Vent Sizing Package is commonly used for sizing relief devices for large scale reaction/fire scenarios. Test results may be applied directly to large scale equipment without correction for the sample container heat losses.

Simple Kinetic Modeling to Obtain Reaction Rate Information

Utilizing rate information will involve some level of kinetic modeling to extrapolate the Reactive Chemicals data to plant conditions. Various reaction schemes may be assumed to determine which provides a "best" fit for Activation Energy and Initial Rate (at the specified Initial Temperature) for batch reactions. Simple kinetic parameters may also be developed from conversion correlated by pressure data and estimated gas generation. Often a simple zero or first order model provides sufficient accuracy in the region of interest for screening of reactivity hazards.

A simple "first-order" kinetic model results from a "best" fit of the test data using Equation 4-3:

$$\textbf{Reaction Rate} = r_0 (1-X) \exp [\Delta E / R (1/T_0 - 1/T)] \qquad \text{Equation 4-3}$$

where:

X = conversion determined by temperature rise, $X=(T-T_0)/(T_{Final}-T_0)$ or by gas evolution.
T, T_0 = temperature and initial temperature respectively (K)
ΔE = Activation Energy (energy/mole)
R = gas law constant (energy/mole K)
r_0 = initial reaction rate at the initial temperature, T_0

Activation Energy, ΔE, determines the slope of reaction rate with temperature. The initial Temperature-Rate pair (T_0, r_0) determines a starting point for the model representing near zero conversion of reactants.

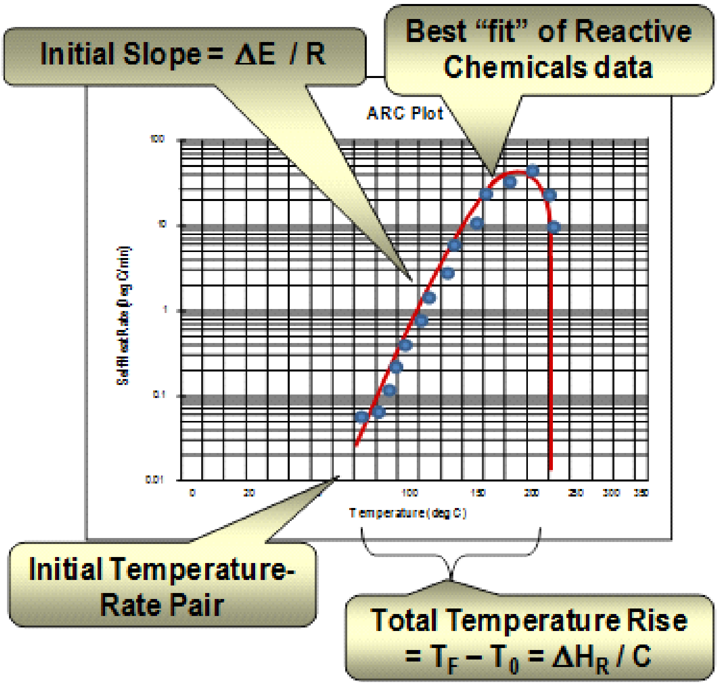


Figure 4.4 Example ARC Temperature Rate vs Temperature Plot

Temperature of No Return

A key to managing reactivity hazard for an exothermic batch reaction is maintaining a normal operating temperature below the temperature at which reaction heat gain exceeds heat loss to the surroundings. Beyond the Temperature of No Return, if no action is taken, the reaction will proceed to a maximum rate (Figure 4.5).

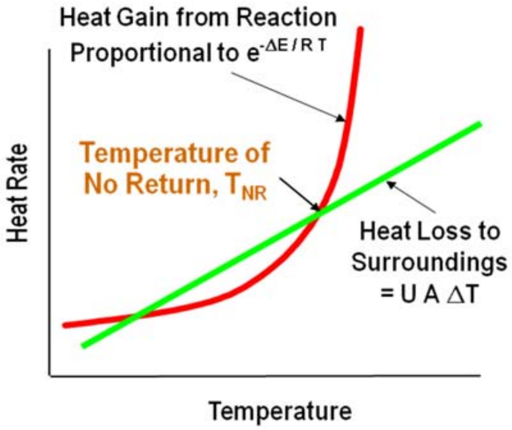


Figure 4.5 Temperature of No Return

The Temperature of No Return, T_{NR}, is commonly used to determine Safe Operating Conditions [34]. It is normally determined by trial-and-error methods or graphically. Of interest is the temperature at which the reaction proceeds in the absence of cooling (when heat loss is by convection to ambient) and the temperature at which control is lost with cooling (when the heat transfer coefficient and temperate reflect that for the cooling media).

The Temperature of No Return is highly dependent on the equipment size. T_{NR} is a function of convective heat loss, which depends on equipment surface area, and effectiveness of insulation. The T_{NR} for small equipment with high surface area to volume may be significantly higher (50 C or more) than for large insulated equipment.

Reactivity Screening

The Time to Maximum Rate, t_{MR}, from any initial temperature may be estimated by integrating the appropriate kinetic rate model. It gives an indication of time frame in which action must be taken to regain control of the reaction system. For a zero-order adiabatic reaction, it is estimated using Equation 4-4 [34]:

$$\mathbf{t_{MR} = R\,T_0^2 / (\,q_0\,\Delta E\,)} \qquad \text{Equation 4-4}$$

where:

q_0 = adiabatic self heat rate at the initial temperature (degree/time)
T_0 = initial temperature respectively (K)
ΔE = Activation Energy (energy/mole)
R = gas law constant (energy/mole K)

Autocatalytic Behavior

Reactions exhibiting autocatalytic behavior may appear to be thermally stable due to an “induction period”. For these systems, the self-heat rate is near zero initially (at zero conversion) and accelerates to a maximum rate under isothermal conditions. Another indication of autocatalytic behavior is an unusually high Activation Energy for simple first-order fit to temperature rate data. *The simple screening correlations for Temperature of No Return and Time to Maximum Rate are not valid for chemicals exhibiting Autocatalytic Behavior* such as an inhibited monomer.

Evaluation of Common Process Upsets involving Reactions

In some cases, an estimation of the impact of a process upset may be evaluated by adjustment of appropriate kinetic parameters. Common process upsets of interest are:

- External heat plus reaction
- Misloading or Recipe Deviation
- Catalytic effects
- “Pooling” of reactants

External heat may result from a heat transfer surface, mechanical energy such as an agitator or circulating pump, or a fire. The primary impact of external heat is an increase in temperature without consuming reactants. At temperatures where reaction heat rate is much less than the external heat input, reaction conversion is essentially zero and total heat rate is only attributed to the external source. The maximum reaction temperature, pressure, and heat rate are much higher with external heat input.

Misloading or Recipe Deviation may result in a change in heat of reaction per mass which affects the maximum temperature and the heat rate. More concentrated exothermic reactions generate more total reaction heat per mass.

Introduction of a *Catalytic Impurity* may significantly increase the rate constant and overall self heat rate for exothermic reactions (such as metals contamination of peroxides). Chemicals normally maintained within safe operating limits may quickly progress to potential runaway conditions upon the addition of impurities or loss of inhibitors.

A common means for controlling an exothermic reaction is by slow addition of a limiting reagent such that the overall reaction heat rate is proportional to the addition rate. ***"Pooling" of reactants*** occurs if the concentration of limiting reagent is allowed to increase – typically by loss of mixing or low temperature.

5. OTHER HAZARDS

Process Hazards

Since process safety risk reduction efforts focuses on hazardous materials and energies, the "process hazards" include both those of the materials and energies handled by specific equipment. Material hazards address acute chemical exposure hazards; exposures to which a single or short duration exposure may cause harm or damage. Flammable or reactive materials may have chemical and explosion hazards, and additional material hazards include the potential for asphyxiation and dermal exposure to corrosive, hot or cold materials as a result of a release. Equipment scale is also important as severity is often related to the quantity of chemical or stored pressure-volume energy that could be released.

The following offers guidance in determining what equipment items should be included in a Hazard Identification and Risk Analysis (HIRA) study based on actual incidents that have occurred in the chemical industry. In addition to these, any equipment items or unit operations that the study teams feel represents a hazard should be included. Note that Chemical Hazards (Flammability, Toxicity and Reactivity) have been in addressed in the previous sections.

Typical Chemical Hazards include:

- Flammability (and Explosivity)
- Toxicity (Inhalation, Dermal, or Environmental)
- Reactivity or Instability

Hazardous Process Conditions include:

- Corrosivity
- High/Low Pressure
- High/Low Temperature
- High/Low Flow
- High/Low Level or Inventory

Equipment Specific Hazards include:

- Fluid Transfer Equipment and Piping
- Fired Equipment (including Boilers, Fired Heaters, etc.)
- Heat Exchangers
- Rotating Equipment
- Dust Handling Equipment

Contributing Factors include:

- *Scale of Operations*
- *Proximity of People*
- *Proximity of Buildings*
- *Proximity of Ignition Sources*
- *Release area Congestion/Confinement*

Section Objectives

The following objectives are covered in this section:

- To identify hazards associated with operating conditions or specific types of equipment
- To recognize contributing factors effecting hazard severity.
- To recognize common process upsets that impact hazards.

Hazardous Process Conditions

Corrosivity may be thought of in more than one way. A material may be corrosive to skin and eyes, but it may also be corrosive to the vessels and pipes in which it's contained. A corrosive material can cause an unintended release of a hazardous material by corroding away piping and vessels in which it's present. Therefore, it's important to pay attention to whether corrosive materials are compatible with the equipment they're contained in. Some materials of construction may corrode at a slow rate and be utilized, but do not have an indefinite lifetime. Materials that resist corrosion indefinitely are the best choice, but such materials do not always exist or they may not be economical.

In some cases, corrosion resistant coatings or lining are used over a base material (such as carbon steel) that provide equipment strength. Coatings and lining may have limitations such as softening of plastics at elevated temperature or spalling of glass. Loss of protective coatings may be difficult to detect leaving equipment vulnerable to failure in a short period of time.

Hazards Associated with Pressure

When a process vessel (or other equipment) is subject to excessive internal pressure, there can be a danger that such a pressure can exceed the vessel's ability to contain it. The failure of equipment in such situations can have devastating effects on surrounding personnel and property.

Equipment failure due to excessive pressure can result in:

- Exposure of personnel and the surrounding community to hazardous contents, including temperature, pressure, and toxicity;
- Exposure of personnel, equipment, and structures to damaging blast overpressure and flying debris; and
- Secondary effects, such as fires or loss of power and control automation.

There are several overpressure scenarios that can arise in process facilities. Excessive pressurization of equipment can result from, among many causes:

- A broken (or leaking) heat exchanger tube;
- A failed regulator on a gas supply line or a closed vapor outlet valve;
- Positive displacement pumps, compressors, and turbines (discharge side); and
- Leaks into vessel steam jackets of low-pressure design.
- Internal explosion (such as deflagration of flammable vapor or combustible dust)
- Pressurization of low-pressure tank while filling (if not properly vented)

Vacuum Damage

Vacuum can often cause as much damage as an overpressure condition. In vacuum systems the pressure is pushing inward, rather than outward. If a tank is not designed for vacuum, there's a good chance it will be damaged if placed under vacuum. Low pressure storage tanks and railcars are particularly susceptible to such damage. An example of a collapsed tank due to vacuum is shown in Appendix B.1.

Thermal Hazards

The hazards of elevated temperature can lead to a number of consequences, such as:

- Burns to personnel due to hot surface contact;
- Harm to personnel and equipment due to radiation heat;
- Reduction of the material strength of vessels and piping at elevated temperatures; and
- Acceleration of exothermic reactions, leading to possible runaway reactions.

When materials become heated to elevated temperatures for significant periods of time, depending on their chemical properties, they may become weakened. For example, prolonged subjection to elevated temperatures in a process plant can cause distortion or failure of PVC pipe. With a melting point of about 80°C, PVC pipes are prone to bending or failure as the material approaches this temperature. This causes some concerns, not only for the usefulness of the pipe, but also because the pipe's contents are liable to be released into the surroundings.

Elevated temperature is often accompanied by elevated pressure, exacerbating the situation of weakened material strength. The result: possible equipment failure and loss of containment. Many materials – specifically steel – are subject to weakness upon prolonged exposure to elevated temperatures.

Other overpressure conditions that may sometimes be caused by heat input into a closed system include:

- Excessive heat supply (such as an uncontrolled steam supply valve to a column);
- Excessively superheated feed (which vaporizes the vessel contents); and
- Blocked-in sections of liquid-filled lines or equipment which are exposed to heat resulting in thermal expansion.
- Slow heating of a well-insulated tank or equipment item by an agitator or circulating pump causing elevated temperature and vapor pressure.

Thermal Expansion may result in result in failed piping (or gasket failures), piping components (such as swivel joints), heat exchanger tubes and vessel jackets. Examples of piping or equipment where thermal expansion may represent a hazard include:

- Long, uninsulated outdoor pipelines subjected to thermal radiation from the sun
- Indoor pipelines in a heated process area originating from a colder outdoor location
- Equipment or piping which is traced or jacketed
- Heat exchangers

Pool Fire Exposure

Consider the case of a vessel exposed to a pool fire. External fire generally involves a burning pool underneath the vessel. The pool may have been created by overflow of the vessel itself or a leak in the vessel or some of its ancillary equipment – commonly, the piping – or it may have drained there from nearby failed equipment.

Fire initially subjects the vessel to high heat flux. Liquid temperature and vapor space pressure increase. At the relief device set point, vapor begins venting to the outside, allowing the temperature and pressure in the vessel to stabilize. Below the liquid level, boiling liquid absorbs heat and prevents the steel from overheating. However, the vessel's vapor space undergoes a dramatic temperature increase; the unwetted upper portion of the vessel eventually reaches a temperature that the steel cannot withstand. The vessel shell, going beyond its design temperature, is weakened by heat, particularly from thermally induced stresses near the vapor-liquid interface. Combined with high internal pressure, a sudden violent tank rupture may occur.

An example may be found in the investigation of the UA Chemical Safety Board [35]. On April 9, 1998, a broken propane line caused a pool fire beneath a 68,000 liter propane storage tank at Herrig Brothers farm in Albert City, Iowa. After about twenty minutes, there was a catastrophic failure of the vessel, resulting in the deaths of two volunteer fire fighters. After the piping was broken, propane began leaking from the tank and flowed along the ground surface (Figure 5.1). Soon after ignition of the leaking propane, the fire burned out of control in the vicinity of the tank. The fire heated the propane inside the tank, causing it to boil and vaporize. The pressure inside the tank increased as the temperature of the propane increases. When pressure inside the tank reached about 17 bar (250 psi), the relief valve opened to vent the tank. The propane escaping from the relief valves ignited and burned. As boiling continued, the pressure inside the tank exceeded 17 bar (250 psi), the temperature of the unwetted tank wall increased, and the strength of the steel used to construct the tank decreased. At some point, the weakened steel no longer resisted the pressure-induced forces inside the tank so the wall of the tank ruptured, allowing propane to escape rapidly into the surrounding atmosphere. The tank wall separated into at least 36 pieces. Tank fragments were propelled at a high velocity in many different directions. The escaping propane ignited, and a large fireball quickly consuming the remaining propane.

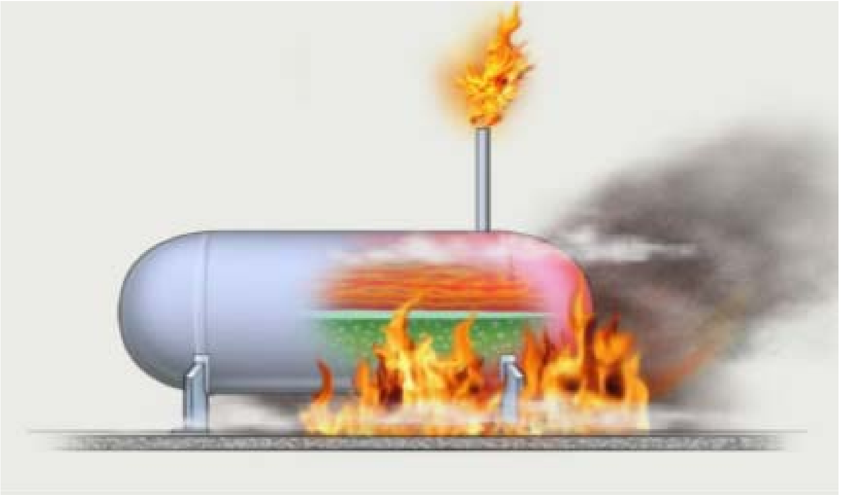


Figure 5.1 Schematic of fire scenario at Herrig Brothers (adapted from [36])

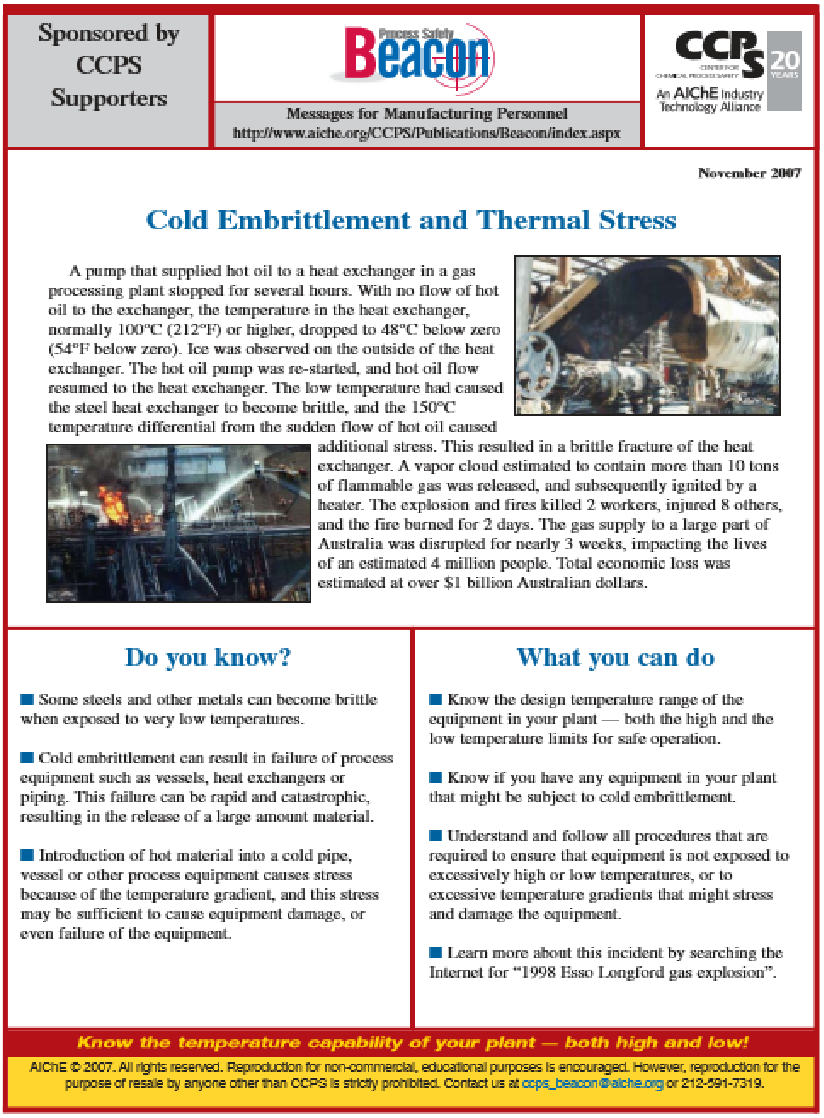
While the relief valve bought time for emergency response, eventually the vessel weakened. So while the relief device may be able to remove the necessary load, it could not keep the vessel from losing its structural strength if the fire continues indefinitely.

Low Temperature Embrittlement

In 1998, a major explosion and fire occurred at a gas processing facility in Victoria, Australia. The facility separated methane from Liquefied Petroleum Gas (or LPG). While the materials present (in this case, hydrocarbons) in this process are inherently hazardous because they are flammable, it was actually the conditions in the process that initiated the release of a large quantity of hydrocarbons.

The exact sequence of events that led to the accident is complicated, but the result was that the temperature in a heat exchanger dropped to minus 48 degrees Celsius. Warm “lean oil” was introduced into the heat exchanger that was cold; the “lean oil” was much hotter than the heat exchanger itself. The large temperature difference between the lean oil and the metal in the heat exchanger created enough stress to cause a brittle fracture.

Normal carbon steel is susceptible to brittle fracture at temperatures below about minus 29 degrees Celsius. Rupture of the heat exchanger led to the release of large quantities of flammable vapor, leading to a subsequent fire and a series of explosions. The fire burned for two days. Two employees were killed and eight were injured. The plant was destroyed and two nearby plants at the same site were damaged [37].



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Process Safety Beacon

Messages for Manufacturing Personnel
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CCPS Center for Chemical Process Safety 20 Years
An AIChE Industry Technology Alliance

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Cold Embrittlement and Thermal Stress

A pump that supplied hot oil to a heat exchanger in a gas processing plant stopped for several hours. With no flow of hot oil to the exchanger, the temperature in the heat exchanger, normally 100°C (212°F) or higher, dropped to 48°C below zero (54°F below zero). Ice was observed on the outside of the heat exchanger. The hot oil pump was re-started, and hot oil flow resumed to the heat exchanger. The low temperature had caused the steel heat exchanger to become brittle, and the 150°C temperature differential from the sudden flow of hot oil caused additional stress. This resulted in a brittle fracture of the heat exchanger. A vapor cloud estimated to contain more than 10 tons of flammable gas was released, and subsequently ignited by a heater. The explosion and fires killed 2 workers, injured 8 others, and the fire burned for 2 days. The gas supply to a large part of Australia was disrupted for nearly 3 weeks, impacting the lives of an estimated 4 million people. Total economic loss was estimated at over $1 billion Australian dollars.

Do you know?

- Some steels and other metals can become brittle when exposed to very low temperatures.
- Cold embrittlement can result in failure of process equipment such as vessels, heat exchangers or piping. This failure can be rapid and catastrophic, resulting in the release of a large amount material.
- Introduction of hot material into a cold pipe, vessel or other process equipment causes stress because of the temperature gradient, and this stress may be sufficient to cause equipment damage, or even failure of the equipment.

What you can do

- Know the design temperature range of the equipment in your plant — both the high and the low temperature limits for safe operation.
- Know if you have any equipment in your plant that might be subject to cold embrittlement.
- Understand and follow all procedures that are required to ensure that equipment is not exposed to excessively high or low temperatures, or to excessive temperature gradients that might stress and damage the equipment.
- Learn more about this incident by searching the Internet for “1998 Esso Longford gas explosion”.

Know the temperature capability of your plant — both high and low!

Hazards Associated with Flow

Operating a centrifugal pump under low flow conditions (pump deadhead) may cause elevated temperature and vapor pressure resulting in failure. Similar process conditions of low flow may also be a problem for heat transfer equipment where material may approach the heating media temperature. See Appendix B.2 for a detailed description of the hazards of pump deadhead even when handling non-hazardous water.

Loss of flow may also be a problem for heat transfer equipment. On December 19, 2007, a powerful explosion and subsequent chemical fire killed four employees and destroyed T2 Laboratories, Inc. (T2), a chemical manufacturer in Jacksonville, Florida (Figure 5.2). It injured 32, including four employees and 28 members of the public who were working in surrounding businesses. Debris from the reactor was found up to one mile away, and the explosion damaged buildings within one quarter mile of the facility. A loss of sufficient cooling during the process likely resulted in the runaway reaction, leading to an uncontrollable pressure and temperature rise in the reactor. The pressure burst the reactor; the reactor's contents ignited, creating an explosion equivalent to 1,400 pounds of TNT.

Figure 5.2 Aerial photograph of T2 damage [38]

Hydraulic Shock

Hydraulic surges are created when the velocity of a fluid suddenly changes and becomes unsteady or transient. Fluctuations in the fluid's velocity are generated by restrictions like a pump starting/stopping, a valve opening/closing, or a reduction in line size. It's sometimes referred to as "water hammer."

Common Types of Hydraulic Shock or "Water Hammer" include:

- Hydraulic Surge - Pressure surge occurs upon sudden change in fluid velocity or direction
- Condensation-Induced Accumulation of Condensate – Region (or "slugs") of liquid resulting from condensation which travels at the speed of vapor. Cavitation - Rapid formation and collapse of vapor within a liquid
- Void-Induced – rapid filling of empty piping with liquid or condensate.

- Fluid Entrainment - Region (or "slugs") of liquid resulting from entrainment which travels at the speed of vapor.

For hydraulic surge, the correlation from Rigid Column Theory (incompressible flow) is represented with Equation 5-1 [39, pp. 72-73]:

$$\mathbf{P_{Max} = P_0 + \rho\, \Delta v\, L / t} \qquad \text{Equation 5-1}$$

where: P_{Max} = Maximum Pressure in the pipeline, kPa
P_0 = initial pressure, kPa which should be the maximum pressure (pump discharge plus any elevation change)
ρ = liquid density, kg/m3
Δ v = velocity change, m/sec
L = pipe length, m
t = apparent valve closure time, seconds (note that v / t assumes the fluid deceleration is constant which is a gross simplification)

Another correlation for Hydraulic Surge is based on an instantaneous change in compressible fluid momentum shown in Equation 5-2 [40, pp. 119-120]:

$$\mathbf{P_{Max} = P_0 + \rho\, a_0\, \Delta v} \qquad \text{Equation 5-2}$$

where: a_0 = wave speed, m/sec (speed of sound in the fluid)
Δ v = change in velocity, m/sec

In August 2010, hydraulic shock of piping led to the release of 15,000 kilograms (32,000 pounds) of anhydrous ammonia at a facility which used ammonia as a refrigerant. Note that it wasn't the properties of ammonia that caused the release; instead, a physical phenomenon was the cause. More information on this incident may be found in the US Chemical Safety Board report no. 2010-13-A-AL.

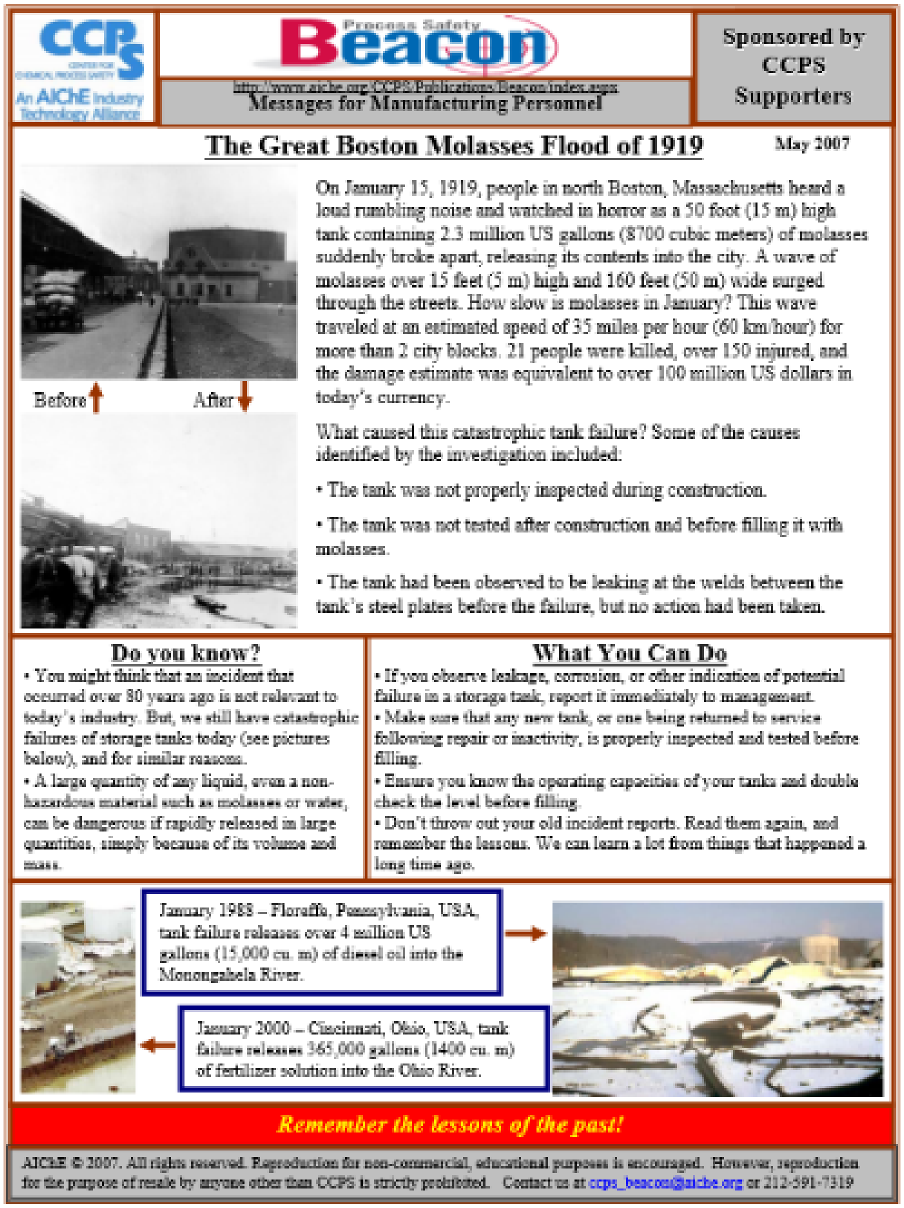
Liquid Level or Inventory Hazards

Level is another condition that needs to be managed. Uncontrolled liquid levels can lead to numerous problems. Some examples include:

- Overflows of toxic and hazardous materials, exposing personnel to respiratory and contact injuries (such as chemical burns, high temperature burns, and cryogenic burns);
- Spilled corrosive materials that can damage facility property and injure personnel; and
- Spilled flammable materials, which can lead to pool fires and vapor cloud explosions.

A well-known example of a high-level incident was the Texas City explosion, caused in large part by the facility's unawareness of a dangerously high liquid level in a distillation column. The column eventually overflowed leading to a flammable release and vapor cloud explosion This incident outcome resulting in numerous fatalities and severe facility damage. More information about this incident may be found in the US Chemical Safety Board report no. 2005-04-I-TX.

Another example is described in the May 2007 Process Safety Beacon. In this incident, the seemingly innocuous material molasses was involved. On January 15, 1919 in north Boston, Massachusetts, a 15 meter (50 foot) high tank containing 8700 cubic meters (2.3 million US gallons) of molasses suddenly broke apart, releasing its contents into the city. 21 people were killed, over 150 were injured, and the financial damage was significant.



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Messages for Manufacturing Personnel

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The Great Boston Molasses Flood of 1919

May 2007

Before ↑ After ↓

On January 15, 1919, people in north Boston, Massachusetts heard a loud rumbling noise and watched in horror as a 50 foot (15 m) high tank containing 2.3 million US gallons (8700 cubic meters) of molasses suddenly broke apart, releasing its contents into the city. A wave of molasses over 15 feet (5 m) high and 160 feet (50 m) wide surged through the streets. How slow is molasses in January? This wave traveled at an estimated speed of 35 miles per hour (60 km/hour) for more than 2 city blocks. 21 people were killed, over 150 injured, and the damage estimate was equivalent to over 100 million US dollars in today's currency.

What caused this catastrophic tank failure? Some of the causes identified by the investigation included:

- The tank was not properly inspected during construction.
- The tank was not tested after construction and before filling it with molasses.
- The tank had been observed to be leaking at the welds between the tank's steel plates before the failure, but no action had been taken.

Do you know?

- You might think that an incident that occurred over 80 years ago is not relevant to today's industry. But, we still have catastrophic failures of storage tanks today (see pictures below), and for similar reasons.
- A large quantity of any liquid, even a non-hazardous material such as molasses or water, can be dangerous if rapidly released in large quantities, simply because of its volume and mass.

What You Can Do

- If you observe leakage, corrosion, or other indication of potential failure in a storage tank, report it immediately to management.
- Make sure that any new tank, or one being returned to service following repair or inactivity, is properly inspected and tested before filling.
- Ensure you know the operating capacities of your tanks and double check the level before filling.
- Don't throw out your old incident reports. Read them again, and remember the lessons. We can learn a lot from things that happened a long time ago.

January 1988 – Floreffe, Pennsylvania, USA, tank failure releases over 4 million US gallons (15,000 cu. m) of diesel oil into the Monongahela River. →

← January 2000 – Cincinnati, Ohio, USA, tank failure releases 365,000 gallons (1400 cu. m) of fertilizer solution into the Ohio River.

Remember the lessons of the past!

Equipment Specific Hazards

Fluid Transfer Equipment

The majority of material in a process plant is moved via piping. While this is extremely reliable, piping still needs to get the same amount of attention as other equipment. Even more so, failures of items like hoses, valves, bellows, seals, and sight glasses, which may seem to be of lesser importance than major equipment items, can result in release of hazardous materials if mismanaged.

An incident at DPC Industries in Festus, Missouri provides a good example of the potential impact of a hose failure (CSB Investigation report no. 2002-04-I-MO) stop the release. They entered the chlorine cloud wearing "Class A" safety gear and climbed on top of the car to close the manual shut off valves (Figure 5.3). Nearby residents either evacuated or sheltered in place. The adjacent Interstate was closed to traffic for 1½ hours. Of the 63 people that sought medical evaluations due to respiratory distress, three were hospitalized. The release also damaged trees and other vegetation in the area.

Figure 5.3 Chlorine Release at Tank Car Station #3 [41]

A review of the 1974 Flixborough incident may be found in the CCPS publication Building Process Safety Culture: Tools to Enhance Process Safety Performance (2005). At a chemical plant in Flixborough, England, cyclohexane was converted in a series of reactors. One of these developed a six-foot crack. Management decided to remove the reactor and replace it with a temporary pipe designed in the maintenance shop without drawings or engineering review. The pipe was held in place by scaffolding (Figure 5.4).

The temporary piping worked for about two months. However, unknown to the operators, it was causing enormous stress to the reactor bellows. Finally, the bellows failed, releasing hot cyclohexane, which ignited. The plant and surrounding homes were extensively damaged. Scores of people were injured and 28 people were killed.

Figure 5.4. Flixborough temporary pipe illustration [42]

Fired Equipment

While not directly contacting process streams, fired equipment can become involved in significant adverse incidents, and requires the same process safety management as process equipment.

An example of a fired heater that was severely damaged during start-up as a result of a fire box explosion is shown in Appendix B.3. The operator had some difficulty with the instrumentation and decided to complete the start-up by bypassing the interlocks, on a one-time-only basis. This allowed the fuel line to be commissioned with the pilots out. The main gas valve was opened and gas filled the heater. Then the heater exploded, destroying the casing and damaging several tubes. Fortunately, no one was injured.

Consider the case of water in a boiler. In boilers, water is transformed into steam by the addition of heat. Furthermore, steam is almost always generated at high pressure. Pressure rises when water is transformed into steam in a closed vessel. If there is no way for the steam to escape, the vessel will explode. Corrosion or overheating can also cause a sudden rupture of the boiler and an explosion

The Grover Shoe Factory explosion was a seminal event, among others, that led to the development of the American Society of Mechanical Engineers (or ASME) Boiler and Pressure Vessel Code. This disaster was an industrial explosion, building collapse and fire that killed 58 people and injured 150 when it leveled the R. B. Grover shoe factory in Brockton, Massachusetts on March 20, 1905 (Figure 5.5). Following a boiler explosion, the four-story wooden building collapsed and the ruins burst into flames, incinerating workers trapped in the wreckage.

Figure 5.5. The Grover shoe factory after the explosion [43]

Heat Exchangers

A primary consideration in the operation of heat exchangers is to assure that there is no contact between the two materials transferring their heat. If the shell side and tube side materials in a leaking heat exchanger are incompatible and reactive, this could initiate a serious incident. Heat and pressure can develop, with possible equipment failure and escape of highly toxic or flammable materials. Even without this safety concern, there is the risk of product or cooling water contamination, which could then progress to a safety concern, often somewhere else in the system.

With so much surface area, corrosion can be a serious hazard in heat transfer equipment; this is a prime focus of Asset Integrity programs. In April 2010, the Tesoro refinery in Washington State, USA experienced a catastrophic explosion due to the rupture of one of its heat exchangers [44]. As a result, there were seven fatalities and massive damage to the facility. Table 5.1 provides some additional failure scenarios for heat exchangers.

Table 5.1 Failure Scenarios for Heat Transfer Equipment

No.	Operational Deviations	Failure Scenarios	Potential Design Solutions		
			Inherently Safer/Passive	Active	Passive
1 (T)	Overpressure	Corrosion/erosion of exchanger internals resulting in a heat transfer surface leak or rupture and possible overpressure of the low pressure side	• Double tube sheets • Seal welding of tubes to tubesheets • Open low pressure side return • Design changes to reduce erosion (e.g., lower velocities, inlet baffle) • Secondary heat transfer fluid • Design pressure of low pressure side equal to design pressure of high pressure side • Use of more corrosion resistant alloys • Use of less corrosive heat transfer media	• Emergency relief device on low pressure side	• Corrosion detection device (e.g., coupons) • Periodic inspection/ analysis of low pressure fluid for high pressure fluid leakage
2 (T)	Overpressure (Shell and Tube Exchanger)	Differential thermal expansion/ contraction between tubes and shell resulting in tube leak/rupture (Fixed Tubesheet)	• U-tube exchanger design • Shell expansion joint or internal floating head • Design pressure of low pressure side equal to design pressure of high pressure side • Use of designs other than shell and tube (e.g., spiral, plate and frame)	• Emergency relief device on low pressure side • Automatic control of introduction of process fluids on start-up and shutdown	• Procedural control of introduction of process fluids on start-up and shutdown • Periodic inspection/ analysis of low pressure fluid for high pressure fluid leak
3 (T)	Overpressure (Shell and Tube Exchanger)	Excessive tube vibration resulting in tube leak/rupture and possible overpressure of the	• Mechanical design (e.g., proper baffle spacing) accommodating maximum anticipated inlet feed pressure/velocity • Design pressure of low pressure side	• Emergency relief device on low pressure side	• Periodic inspection/ analysis of low pressure fluid for high pressure fluid leak

Rotating Equipment

Failure of rotating equipment may be caused by vibration damage, excessive speed, or other process upsets. On 17 August 2009, a turbine of the Sayano-Shushenskaya hydroelectric power station near Sayanogorsk. Russia failed catastrophically, flooding the building and killing 75 people (Figure 5.6). A section of the roof of the turbine hall collapsed; all but one of the ten turbines were damaged or destroyed. The entire plant output, totaling 6,400 MW – a significant portion of the supply to the local area – was lost, leading to widespread power outages.

The turbine was not properly rebalanced after repairs, following which turbine 2 had increased vibrations, ca 0.15 mm (0.0059 in) for the main bearing during the full load of the turbine. While this did not exceed specifications, the increased vibrations were unacceptable for long term use. The elevated vibration levels compared to other turbines were apparent for turbine 2 before the repair as well. The vibrations exceeded the allowed specification in the beginning of July and continued to increase with accelerated speed.

Figure 5.6 The power station after the accident, with the roof of the turbine hall partially collapsed

Dust Handling Equipment

It's not unusual for combustible dusts to ignite and explode. In this case, the material is present as a fine powder or dust dispersed in air which renders it susceptible to an explosion. Common combustible materials, which seem innocuous, can be dangerous when they are finely divided and dispersed in air. Grain silos have exploded because they contain grain dust suspended in air. Similar events can occur in industrial operations where combustible dusts are handled.

On February 7, 2008, a series of dust explosions and subsequent fires occurred at the Imperial Sugar manufacturing facility in Port Wentworth, Georgia, destroying much of the plant (Figure 5.7). As a result:

- 14 workers were killed;
- 36 other workers were seriously injured;
- Extensive facility damage occurred beyond the initial ignition point as a result of massive secondary explosions and fires;
- 7.6 centimeter thick concrete floors were shattered; and
- Packing buildings, granulated sugar silos, and a palletizer room were destroyed, and the bulk sugar loading and refinery area were severely damaged.

The initiating event was airborne sugar inside an enclosed steel belt conveyor reaching an explosible concentration and contacting an ignition source (thought to be an overheated bearing) inside the conveyor.

- The sugar and cornstarch conveying equipment was not designed or maintained to minimize the release of sugar and sugar dust into the work area.
- Inadequate housekeeping practices resulted in significant accumulations of combustible sugar and sugar dust on the floors and elevated surfaces throughout the packing buildings.
- Airborne combustible sugar dust accumulated above the minimum explosible concentration (MEC) inside the newly enclosed steel belt assembly.

- The primary dust explosion inside the enclosed steel conveyor belt led to massive secondary dust explosions and fires throughout other buildings.
- The 14 fatalities were most likely the result of the secondary explosions and fires.

Secondary explosions knocked out much of the emergency lighting and fire suppression piping.

Figure 5.7. Damage from dust explosion at the Imperial Sugar Company [45]

Contributing Factors to the Severity of Hazards

Impact of Size or Scale

The size of a system influences how hazardous it is. Naturally, large systems can have a larger impact than small systems. The impact of a release of a hazardous material can have a significant impact and can endanger not only employees but members of the public.

Ammonium nitrate is commonly used as a fertilizer on farms, and it may be present in small quantities in an ordinary home. Most people would hardly consider a bag of fertilizer to be dangerous. In fact, ammonium nitrate is quite safe at ambient temperature and pressure. It doesn't burn. In small amounts, it's harmless. But when ammonium nitrate is heated in a confined space, it can decompose rapidly and detonate.

On April 17, 2013 a fire broke out in a fertilizer storage and distribution facility in the town of West, Texas. The facility stored large amounts of ammonium nitrate for use as a fertilizer. The fire caused approximately 27 metric tons of ammonium nitrate to detonate. The site itself and buildings near the site were destroyed. The explosion led to extensive damage and destruction in the town of West, Texas. It also caused 15 fatalities and many more injuries.

Another example of the impact of size involves Liquefied Petroleum Gas (or LPG). LPG is a fuel which is especially useful for cooking and heating (and so it's naturally flammable). It's used in both homes and industry. Like other materials, it's stored in large quantities at facilities where it's produced or at facilities that distribute LPG to customers.

The Mexico City facility had six spherical storage tanks and 48 smaller horizontal cylindrical tanks. On November 19th, 1984 an LPG leak occurred at the Mexico City terminal. The exact cause could not be determined with certainty after the event because of the extent of the damage to the site. The LPG leak continued for five to ten minutes and a cloud of LPG vapor estimated to be 200 meters by 150 meters by two meters high formed. The cloud ignited. The explosion knocked storage tanks off their supports and ruptured piping, causing more LPG to be released.

A series of explosions which destroyed the site followed. In addition to destroying the facility, the fire and explosions killed 600 people and injured 7000 others. Most of the casualties were members of the public living in surrounding communities. So the explosion of a home LPG tank might cause damage a few houses away whereas the explosion of a large LPG tank, by contrast, might damage or destroy entire communities.

Impact of the Proximity of Personnel

There are several other factors that may influence the severity of a hazard. These hazards are often created or made worse by conditions not directly associated with the normal operation of the process, including conditions outside the equipment in the process and even outside the plant fence line. These conditions include:

- Proximity of members of the public;
- Location of onsite buildings;
- Confinement of materials released from the process;
- Confinement during vessel entry; and
- The presence of sources of ignition.

Having large numbers of people living or working nearby can result in large numbers of fatalities in the case of an accidental chemical release, fire, or explosion. The Mexico City LPG explosion in particular (people were living as close as 130 meters from the terminal, and there were hundreds of fatalities). Also, communities were nearby the West Fertilizer facility where the ammonium nitrate explosion occurred.

Impact of Building Location

Building locations are also important. Public buildings or private residences, which may be located offsite but nearby (as in the case of the Mexico City LPG explosion), can be vulnerable to explosions. Likewise, locations of onsite buildings can significantly affect the safety of workers. People inside buildings are in danger of being killed or injured from building collapse, flying debris, and shattered glass in the event of an explosion. They may also be vulnerable to a toxic gas release.

The proximity of onsite buildings has played an important part in the outcome of several notable incidents, including the one in Texas City in March 2005. In this incident, the CSB noted that the “placement of occupied trailers close to the ISOM unit was a key factor leading to the fatalities from this disaster [46].” This incident has also been provided as a case study using RAST [1]. Trailers were used as temporary buildings for use by contractors at the site. Some of these trailers were located 37 meters from the process. The accident resulted in 15 fatalities, all of them contractors working in or around the trailers.

Confinement of Hazardous Releases

If the materials are released from a process, they’re sometimes more dangerous if they’re confined rather than allowed to disperse freely in the atmosphere. Situations of particular importance include:

1. Confinement of flammable or toxic vapors inside buildings; and
2. Confinement of flammable vapors outdoors but between buildings or plant equipment.

Vapor (or a liquid with a high enough vapor pressure) that escapes from piping or equipment enclosed in a building will accumulate. The concentration of the vapor in the air in the building will increase. The maximum concentration depends on building ventilation and the rate that the substance escapes into the building. The air within the building may increase above the concentration that would be attained outdoors unless the ventilation is capable of providing enough air to control the concentration increase.

If the substance is flammable, confinement within a building can cause the concentration to exceed the lower flammable limit and an explosion can occur. The explosion may be more energetic than if the vapor were released outdoors because confinement makes a detonation (in which the shockwave moves at the speed of sound) possible. Examples of confined vapor cloud explosions, such as events in Danvers, Massachusetts and Perth Amboy, New Jersey, can be explored by clicking the book icons.

Also, remember that confinement of something seemingly harmless, such as nitrogen, in a building is dangerous because it creates the risk of asphyxiation. The need to enter a space not normally intended for continuous human occupation; is “confined space entry.” Sometimes there is a need to enter vessels to clean them, to inspect them, or to perform other maintenance.

There are a number of problems that can occur during confined space entry:

- Asphyxiation by nitrogen used to purge the vessel or by other gases (like CO2) which are either used for purging or which leak into the vessel;
- Exposure to the effects of residual chemicals;
- Exposure to chemicals accidentally introduced into the vessel; and
- Engulfment (for instance, by falling into or being buried in solids already present in the vessel).

The main thing to remember about confined spaces is that they create conditions in which people entering them could be at risk for asphyxiation or exposure to toxic or flammable substances.

Ignition Sources

Where flammable gases or liquids are present, there’s a danger of a fire or explosion. Therefore, it’s necessary to reduce or eliminate oxygen or to eliminate ignition sources. In processes where flammable materials are present, small leaks to the atmosphere often cannot be entirely eliminated. Since atmospheric air contains oxygen, it’s important to identify ignition sources that can ignite flammable materials leaking to the atmosphere and initiate a fire or explosion.

It’s especially important to recognize that electrical equipment that is not intended for use in environments where flammable materials might be present can be a source of ignition. Electrical equipment includes the electrical devices normally present in a plant (such as motors, switches, power outlets, lights, and electrically operated controls). Electrical equipment not suitable for environments where flammable atmospheres are possible includes cell phones, computers, and similar electronic devices.

Static electricity is a hazard that can result in explosions and flash fires when there is contact with flammable liquids, gases, vapors, or dusts. Consider these static electricity hazards:

- The use of power or conveyor belts in which non-conductive materials move over or between pulleys and rollers;
- Pulverized materials or dusts passing through chutes or being conveyed pneumatically;
- The flow of fluids through pipes or conduits (as we saw near the end of Section 3) or from orifices into tanks or containers (known as splash filling);
- The flow of gases from orifices;
- The use of rubber-tired vehicles;

- The general accumulation of static charge on personnel in the work place, particularly when they wear overalls made of synthetic materials; and
- Sparks arising from the use of tools or friction in machinery.

The generation of static electricity is illustrated a case study described in Appendix B.4. A fire and series of explosions occurred in a chemical distribution facility. The fire started in a packaging area while a portable steel tank (a "tote") was being filled with ethyl acetate, a flammable material. An operator placed the fill nozzle in the opening on top of the tote and suspended a steel weight on the nozzle to keep it in place. As the tote was filling, it burst into flames. The fire spread to a warehouse, igniting other stored flammable and combustible liquids. To make matters worse, the fire propagated and spread to a tank farm area.

It was determined that static electricity likely was generated, accumulated and was discharged, igniting the vapor that accumulated around the fill opening during filling. A static electric charge can be created by liquid freely falling through air, and can result in sparks such as from an ungrounded conductor.

6. HAZARD SCREENING

The Hazard Screening step (What are the Hazards) are addressed with the first two elements in the HIRA Workflow (Figure 6.1). The handling of any chemical at a wide range of process conditions involves risk. However, it is important to narrow the scope of risk analysis to those chemicals and processing units representing significant hazard. Prior to performing Hazard Identification and Risk Analysis (HIRA) study, the process hazards must be identified and screened to determine which equipment or unit operations should be analyzed.

Each company may have hazard screening criteria. Note that CCPS does not endorse any specific criteria but provides guidance for the company to consider. If hazard severity is considered reasonably low, then a HIRA study may not be required (or "screened out"), provided there is no regulatory or other requirement.

Figure 6.1 The Hazard Screening Step in the HIRA Workflow Process

Hazard Definition

As noted in Section 1, a hazard is defined as an inherent physical or chemical characteristic that has the potential for causing harm to people, property, or the environment [4].

Based on experience and general observation, the guidelines in this section are provided as examples that may be used in determining what equipment items usually are not included in a Hazard Evaluation study when all of the conditions are met.

Flammable Hazard sufficient for evaluation *does not exist* for equipment, vessels, transport containers, or piping handling chemicals if:

- Flash Point > 60 C *and*
- The maximum process temperature (under normal or upset conditions) is less than the flash point less 5 C *and*
- There are no "hot" surfaces in the immediate area that liquid could contact exceeding the flash point less 5 C *and*
- The chemical is not considered a combustible dust or a combustible liquid that could be released as a small droplet aerosol or mist.

Toxicity Hazard sufficient for evaluation *does not exist* for equipment, vessels, transport containers, or piping handling chemicals if:

- ERPG-3 is higher than an established level related to serious human health effects (e. g., ERPG-3 > 1000 ppmv) for gases or vapors *and*
- Chemical is not labeled or considered by a regulatory agency to be toxic if inhaled, toxic in contact with skin, or toxic to the environment.

Reactivity Hazard sufficient for evaluation *does not exist* for equipment, vessels, transport containers, or piping where intended or unintended reactions may occur (including reaction with water or any other chemical which may be inadvertently added) if:

- Heat of Reaction / Mass is minimal (e. g., less exothermic than –50 J/g or 25 C adiabatic heat rise) *and*
- There is no evidence of highly volatile or gaseous products generated - *and*
- The chemical is not considered or labeled as Explosive, Pyrophoric, Oxidizing, Water Reactive or otherwise Unstable.

Equipment: Hazardous Conditions sufficient for evaluation *do not exist* for, vessels, piping, or other equipment handling chemicals if:

- The maximum process temperature that does not pose a thermal hazard to human tissue under normal, upset, or reaction conditions (e. g., less than 60 C for liquids, less than 93 C for vapors and material temperature is greater than -23 C) *and*
- The chemical handled is not corrosive to human tissue *and*
- The maximum process pressure or vapor pressure (under normal, upset, or reaction conditions) does not exceed the MAWP or relief device set pressure *and*
- The equipment or piping is not located within an enclosed area that a release could pose an asphyxiation hazard

Other Types of Hazards

Other hazards that may be evaluated include potential for thermal burns, chemical burns, equipment rupture, relief device activation, and asphyxiation in addition to flammability, toxicity, and reactivity noted in this section. When in doubt if a hazard sufficient to include equipment, vessels or piping in the evaluation; *include it*. There are steps later in the proposed Hazard Identification and Risk Analysis work process when scenarios or incident outcome will be screened out from further evaluation.

7. HAZARD EVALUATION

Hazard Evaluation is an organized effort to identify and analyze “what can go wrong” in a chemical process (Figure 7.1). Fortunately, the number of catastrophic incidents is very small relative to the total number of incidents or near misses each year. Fortunately, not everyone personally experiences a catastrophic incident during their career. This may present a challenge in appreciating the importance in developing a thorough Hazard Evaluation.

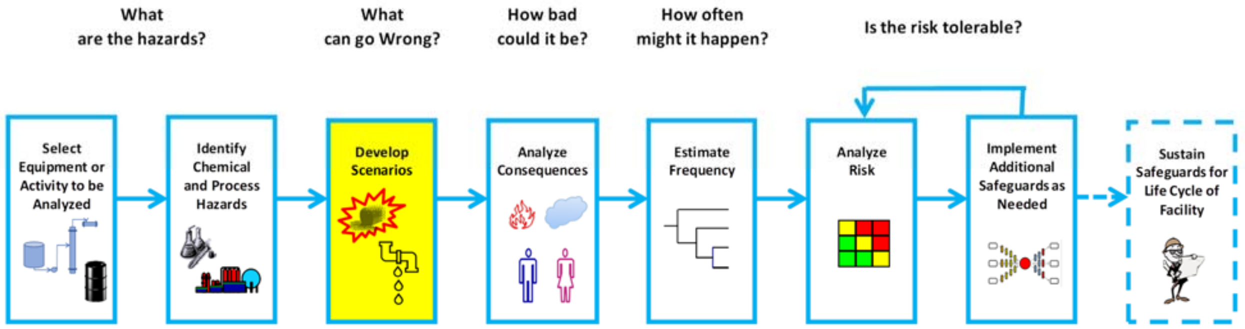


Figure 7.1 The Scenario Developing Step in the HIRA Workflow Process

Section Objectives

The following objectives are covered in this section:

- Understand when to begin Hazard Evaluation.
- Understand what information is needed for Hazard Evaluation.
- Recognize Fire and Explosion Index and Chemical Exposure Index.
- Be able to define a Scenario.
- Match phrases related to the concepts of a Hazard and Operability (HAZOP) Study.
- Be able to use HAZOP keywords to identify process upsets that could lead to an incident.
- Understand basic concepts for screening feasible scenarios.

Non-Scenario and Scenario Based Hazard Evaluation Techniques

Hazard Evaluation involves both experience-based and predictive techniques[1]. It should be performed several times throughout the life of a process. Non-scenario-based techniques rely primarily on experience and focus on major risks within process units. These techniques may also identify design criteria or alternatives that could reduce hazards.

Non-Scenario Based Techniques

- Reactive Chemicals/Process Hazard Reviews
- Checklist Analysis
- Relative Ranking Indices

Scenario Based Techniques

- Defining a Scenario
- What-If Analysis
- Hazard and Operability Analysis (HAZOP)
- Other Methods (Fault Tree, Event Tree, etc.)

Scenario based techniques are predictive and commonly used in performing more detailed analysis of a wide range of hazards during the design phase of a process and during routine operation. As these techniques are based on a common denominator, the scenario, the analysis may be used to systematically determine what can go wrong. Results are often scenarios appropriately structured for continuation into Barrier Analysis, Layers of Protection Analysis, or Quantitative Risk Analysis.

Each method or technique has strengths and weaknesses. Different techniques may be better suited for highly hazardous portions of the process (versus less hazardous units). It is best to combine methods to gain the advantages of creative techniques such as brainstorming with more structured approaches such as checklists and HAZOP. Each technique is more thorough and effective when performed by an experienced team.

When to Perform Hazard Evaluation

Hazard Evaluation should be performed several times throughout the life of a process.

- For capital projects, start “non-scenario based” techniques early as the plant is beginning the equipment layout. Continue updating the Hazard Identification as design information becomes available.
- Begin using “scenario based” techniques as equipment design pressure and relief device set pressure is determined
- Finalize the Hazard Evaluation once Piping and Instrument Diagrams are complete and equipment interconnectivity is known (and before final capital authorization)
- Update the Hazard Evaluation for existing facilities as part of periodic revalidation.

Preparing for Hazard Evaluation

The appropriate objective for a hazard evaluation depends upon several factors, including the life cycle phase the project is in when the hazard evaluation is performed. As a project evolves, the types of hazardous situations investigated change from general questions about basic process chemistry to more detailed questions about equipment and procedures. If the hazard evaluation is being done to comply with regulatory requirements, the process covered by regulation must clearly be identified. Depending on the objectives, the boundaries of the study may be drawn to include only injury impacts or, more broadly to include non-injury community impacts, property damage, business interruption, and/or environmental impacts, with a threshold severity also drawn for each additional type of impact.

The composition of the team performing a hazard evaluation is essential to the success of the study. The level and types of skills that personnel must have to participate in hazard evaluations depend upon several factors, including the type and the complexity of process or operation analyzed, the hazard evaluation technique selected, and the objective of the analysis.

- The *team leader* (or facilitator) provides direction for the analysis, organizes and executes analysis activities, and facilitates any team meetings that may be held as part of the study.
- A *scribe* or note taker is typically designated to formally document the discussions that take place during studies. If using a computer-based means of documenting the hazard evaluation, this individual will also need to be proficient in the use of both the hardware and the software that is employed.
- The remainder of the evaluation team is composed of *contributors* or experts in various aspects of the design and operation of the process being evaluated.

Process Equipment to Include in a Hazard Evaluation Study

Process hazards typically depend upon a chemical or physical property (such as a flammable limit or vapor pressure), process conditions (such as temperature, pressure, or flow rate) and equipment parameters (such as volume and maximum allowable working pressure). Any unit operation (or major equipment item) within the scope or boundaries of the chemical process where a hazard is recognized is typically included in the scope of the Hazard Evaluation study. Process hazards typically depend upon a chemical or physical property (such as a flammable limit or vapor pressure), process conditions (such as temperature, pressure, or flow rate) and equipment parameters (such as volume and maximum allowable working pressure). Any unit operation (or major equipment item) within the scope or boundaries of the chemical process where a hazard is recognized is typically included in the scope of the Hazard Evaluation study.

Hazard Identification typically begins with a review Index Flowsheets, Process Flowsheets (Figure 7.2), or Block Flow Diagram of the process (using whatever level of detail is available). Ultimately, Piping and Instrument Diagram (P&ID) level details may be needed to pinpoint potential backflow and other interconnectivity issues.

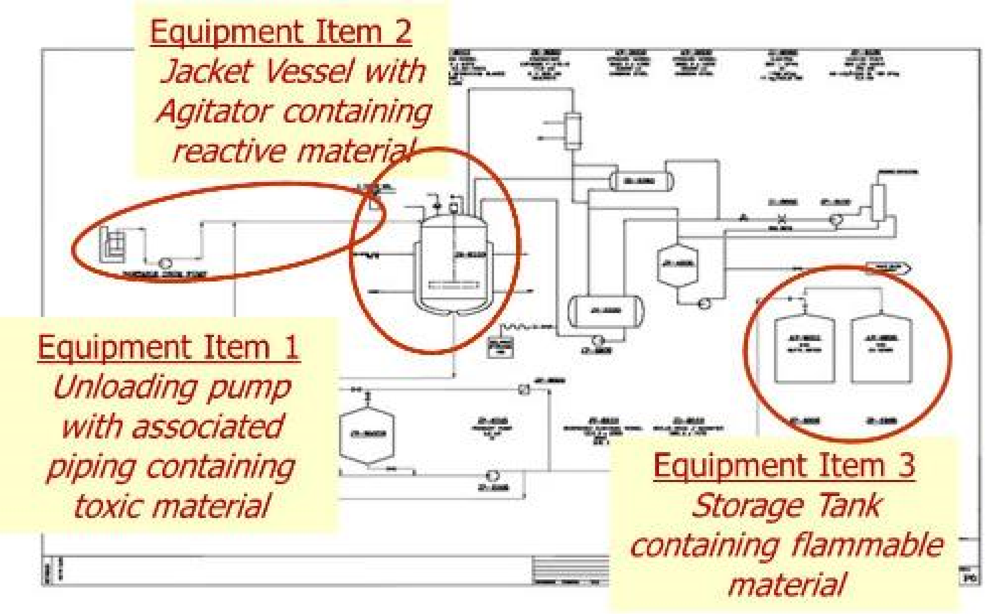


Figure 7.2 Example Equipment Depiction on Process Flowsheet

Key Process Information Needed for Hazard Evaluation

The more information and knowledge one has about a process, the more thorough and valuable the hazard identification can be. Ultimately, the quality of any hazard evaluation depends directly on the quality of the information available to the analysis team.

Process Description – A compilation of information needed as input for process risk analysis including:

- Chemical related properties
- Process conditions
- Equipment design parameters
- Site and plant layout
- Procedures and policies

Chemical related properties include molecular weight, physical state, vapor pressure, liquid density, liquid heat capacity, and heat of vaporization. Chemical properties also include flash point, flammable limits, minimum ignition energy, Emergency Response Planning Guideline (ERPG) concentrations, NFPA ratings or European Risk Phrases, and other chemical information one might find associated with a Material Safety Data Sheet.

Process conditions include temperature, pressure, feed rate and feed pressure. Batch versus continuous operation, batch processing steps, maintenance of an inert atmosphere, and potential for plugging or corrosion issues also represent process conditions.

Equipment design parameters include equipment type, volume, design pressure, surface area, pipe diameter and length, motor size, and material of construction. Depending upon the type of equipment, heat transfer area and heating or coolant temperature, relief device type and set pressure, and type of insulation are also equipment parameters.

Site and plant layout includes spacing to occupied buildings and number of occupants, distance to local (off-site) population, size of spill containment, volume of indoor process areas, and distance to fired equipment. Assessment for access of emergency services, drainage, process area congestion and confinement, and potential to spill to waterways or other layout information may be needed.

Procedures and policies will also impact chemical process risk assessment. The failure frequency for piping and equipment is dependent on design and inspection practices. The effectiveness of return to operations procedures following maintenance or daily equipment checks impacts the frequency of many “loss of containment” events. Corporate standards and regulatory requirements establish many of the policies and procedures that are routinely practiced.

Process Hazard Assessments

Government regulations require periodic Process Hazard Assessments for existing facilities, in addition to unannounced external audits. *There is a good chance that everyone at a plant site will be involved in one or more of these reviews.*

When performed on existing facilities, the Process Hazard Assessment typically involves a walk-through inspection that can vary from an informal, routine visual examination to a formal team examination that takes several weeks. For processes that are still being designed, a design project team might, for example, review a set of drawings during a meeting.

A Process Hazard Assessment includes interviews with people in the plant: operators, maintenance staff, engineers, management, safety staff, and others, depending upon the plant organization. If performed on an existing facility, the review should start with a general orientation tour of the plant and progress to specific inspections and interviews. The review team may cover the relevant emergency procedures with operating personnel in a “roundtable” discussion.

The personnel assigned to the Review must be very familiar with safety standards and procedures. Special technical skills and experience are helpful for evaluating instrumentation, electrical systems, pressure vessels, process materials and chemistry, and other special-emphasis topics.

Checklist Analysis

The Checklist Analysis approach is easy to use and can be applied at any stage of the process's lifecycle.

- Checklists are used primarily to ensure that organizations are complying with standard practices.
- Checklists are limited by their authors' experience; therefore, they should be developed by authors with varied backgrounds who have extensive experience with the systems they are analyzing.

Example checklist questions for the inherent safe design of a facility (typically used during the early design phase) [47]:

Substitution

- Can a flammable solvent be replaced with water?
- Is it possible to completely eliminate hazardous raw materials, process intermediates, or by-products by using an alternative process or chemistry?

Minimization

- Can hazardous finished product inventory be reduced?
- Can alternative equipment with reduced hazardous material inventory be used, such as
- Flash dryers in place of tray dryers?
- Continuous in-line mixers (static mixers) in place of mixing vessels or reactors?

Moderation

- Is it possible to limit the supply pressure of raw materials to less than the maximum allowable working pressure of the receiving equipment?
- Is it possible to make the reaction conditions (temperature, pressure) less severe by using a catalyst or a better catalyst?

Simplification

- Can equipment be designed such that it is difficult or impossible to create a potentially hazardous situation due to an operating or maintenance error, such as by
- Easy access and operability of valves to prevent inadvertent errors?
- Elimination of all unnecessary cross-connections?

Relative Ranking

This technique allows hazard analysts to compare the attributes of several processes or activities to determine whether they possess hazardous characteristics that are significant enough to warrant further study. Relative Ranking methods are used to determine the process areas or operations that are the most significant with respect to the hazard of concern, the potential severity of consequences, or the overall risk in a given study.

- **Fire and Explosion Index (F&EI)** – Evaluates the fire and explosion hazards associated with discrete "process units" considering material properties, process conditions, operating characteristics, distance from adjoining areas, the existence of safety and fire protection systems, etc.
- **Chemical Exposure Index (CEI)** – Addresses factors that can influence the effects of a chemical release: acute toxicity, volatile portion of material that could be released, distance to areas of concern, and various process parameters such as temperature, pressure, reactivity, etc.

Scenario-Based Hazard Evaluation Definitions

Definitions used in Scenario-based evaluations, consistent with several publications from the Center for Chemical Process Safety literature include:

- **Event** – An occurrence involving a process that is caused by equipment performance or human action or by an occurrence external to the process.
- **Event Sequence** – A specific, unplanned series of events composed of an initiating event and intermediate events that may lead to an incident.
- **Loss Event** – Point in time in an abnormal situation when an irreversible physical event occurs that has the potential for loss and harm impacts. Examples include release of a hazardous material, ignition of flammable vapors or ignitable dust cloud, and over-pressurization rupture of a tank or vessel.
- I**nitiating Event** – the first event in an event sequence and marks the transition from a normal to an abnormal situation.
- **Incident Outcome** – The physical manifestation of the incident: for toxic materials, the incident outcome is a toxic release, while for flammable materials; the incident outcome could be a boiling liquid expanding vapor explosion (BLEVE), flash fire, vapor cloud explosion (VCE), etc.
- **Scenario** – A detailed description of an unplanned event or incident sequence that results in a loss event and its associated impacts, including the success or failure of safeguards involved in the incident sequence.

Scenario Development

Scenario development is the step in which the team or analyst constructs a series of events, including initiating events that lead to a loss event with undesired consequence (Figure 7.3).

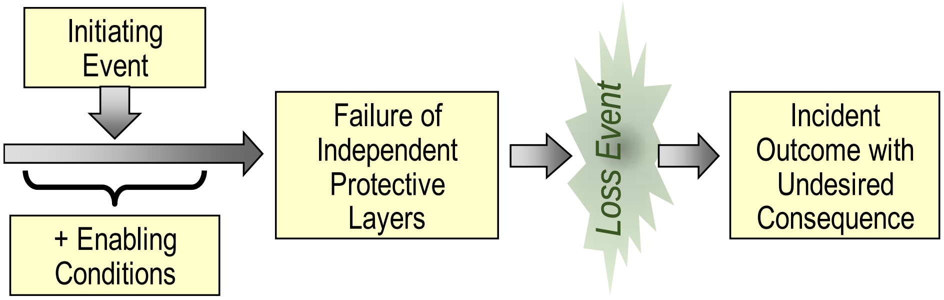


Figure 7.3 Hazard Scenario

Scenario development is sometimes referred to as “structured scenario analysis”. Ideally, a project team begins Hazard Identification early in the design and completes the Scenario-Based approach as Piping and Instrument Diagrams are being finalized. This will help to ensure that issues are resolved before final authorization of capital funds.

Inherently safer concepts attempt to reduce risk by eliminating scenarios, usually by preventing or limiting the magnitude of the loss event. For example, if a process is modified to significantly reduce the inventory of a toxic material that could be released, the consequence, and thus the risk, associated with a vessel rupture can be significantly reduced. Again, if a vessel is designed to resist an internal explosion, or the shut-off head pressure of a pump, or a relief flow is passed to a flare rather than directly to the atmosphere; the risk associated with these scenarios may be reduced or eliminated.

Initiating and Loss Events

The initiating and loss events that affect the scenario development are depicted in Figure 7.4.

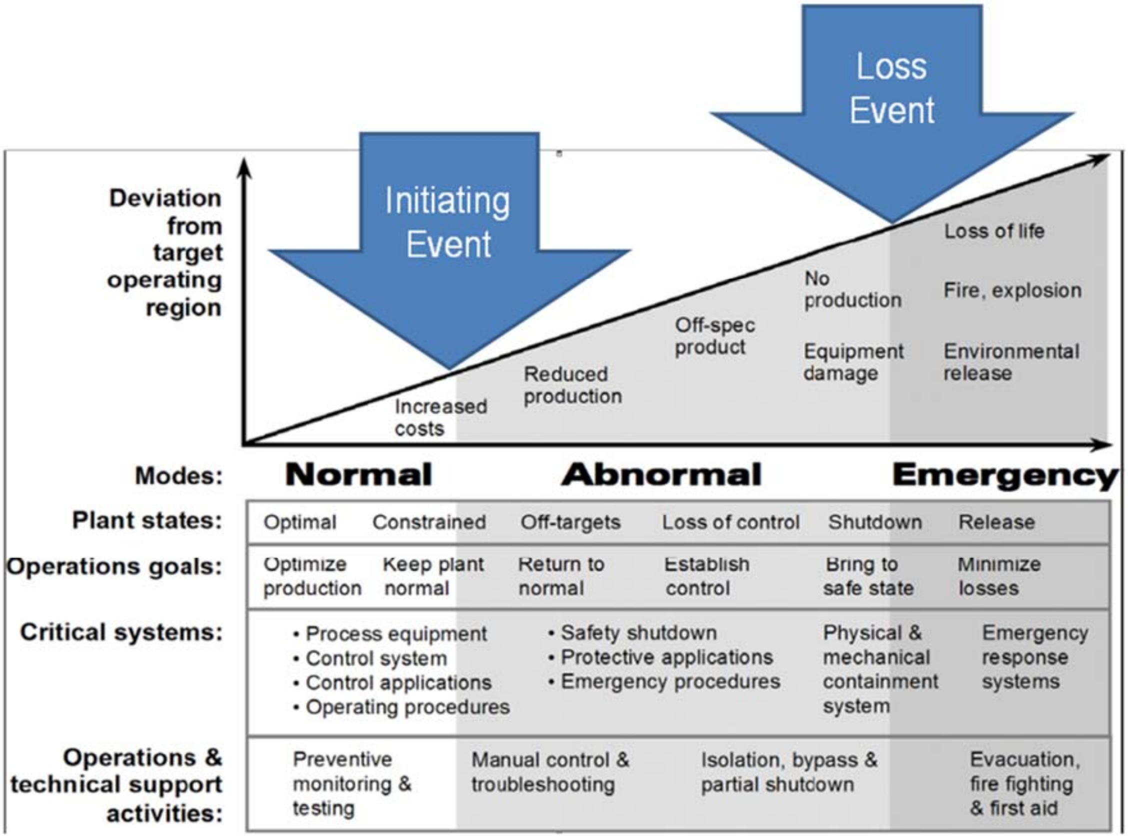


Figure 7.4 Common Operating Modes (adapted from [5, p. 23])

Initiating Events

Initiating Events typically fall into broad categories [6]:

- **External events** include natural phenomena such as earthquakes, tornadoes, or floods, and third-party intervention such as mechanical impact on equipment or supports by motor vehicles, or construction equipment. Sabotage and terrorism are initiating events that require special treatment, because a true saboteur may defeat, or attempt to defeat, Protective Layers.
- **Equipment-related initiating events** can be further classified into control system failures and mechanical failures. Control system failures include, but are not limited to:
    - basic process control system (BPCS) component or software failures,
    - failure of control support systems or utilities (e.g., electricity, instrument air).

Similarly, **mechanical failures include**, but are not limited to:

  - vessel or piping failure caused by wear, fatigue, or corrosion;
  - vessel or piping failure caused by overpressure (e.g., thermal expansion, pigging/blowing) or under-pressure (vacuum collapse);
  - vibration-induced failures (e.g., in rotating equipment);
  - failures caused by design defects or inadequate maintenance/repair (including substitution of improper materials of construction)
  - failures resulting from high temperature (e.g., fire exposure, loss of cooling) or low temperature and resulting brittle fracture (e.g., auto-refrigeration, low ambient temperature);
  - failures resulting from flow surge or hydraulic hammer; and

- **Human failures** are either errors of omission or errors of commission, and include but are not limited to:
  - failure to execute the steps of a task properly, in the proper sequence or omitting steps (something not done), or
  - failure to observe or respond appropriately to conditions or other prompts by the system or process (something done wrongly).

In addition, **Domino Effects** across the facility from fires or explosions in adjacent equipment as a cause or Initiating Event may need to be considered.

Loss Events

A Loss Event is essentially the “unintended release of a hazardous material or energy”; or loss of containment from:

- Gasket leak
- Connection failure
- Piping leaks
- Pump Seal leaks
- Inadvertently opened valve
- Relief Device activation
- Equipment rupture

In some Hazard Evaluation studies, the Loss Event is often qualitative and may not always be well differentiated from the causes or Initiating Events. Where additional clarity is needed (such as Quantitative Risk Analysis), Loss Events may be categorized by the type of discharge model used to determine the rate of release.

- **Hole Size** – many release situations may be estimated as an orifice or short pipe calculation
  - 5 to 10 mm to represent gasket failure or seal leak.
  - 100 mm to full bore diameter to represent pipe or equipment nozzle failure.

- **Fill Rate** used for overflow and backflow situations.
- **Excessive Heat** determined by an energy balance as the rate of heat input divided by heat of vaporization.
- **Catastrophic Failure or Rupture** as a sudden release of entire equipment contents and corresponding release of reaction or pressure-volume energy.

Incident Outcome

A single incident may have several potential outcomes. For continuation of Scenario Identification, the Incident Outcome, Impact or Consequence may need to be estimated in terms of human injury, damage, or economic loss. This is discussed in more detail as part of the Consequence Analysis topics (Impact Assessment).

Flammable Outcome:
- Flash Fire or Fireball
- Vapor Cloud Explosion
- Building or Confined Space Explosion

Toxic Outcome:
- Off-site toxic exposure
- On-site toxic exposure
- Toxic infiltration of occupied buildings
- Chemical Exposure

Other Outcome:
- Physical Explosion
- Environmental Incident
- Equipment Damage/Business Loss

Note that pool fire and jet fire are other possible flammable outcome that usually starts with a flash fire. Flash fire typically involves a greater effect zone than pool or jet fires.

What-If Analysis

The What-If Analysis technique is a brainstorming approach in which a group of experienced people familiar with the subject process ask questions or voice concerns about possible undesired events.

What-If Analysis is not as inherently structured as some other techniques such as a HAZOP study. The concept encourages the hazard evaluation team to think of questions that begin with “What-If.” However, any process safety concern can be voiced, even if it is not phrased as a question. The technique can also be used to evaluate hazards in a safety review.

Ideally “What if” questions represent potential Initiating or Loss Events in a Scenario. For example, “What if the unloading connection comes apart when the transfer begins?” represents an Event which could be caused by mechanical failure or human error. The team would brainstorm process deviation scenarios and identify inherent safety improvements for reducing or eliminating the potential for the scenario to develop. The strategies of substitution, minimization, moderation and simplification can be used to determine the safety improvement.

What-If Checklist

What-If Checklists provide the team with a list of thought-provoking issues to help reduce the time commitment to identify scenarios while improving the quality of the analysis (Figure 7.5).

Releases of materials to the surroundings that could result in pool fires, flash fires, vapor cloud explosions or toxic vapor clouds, dust clouds, or mist clouds, with significant acute exposure to personnel.

1. Vessel Failure
- ☐ a. Installation
  - 1) vibration
  - 2) fatigue
  - 3) embrittlement (e.g., cast iron/ steel, hydrogen)
- ☐ b. Impingement
  - 1) crane drop
  - 2) heavy equipment impact
  - 3) vehicle impact
  - 4) railcar/barge/tank truck collision
- ☐ c. Overpressure from
  - 1) process upsets
  - 2) common vent header
  - 3) pump/compressor
  - 4) nitrogen supply
  - 5) blowing lines into vessel
  - 6) steaming to clean
  - 7) ruptured tube
  - 8) homogeneous nucleation/ low boilers with high boilers
  - 9) overfill
  - 10) liquid filled/valved-in
  - 11) hydraulic hammer
  - 12) water freezing
- ☐ d. Natural forces
  - 1) lightning
  - 2) earthquake
  - 3) hurricane
  - 4) ice/snow load
- ☐ e. Corrosion/erosion
  - 1) wrong MOC
  - 2) stress corrosion cracking
  - 3) crevice corrosion/pitting
  - 4) internal wall
  - 5) external sweat zone
  - 6) lining/jacket failure
  - 7) erosion
  - 8) high temp. corrosion
- ☐ f. Vacuum collapse:
  - 1) sudden cooling and vapor cooling/condensation
  - 2) plugged filters/lines
  - 3) vacuum systems
  - 4) pumping contents from closed-in vessel
- ☐ g. High temperature:
  - 1) fire exposure/BLEVE
  - 2) heater malfunction
  - 3) operation above maximum allowable working temperature
- ☐ h. Low temperature fracture:
  - 1) embrittlement - operating below minimum design metal temp.
  - 2) low pressure flashing
  - 3) low ambient temperature

2. Piping System Failure
- ☐ a. Installation
  - 1) improper material of construction
  - 2) improper installation
  - 3) vibration
  - 4) fatigue
- ☐ b. Impingement
  - 1) crane drop
  - 2) heavy equipment impact
  - 3) vehicle impact
  - 4) third party intervention (e.g., backhoe)
- ☐ c. Natural forces
  - 1) earthquake
  - 2) high winds
- ☐ d. Corrosion/erosion
  - 1) chemical – improper material of construction
  - 2) stress cracking
  - 3) internal wall
  - 4) external wall (e.g., under insulation)
  - 5) lining failure
  - 6) erosion
  - 7) high temperature corrosion
- ☐ e. Overpressure from
  - 1) common vent header
  - 2) high pressure pump/ compressor
  - 3) reaction in line
  - 4) nitrogen supply
  - 5) blowing lines
  - 6) steaming to clean
  - 7) hydraulic expansion
  - 8) hydraulic hammer
  - 9) water freezing in
  - 10) solids plugging line/filter
- ☐ f. Temperature too high from
  - 1) fire exposure
  - 2) loss of coolant
  - 3) loss of fluid flow (e.g., in furnace tube)
- ☐ g. Temperature too low from
  - 1) liquid flashing
  - 2) low temperature fluid impingement
- ☐ h. Open vents and drains
  - 1) left open
  - 2) inadvertently opened
- ☐ i. Valve failure
  - 1) bonnet gasket/bolts failure
  - 2) packing blowout
  - 3) line gasket failure
  - 4) reactive/cryogenic material trapped in ball valve

3. Other Releases
- ☐ a. Sight glass b. Expansion joints
  - c. Swivel joints d. Hoses
  - e. Flare outage
  - f. Scrubber breakthrough
  - g. Incinerator failure
- ☐ h. Heat exchanger failure
  - 1) tube rupture – release through heating or cooling system
  - 2) tube rupture followed by jacket hydraulic failure
- ☐ i. Compressed gas cylinder failures
  - 1) valve broken off
  - 2) propelled if unsecured
  - 3) fusible plug melted/dislodged
  - 4) inappropriate heating
  - 5) wrong regulator/tubing used
- ☐ j. Pump failures
  - 1) packing blowout
  - 2) single mechanical seal rupture
  - 3) rupture of both double/tandem mechanical seals
  - 4) deadheaded
  - 5) positive displacement blocked in
- ☐ k. Compressor wreck
  - 1) liquid in suction
  - 2) lubrication failure
  - 3) sudden loss of load
  - 4) vibration
  - 5) turbine overspeed
  - 6) discharge blocked in (reciprocating)
- ☐ l. Drums
  - 1) improper (splash) filling
  - 2) loss of inerting
  - 3) overpressure with N2/Air
  - 4) puncture with forklift
  - 5) stacking too high
  - 6) improper thawing (e.g., glacial acrylic acid)
- ☐ m. Loss of utilities
  - 1) cooling
  - 2) heating
  - 3) electricity
  - 4) instrument air
  - 5) nitrogen
  - 6) steam
- ☐ n. Relief device, spurious opening
- ☐ o. Interfaces with
  - 1) raw materials
  - 2) waste streams
  - 3) distribution
  - 4) blowback
  - 5) energy systems
  - 6) laboratory
  - 7) product storage/handling

Figure 7.5 Example What-If Checklist [5, p. Appendix A]

Hazard and Operability Study (HAZOP)

The Hazard and Operability Study (HAZOP) is a structured method for identifying hazard scenarios and is well accepted across the chemical industry[1]. The method begins with identification of "nodes" or a process location where deviations from the design intent will be evaluated. Standard guidewords are used to suggest possible deviations.

HAZOP Study Terms

- **Node** is a location on a process diagram at which process parameters are investigated for deviations. Node examples:
    - A pipeline transferring material from one process unit to another
    - A specific tank or vessel
- **Design Intent** defines how the system is expected to operate at the nodes. It provides the reference point for developing deviations.
- **Parameter** is an aspect of the process that describes it physically, chemically or in terms of what is happening.
    - Specific parameters: flow, temperature, pressure, etc.
    - General parameters: addition, reaction, maintenance, relief, etc.
- **Deviations** are discovered by systematically applying the guidewords to each parameter at each node (e.g., more + temperature = higher temperature).

Selecting the correct node size is important for an efficient HAZOP. Too small the same discussion with the same deviations will be repeated. Too large and the team will be confused about what is the actual deviations being discussed or scenarios may be missed.

For HAZOP Studies performed as part of a larger Risk Analysis, it is convenient to define a *Node* as a specific equipment item such as a column, tank or vessel, pipeline, heat exchanger, pump, etc. All material and energy inputs into the equipment item would be included in the Node. This approach facilitates estimating release rate used for determining incident outcomes.

Design Intent is typically summarized as a sentence which includes:

- Material or chemical involved include its physical state, quantity, temperature and pressure.
- Activity such as heating, reacting, vaporizing, condensing, freezing, transferring (flow rate), etc.
- Location:
    - From a tank, vessel, reactor
    - At a tank, vessel, reactor
    - Through a pump, compressor, filter
    - To a reactor, vessel, column

Development of the Design Intent is a very valuable exercise whether HAZOP is being used or not. Having a good Design Intent statement helps the analysis team agree on how the process node or equipment item is intended to operate and provides insight into how deviation of various parameters may pose serious issues.

Guidewords are simple words or phrases used to qualify or quantify the design intent and associated parameters in order to discover deviations (Figure 7.6).

Guidewords ⇒ Parameter ⇓	More	Less	None	Reverse	Part Of	As Well As	Other Than
Flow	High flow	Low flow	No flow	Back flow			Loss of containment
Pressure	High pressure	Low pressure	Vacuum		Partial pressure		
Temperature	High temperature	Low temperature				Cryogenic	
Level	High level	Low level	No level				Loss of containment
Composition State	Additional phase	Loss of phase		Change of state	Wrong concentration	Contaminants	Wrong material
Reaction	High reaction rate	Low reaction rate	No reaction	Reverse action	Incomplete reaction	Side reaction	Wrong reaction

Figure 7.6 HAZOP Guidewords

Useful alternative interpretations of the original guidewords include:

- Sooner or for OTHER THAN when considering time.
- Where Else for OTHER THAN when considering position, sources, or destination
- Higher and Lower for MORE and LESS when considering levels, temperature, or pressure

Simple HAZOP Example Node, Parameter and Deviation

Using an equipment item in a specific chemical service as a “node” may be used to streamline the scenario identification process so that the analysis team can focus on the less common process upsets (Figure 7.7). The analysis team may be able to build upon a pre-determined list of reasonable scenarios to more quickly identify other scenarios to consider.

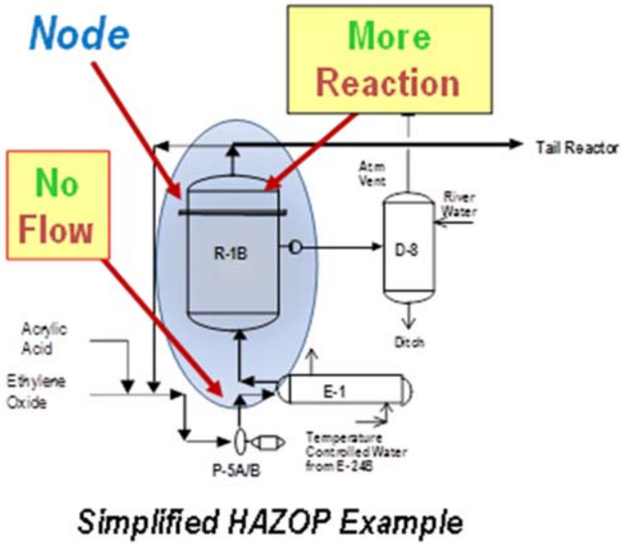


Figure 7.7 Example HAZOP Node

Not all possible deviations are meaningful. It is the HAZOP team's job to identify meaningful deviations with credible causes.

Additional HAZOP Study Terms

- **Causes** are the reasons why deviations may occur. Causes can be equipment failure, human error or external events.
- **Consequence** may be documented as the Loss Event or Impacts resulting from the Loss Event.
- **Recommendations** are suggested actions to prevent or mitigate the consequence of deviation, or to obtain further information.
- **Safeguards** are the systems in place that reduce the probability of the deviation occurring or mitigate the severity of the consequences. Examples include:
  - Dikes
  - Drainage
  - Instrument systems
  - Fire protection systems
  - Documented mechanical integrity programs
  - Documented sampling or other procedures

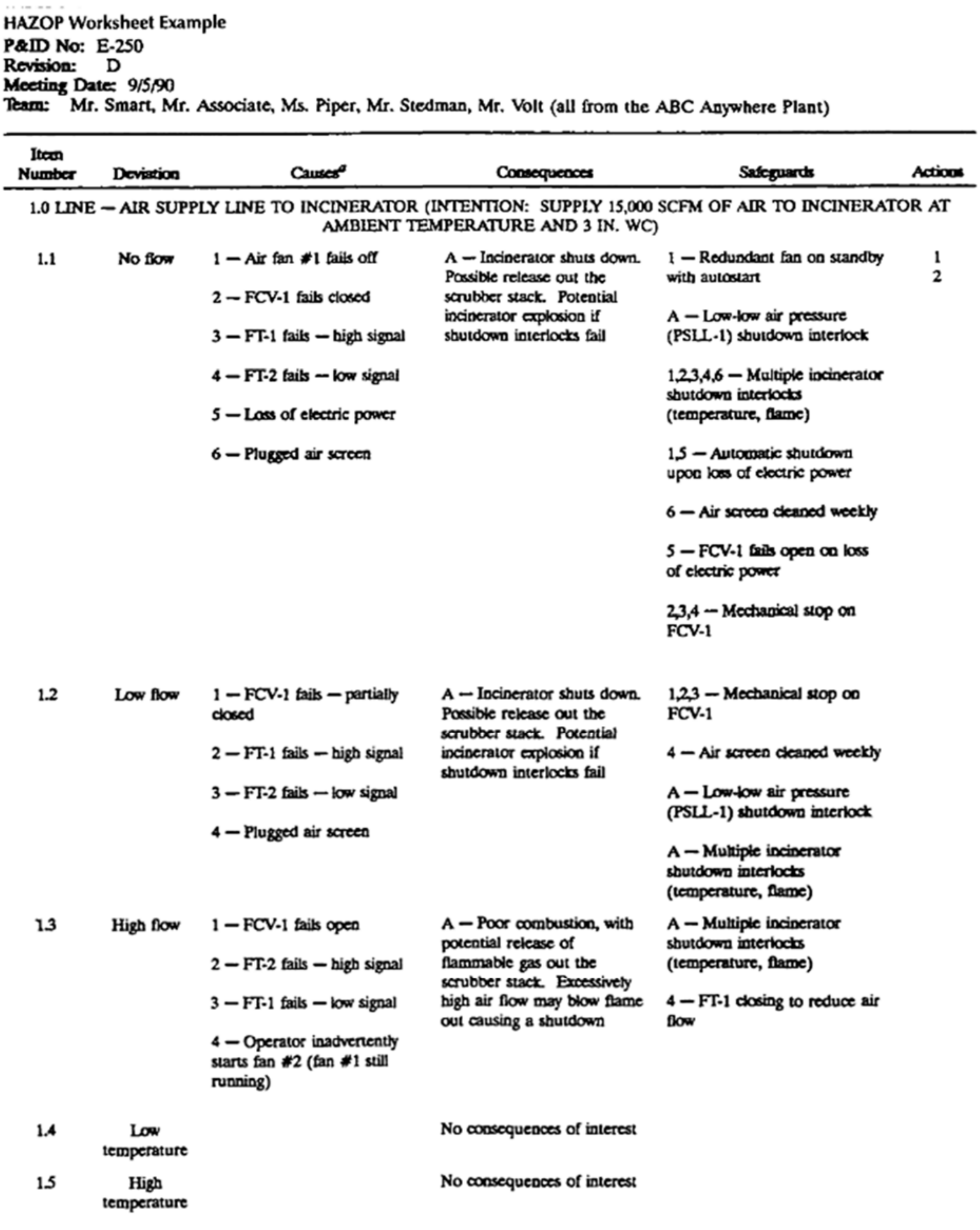
A *Preventive* Safeguard is one that intervenes between an Initiating Event and the Loss Event – it prevents the Incident from occurring. A *Mitigating* Safeguard is one that is designed to reduce the Loss Event impact.

HAZOP Documents

The recording process is an important part of the HAZOP Study (Figure 7.8). The person assigned to scribe the meetings must be able to distill the pertinent results from the myriad of conversations that occur during the meetings. It is impossible to manually record all that is said during the meetings, yet it is very important that all important ideas are preserved.

Each Deviation of a Design Intent is documented with the Possible Causes, Consequences, Safeguards and Recommendations.

Software is available to aid in Identification of Parameter Deviations and Documentation of HAZOP Study Results.



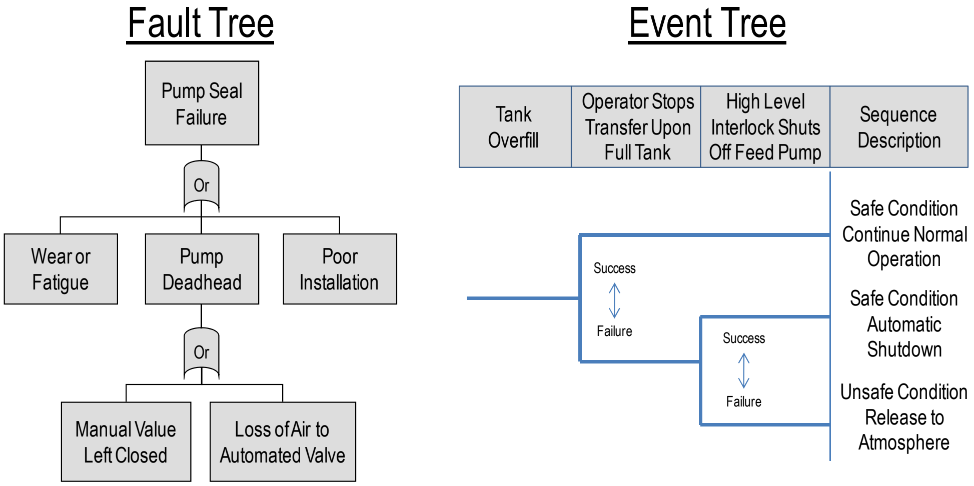
HAZOP Worksheet Example
P&ID No: E-250
Revision: D
Meeting Date: 9/5/90
Team: Mr. Smart, Mr. Associate, Ms. Piper, Mr. Stedman, Mr. Volt (all from the ABC Anywhere Plant)

Item Number	Deviation	Causes[a]	Consequences	Safeguards	Actions
1.0 LINE — AIR SUPPLY LINE TO INCINERATOR (INTENTION: SUPPLY 15,000 SCFM OF AIR TO INCINERATOR AT AMBIENT TEMPERATURE AND 3 IN. WC)					
1.1	No flow	1 — Air fan #1 fails off 2 — FCV-1 fails closed 3 — FT-1 fails — high signal 4 — FT-2 fails — low signal 5 — Loss of electric power 6 — Plugged air screen	A — Incinerator shuts down. Possible release out the scrubber stack. Potential incinerator explosion if shutdown interlocks fail	1 — Redundant fan on standby with autostart A — Low-low air pressure (PSLL-1) shutdown interlock 1,2,3,4,6 — Multiple incinerator shutdown interlocks (temperature, flame) 1,5 — Automatic shutdown upon loss of electric power 6 — Air screen cleaned weekly 5 — FCV-1 fails open on loss of electric power 2,3,4 — Mechanical stop on FCV-1	1 2
1.2	Low flow	1 — FCV-1 fails — partially closed 2 — FT-1 fails — high signal 3 — FT-2 fails — low signal 4 — Plugged air screen	A — Incinerator shuts down. Possible release out the scrubber stack. Potential incinerator explosion if shutdown interlocks fail	1,2,3 — Mechanical stop on FCV-1 4 — Air screen cleaned weekly A — Low-low air pressure (PSLL-1) shutdown interlock A — Multiple incinerator shutdown interlocks (temperature, flame)	
1.3	High flow	1 — FCV-1 fails open 2 — FT-2 fails — high signal 3 — FT-1 fails — low signal 4 — Operator inadvertently starts fan #2 (fan #1 still running)	A — Poor combustion, with potential release of flammable gas out the scrubber stack. Excessively high air flow may blow flame out causing a shutdown	A — Multiple incinerator shutdown interlocks (temperature, flame) 4 — FT-1 closing to reduce air flow	
1.4	Low temperature		No consequences of interest		
1.5	High temperature		No consequences of interest		

Figure 7.8 Example HAZOP Document [48]

Other Hazard Identification Methods

Fault Tree and **Event Tree** methods can be applied qualitatively or quantitatively[1]. They provide a format to document logical possibilities to which quantitative information may be added. Fault Tree may be used to identify all potential Initiating Events for a specific Loss Event. Event Tree may be used to identify feasible Incident Outcome for a specific Loss Event. These event trees are depicted in Figure 7.9.



For Illustration Only – these diagrams do not reflect complete results

Figure 7.9 Example Fault Tree and Event Tree

Quantitatively, these methods can provide likelihood information for an event sequence. This will be discussed further in the Likelihood Analysis Section.

Scenario Libraries

Most chemical process facilities utilize the same basic equipment types such as vessels or tanks, pumps, piping, heat exchangers, columns, scrubbers, etc. Development of HAZOP Libraries may help to reduce the time required for analysis.

Through operational experience, incident history, and risk analysis history; common process upsets or scenario categories for the various equipment types may be categorized such as:

- Overfill
- Drains/Vents left open
- Overpressure/Relief Activation
- Excessive Heating
- Physical Damage
- Hose Failure
- Mechanical Integrity Failures (erosion, corrosion, fatigue)
- Low Temperature Embrittlement
- Hydraulic Surge
- Uncontrolled Reaction
- Others

These scenario categories represent some of the common parameter deviations from the design intent.

No Scenario Library is Perfect. Facilitators should always ask Evaluation Teams to add scenarios based on their personal experience and plant or industry history.

Example Scenario Library

Parameters, Deviations, Initiating Events, Loss Events and potential Incident Outcome may be related to an overall Scenario Category. This technique provides a framework for a Scenario Library such that scenarios may be easily added and updated. An example of a scenario listing for chemical process equipment is shown in Table 7.1; for dust handling equipment in Table 7.2; and for fired equipment in Table 7.3 [1, p. From RAST].

Scenario or Hazard Category	**Parameter/Deviation**	**Applicable Equipment**	**Initiating Events** *(Partial List)*	**Loss Event***	**Incident Outcome**
Blocked-In with Thermal Expansion	Flow-No	Drum Oven Heat Exchanger Piping, Pump**	Procedure Failure (Human Error) Flow Control Failure	Gasket Leak Equipment Rupture Equipment Damage	Flammable Release Toxic Release Chemical Exposure
Casing or Containment Failure	Flow-Loss of Containment	Pump	Canned or Magnetic Drive Failure	Small Hole Leak	Flammable Release Toxic Release Chemical Exposure
Connection Failure	Flow-Loss of Containment	Durm/IBC Handling Tank Truck/Rail Car/Tote	Procedure Failure (Human Error)	Gasket Leak	Flash Fire or Fireball Chemical Exposure
Damage from Movement	Flow-Loss of Containment	Tank Truck/Rail Car/Tote	Procedure Failure (Human Error)	Full-Bore Leak	Flammable Release Toxic Release Chemical Exposure
Drain or Vent Valve Open	Flow-Loss of Containment	All	Procedure Failure (Human Error) Flow Control Failure	Drain or Vent Leak	Flammable Release Toxic Release Chemical Exposure
Dust Accumulation in Process Area	Flow-Loss of Containment	All Solids Handling Equipment	Any scenario that could dislodge accumulated dust (explosion within nearby equipment, etc.)	Secondary Dust Release	Building Explosion
Excessive Heat Input - Heat Transfer	Temperature-High Pressure-High Heat Input-High	All with Heat Transfer Capability	Temperature Control Failure Residence Time Failure (Solids) Feed rate Control Failure	Relief Venting Equipment Rupture Equipment Damage	Flammable Release Toxic Release Flash Fire or Fireball Physical Explosion Business Loss
Excessive Heat Input - Mechanical or Frictional	Temperature-High Pressure-High Heat Input-High	All with Mixing, Fluid Movement, or Electric Heating	Bearing or Seal Failure Mechanical Failure Speed Control Failure	Relief Venting Equipment Rupture Equipment Damage	Flammable Release Toxic Release Flash Fire or Fireball Physical Explosion Business Loss
Excessive Heat Input - Pool Fire Exposure	Temperature-High Pressure-High Heat Input-High	All	Scenarios involving spill plus ignition in nearby liquid-containing equipment	Relief Venting Equipment Rupture Equipment Damage	Flammable Release Toxic Release Flash Fire or Fireball Physical Explosion Business Loss
Excessive Pad Gas Pressure	Flow-High	All	Flow Control Failure Pressure Control Failure Procedure Failure (Human Error)	Gasket Leak Relief Venting Equipment Rupture	Flammable Release Toxic Release Physical Explosion Business Loss
Exhaustion of Scrubbing Media	Composition-Wrong Concentration	Adsorber/Scrubber Vapor Quench	Flow Control Failure Procedure Failure (Human Error)	Vent Release	Flammable Release Toxic Release

Table 7.1 Example List of Scenarios for Common Chemical Process Equipment

Scenario or Hazard Category	Parameter/Deviation	Applicable Equipment	Initiating Events *(Partial List)*	Loss Event*	Incident Outcome
Hose or Loading Arm Connection	Flow-Loss of Containment	Drum/IBC Handling Tank Truck/Rail Car/Tote	Procedure Failure (Human Error)	Gasket Leak	Flammable Release Toxic Release Chemical Exposure
Hydraulic Surge	Flow-Loss of Containment	Piping Pump**	Flow Control Failure Procedure Failure (Human Error)	Gasket Leak	Flammable Release Toxic Release Chemical Exposure
Ignitable Headspace	Composition-Wrong Concentration Electrostatic Charge-High Electrical Conductivity-Low	All but Liquid-Full Equipment	Flow Control Failure Failure of Bonding or Grounding Particle Size Control Failure (Solids) Wrong Type or Damaged Bag, Pak or Drum (Solids) Improper Changing Dust Collector Bag or Screen (Solids)	Gasket Leak Equipment Rupture Equipment Damage	Flammable Release Toxic Release Flash Fire or Fireball Physical Explosion Business Loss
Introduction of Foreign Material	Composition-Contaminants	Rotating Equipment Mechanical Conveyor (Solids)	Mechanical Failure Procedure Failure (Human Error)	Equipment Rupture Equipment Damage	Flash Fire or Fireball Physical Explosion Business Loss
Liquid in Vapor Feed	Level-High	Compressor or Blower Turbine or Gas Expander	Level Control Failure	Flaming Liquid Release	Chemical Exposure
Loss of Flow - Adsorber or Scrubber	Flow-Low	Adsorber/Scrubber Vapor Quench	Flow Control Failure Pump Failure	Vent Release	Flammable Release Toxic Release
Low Temperature Embrittlement	Temperature-Low	All	Temperature Control Failure Leak of Liquified Gas	Full-Bore Leak	Flammable Release Toxic Release
Mechanical Integrity Failure - Very Large	Flow-Loss of Containment	All - to address Residual Failures	Residual Failure	Very Large Hole Size Leak	Flammable Release Toxic Release Chemical Exposure
Mechanical Integrity Failure - Very Small	Flow-Loss of Containment	All - to address Residual Failures	Residual Failure	Very Small Hole Size Leak	Flammable Release Toxic Release Chemical Exposure
Overfill, Overflow, or Backflow	Level-High Flow-Backflow	All Liquid Containing Equipment	Level Control Failure Procedure Failure (Human Error)	Overflow Release Equipment Damage Equipment Rupture	Flammable Release Toxic Release Physical Explosion Business Loss
Overflow - Flooding or Plugging	Level-High	Adsorber/Scrubber Distillation Vapor Quench	Level Control Failure Pressure Control Failure Flow Control Failure	Overflow Release Equipment Damage Equipment Rupture	Flammable Release Toxic Release Physical Explosion Business Loss
Physical Damage or Puncture	Flow-Loss of Containment	Drum/IBC Handling Piping Pump**	Procedure Failure (Human Error)	Full-Bore Leak Solids Spill	Flammable Release Toxic Release

Table 7.1 (Continued) Example List of Scenarios for Common Chemical Process Equipment

Scenario or Hazard Category	Parameter/Deviation	Applicable Equipment	Initiating Events *(Partial List)*	Loss Event*	Incident Outcome
Piping or Equipment Leak - Full Bore	Flow-Loss of Containment	All	Hose Failure Pipe Failure Mechanical Failure (nozzle)	Full-Bore Leak	Flammable Release Toxic Release Chemical Exposure
Piping or Equipment Leak - Small	Flow-Loss of Containment	All	Procedure Failure (Human Error) Mechanical Failure (Loading Arm, etc.)	Small Hole Size Leak	Flammable Release Toxic Release Chemical Exposure
Pressure Damage	Pressure-High	All Dust Handling Equipment	Pressure Control Failure Regulator Failure	Solids Spill Equipment Rupture	Flammable Release Toxic Release Physical Explosion Business Loss
Pump Deadhead	Flow-No Temperature-High	Pump	Flow Control Failure Procedure Failure (Human Error) Utility Failure	Equipment Rupture	Flammable Release Toxic Release Physical Explosion Business Loss
Relief Device Failure	Flow-Loss of Containment	All	Mechanical Failure	Relief Hole Size Leak	Flammable Release Toxic Release Chemical Exposure
Rotating Equipment Damage	Speed-High	All Rotating Equipment	Speed Control Failure Mechanical Failure	Equipment Rupture Equipment Damage	Flammable Release Toxic Release Flash Fire or Fireball Physical Explosion Business Loss
Seal Leak	Flow-Loss of Containment	Compressor or Blower Pump, Turbine or Gas Expander Stirred Reactor/Crystallizer	Mechanical Seal Failure Utility Failure Procedure Failure (Human Error)	Mechanical Seal Hole Size Leak	Flammable Release Toxic Release Chemical Exposure
Tube Failure	Flow-Loss of Containment	Heat Exchanger	Heat Exchanger Tube Failure	Tube Hole Size Leak	Flammable Release Toxic Release Business Loss
Uncontrolled Reaction	Reaction-High Rate Temperature-High Composition-Wrong	All	Flow Control Failure Temperature Control Failure	Relief Venting Equipment Rupture	Flammable Release Toxic Release Flash Fire or Fireball Physical Explosion Business Loss
Uncontrolled Reaction - Incompatible Materials	Reaction-Wrong Reaction	All	Addition of Wrong Recipe (Human Error) Addition of Wrong Material (Human Error)	Equipment Rupture	Flammable Release Toxic Release Flash Fire or Fireball Physical Explosion Business Loss
Vacuum Damage	Pressure-Low	All	Pressure Control Failure Mechanical Failure	Full-Bore Leak Equipment Damage	Flammable Release Toxic Release Business Loss

*Each Loss Event represents separate Scenarios
**Where Piping included with Pump
***Equipment Failure represents total loss of containment without Physical Explosion

Table 7.1 (Continued) Example List of Scenarios for Common Chemical Process Equipment

Scenario or Hazard Category	Parameter/Deviation	Applicable Equipment	Initiating Events *(Partial List)*	Loss Event*	Incident Outcome
Connection Failure	Flow-Loss of Containment	All Dust Handling Equipment	Boot or Flex Hose Failure (Solids)	Gasket Leak Solilds Spill	Flash Fire or Fireball Chemical Exposure
Dust Accumulation in Process Area	Flow-Loss of Containment	All Solids Handling Equipment	Any scenario that could dislodge accumulated dust (explosion within nearby equipment, etc.)	Secondary Dust Release	Building Explosion
Excessive Heat Input - Heat Transfer	Temperature-High Pressure-High Heat Input-High	All with Heat Transfer Capability	Temperature Control Failure Residence Time Failure (Solids) Feed rate Control Failure	Relief Venting Equipment Rupture Equipment Damage	Flammable Release Toxic Release Flash Fire or Fireball Physical Explosion Business Loss
Excessive Heat Input - Mechanical or Frictional	Temperature-High Pressure-High Heat Input-High	All with Mixing, Fluid Movement, or Electric Heating	Bearing or Seal Failure Mechanical Failure Speed Control Failure	Relief Venting Equipment Rupture Equipment Damage	Flammable Release Toxic Release Flash Fire or Fireball Physical Explosion Business Loss
Ignitable Headspace	Composition-Wrong Concentration Electrostatic Charge-High Electrical Conductivity-Low	All but Liquid-Full Equipment	Flow Control Failure Failure of Bonding or Grounding Particle Size Control Failure (Solids) Wrong Type or Damaged Bag, Pak or Drum (Solids) Improper Changing Dust Collector Bag or Screen (Solids)	Gasket Leak Equipment Rupture Equipment Damage	Flammable Release Toxic Release Flash Fire or Fireball Physical Explosion Business Loss
Introduction of Foreign Material	Composition-Contaminants	Rotating Equipment Mechanical Conveyor (Solids)	Mechanical Failure Procedure Failure (Human Error)	Equipment Rupture Equipment Damage	Flash Fire or Fireball Physical Explosion Business Loss
Propagation of Flame or Burning Ember	Composition-Foreign	All Dust Handling Equipment	Any upstream scenario resulting in explosion or smoldering particles (Solids)	Equipment Rupture	Flammable Release Flash Fire or Fireball Physical Explosion Business Loss
Rotating Equipment Damage	Speed-High	All Rotating Equipment	Speed Control Failure Mechanical Failure	Equipment Rupture Equipment Damage	Flammable Release Toxic Release Flash Fire or Fireball Physical Explosion Business Loss
Uncontrolled Reaction - Incompatible Materials	Reaction-Wrong Reaction	All	Addition of Wrong Recipe (Human Error) Addition of Wrong Material (Human Error)	Equipment Rupture	Flammable Release Toxic Release Flash Fire or Fireball Physical Explosion Business Loss

Table 7.2 Example List of Scenarios for Solids Handling Equipment

Scenario or Hazard Category	Parameter/Deviation	Applicable Equipment	Initiating Events *(Partial List)*	Loss Event*	Incident Outcome
Accumulation of Untreated Vent or Waste	Flow-High	Fired Equipment - Incinerator or TTU Vapor Quench	Flow Control Failure	Vent Release	Flammable Release Toxic Release
Excessive Heat Input - Heat Transfer	Temperature-High Pressure-High Heat Input-High	All with Heat Transfer Capability	Temperature Control Failure Residence Time Failure (Solids) Feed rate Control Failure	Relief Venting Equipment Rupture Equipment Damage	Flammable Release Toxic Release Flash Fire or Fireball Physical Explosion Business Loss
Flash Back of Vent to Fired Equipment	Composition-Wrong Concentration	All	Flow Control Failure Pressure Control Failure Procedure Failure (Human Error)	Equipment Rupture Equipment Damage	Flash Fire or Fireball Physical Explosion Business Loss
Fuel Accumulation during Light Off	Flow-High	Fired Equipment - Combustion Unit Fired Equipment - Fire Tube Unit Fired Equipment - Incinerator or TTU	Flow Control Failure Mechanical Failure (Damper or Blower)	Equipment Rupture Equipment Damage	Flash Fire or Fireball Physical Explosion Business Loss
Fuel Accumulation during Operation	Flow-High	Fired Equipment - Combustion Unit Fired Equipment - Fire Tube Unit Fired Equipment - Incinerator or TTU	Flow Control Failure Mechanical Failure (Damper or Blower)	Equipment Rupture Equipment Damage	Flash Fire or Fireball Physical Explosion Business Loss
Fuel Accumulation while Down	Flow-High	Fired Equipment - Combustion Unit Fired Equipment - Fire Tube Unit Fired Equipment - Incinerator or TTU	Flow Control Failure Procedure Failure (Human Error)	Vent Release Equipment Rupture Equipment Damage	Flash Fire or Fireball Physical Explosion Business Loss
High Fuel Flow or Energy Content	Flow-High	Fired Equipment - Combustion Unit Fired Equipment - Fire Tube Unit Fired Equipment - Incinerator or TTU	Flow Control Failure	Equipment Damage	Flash Fire or Fireball Physical Explosion Business Loss
High Temperature Failure	Temperature-High	Vapor Quench	Flow Control Failure	Equipment Failure	Toxic Release Physical Explosion Business Loss
Loss of Pilot or Ignition	Composition-Wrong Concentration	Fired Equipment-Flare	Flow Control Failure Mechanical Failure (Ignitor)	Vent Release	Flammable Release Toxic Release
Loss of Vacuum - Thermal Oxidizer	Pressure-Low	Fired Equipment-Incinerator or TTU	Pressure Control Failure Mechanical Failure (Blower)	Vent Release	Flammable Release Toxic Release
Plugged or Frozen Vent Line	Flow-No	Fired Equipment-Flare	Temperature Control Failure Utility Failure	Equipment Damage	Business Loss

Table 7.3 Example List of Scenarios for Fired Equipment

Scenario Screening

Scenario screening is often based on a qualitative assessment. In order to narrow the list to those of greatest significance, screening criteria based on chemical properties, process capability and equipment design may be helpful (Figure 7.10).

Flammability
Flash Point
Lower Flammability Limit
Minimum Ignition Energy

Toxicity
Inhalation Toxicity
Dermal Toxicity
Aquatic Toxicity

Reactivity
Heat of Reaction
Detected Onset Temperature
Gas Generation

Fire and Explosion
Process Temperature > Flash Point
Max Concentration > Lower Flammable Limit
Ignition Source > Minimum Ignition Energy

Toxicity
Max Vapor Concentration > ER Value
Potential For Dermal Exposure
Potential for Environmental Damage

Reactivity
Max Pressure > MAWP or Relief Set
Max Process or Heating Temp > Temp of No Return

Figure 7.10 Scenario Screening

Many deviations for key process parameters have maximum or minimum limits easily estimated from process or equipment capability noted in the system description. Such estimates may be captured in a spreadsheet (see generic list inTable 7.1). For example, the minimum and maximum level limit may be zero and 100% full while the minimum and maximum flow rate may be zero and 75 gallons per minute. Deviations from normal composition should consider maximum and minimum limits of feed rate when multiple materials are fed, the impact of back flow and reaction chemical products. If there is sufficient material to exceed the equipment volume then an *overfill* loss event may result as a release through the outlet or vent. If the down-stream equipment pressure exceeds the normal operating pressure, then a *back-flow* loss event may result. Furthermore, if the feed pressure (or downstream equipment pressure in the case of back flow) exceeds the relief device set pressure, a release through the relief device may also occur.

8. INTRODUCTION TO CONSEQUENCE AND RISK ANALYSIS

Risk Analysis is the development of qualitative or quantitative estimates of risk based on engineering evaluation and mathematical techniques for combining estimates of incident consequences and frequencies. Risk Analysis tends to be more quantitative than Hazard Evaluation. Examples of simple correlations used for evaluation of Consequence include of estimation of airborne quantity, vapor dispersion concentration, and explosion overpressure are presented in the subsequent sections. It is not the intent that all members of Risk Analysis Teams perform these calculations but that the key variables, limitations, and when to engage more detailed modeling techniques are understood.

Risk Analysis involves selecting potential scenarios, evaluating and combining the expected frequency and impact of each scenario having a consequence of concern, and then summing the scenario risks (if necessary) to obtain the total risk estimate for the level at which the risk analysis is being performed.

The selection of some inputs or conditions may depend on the purpose for the specific study. During an *Incident Investigation*, estimates are often made to better understand actual events. Information such as release rate, wind direction, weather conditions and location of personnel are typically known and used as inputs. *Risk Analysis* involves anticipating possible incidents and estimating the consequence severity to people, facilities or the environment. Information such as release rate, wind direction, weather conditions, and location of personnel are assumed based on typical or “worst case” conditions (or on a company’s protocol for Risk Analysis).

Risk Analysis Approach

- Various Risk Analysis techniques may be used to compare process risk with corporate or regulatory criteria. General practice is to use as simple a technique as possible, but that is appropriate to the hazard, to more complex techniques as needed. The general progression (Figure 8.1) would be: Qualitative Risk Analysis, which is based primarily on description and comparison using historical experience and engineering judgment, with little quantification of the hazards, consequences, likelihood, or level of risk.
- Simplified Quantitative Risk Analysis such as simple consequence models, Layers of Protection Analysis (LOPA) or Bow Tie Analysis.
- Quantitative Risk Analysis, with fault tree analysis, event tree analysis, complex consequence modeling tools, and full QRA that systematically develops numerical estimates of the expected frequency and severity of potential incidents associated with a facility or operation based on engineering evaluation and mathematical techniques [21] [49].

Companies and/or regulatory agencies often establish the criteria for which risk analysis technique should be used.

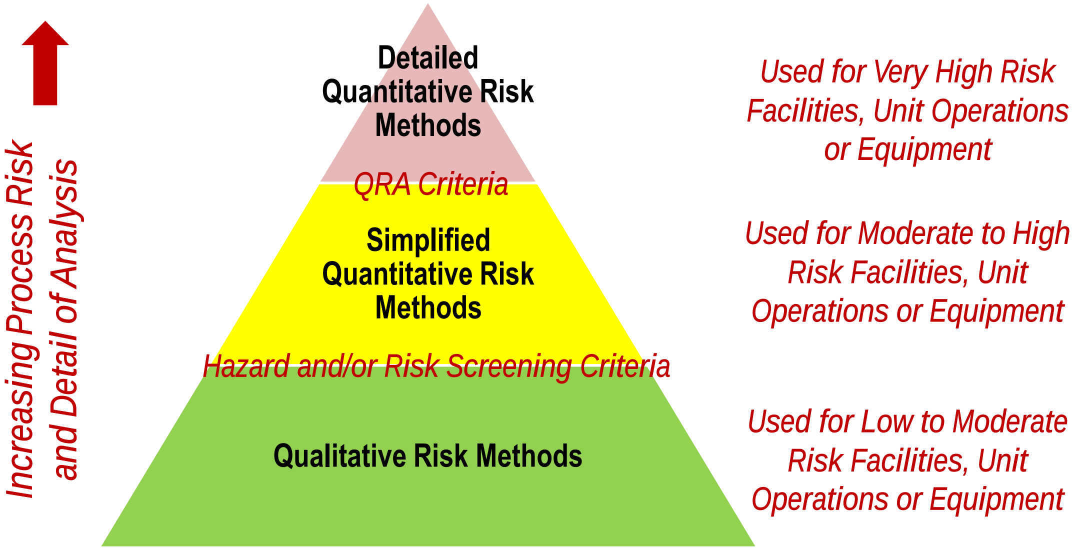


Figure 8.1 Risk Analysis Techniques

There are several approaches that may be used to categorize consequence severity for risk analysis.

- **Categories without Direct Reference to Human Harm**: Categories are often based on release quantity of a specific hazard level such as a 1000 kg release of highly toxic material. The release quantity may be estimated qualitatively or quantitatively. Categories may also be based on results of simple dispersion or explosion models such as a release where the distance to ERPG-2 concentration exceeds 1000 m or where the distance to 1 psi blast overpressure exceeds 500 m.

  This approach avoids estimating the number of potential injuries or fatalities which may appear to imply that injuries or fatalities are tolerable. This approach also recognizes the difficulty in estimating the number of people who may be harmed and how severe the harm might be. For example, a toxic release may result in one or more fatalities or no harm at all, depending on the proximity of people to the release location and capability they have to escape.

- **Qualitative Estimates of Human Harm**: This approach uses the final impact to humans as the consequence of interest, but arrives at the value using qualitative judgment from past experience or knowledge of prior detailed modeling of similar releases.

  Many people tend to understand consequence in terms of human harm rather than release size or release characteristics. The resulting risk of injury or fatality estimate can typically be compared directly to a company's risk tolerance criteria. However, qualitative estimates may vary significantly between different analysts.

- **Quantitative Estimate of Human Harm**: This method involves the use of mathematical models to simulate the release, the subsequent dispersion, and toxic or blast effects. Models may be relatively simple to very complex. In addition to direct comparison with a company's risk tolerance criteria, quantitative methods provide better consistency between different analysts.

  It must be recognized that the results of real-world events have been both significantly less and significantly greater than those calculated. A set of assumptions such as weather conditions, wind direction, and release orientation are typically needed to determine a "worst" consequence that may not represent real-world events.

Quantitative or Simplified Quantitative Consequence Analysis involves several models that will be discussed in subsequent sections in this document (Figure 8.2).

- Source models are used to quantify the release scenario by estimating discharge rates, total quantity released, extent of flash, and evaporation from a liquid pool and/or aerosol formation.
- Dispersion models estimate concentration at distances downwind from the release source.
- Explosion models estimate the blast energy while fireball models estimate thermal energy at distances from the source.
- Effect models are used to assess the impacts to people, property or the environment of release scenarios.

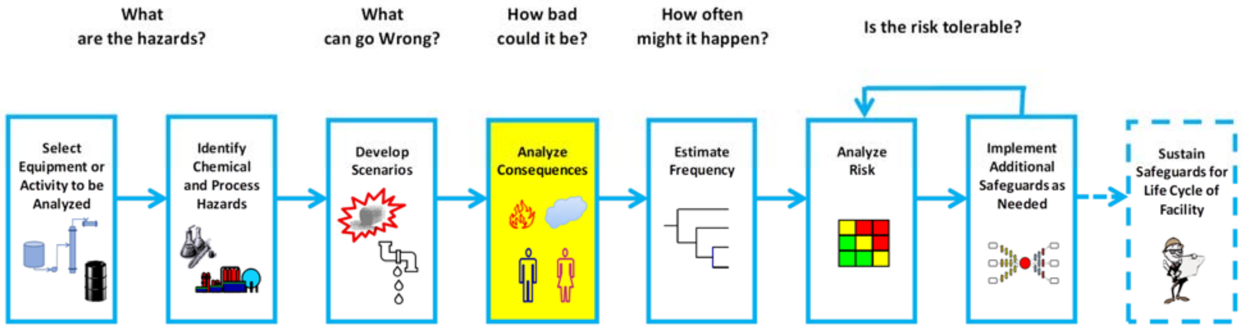


Figure 8.2 The Consequence Analysis Step in the HIRA Workflow Process

Likelihood Evaluation provides an estimate of the expected probability or frequency of an event. The frequency of the Initiating Event is combined with the probabilities of occurrence of other events or conditions within an event sequence to obtain an estimated scenario frequency.

Chemical Process Risk

Risk is a measure of human injury, environmental damage or economic loss in terms of both the likelihood and the magnitude of the loss or injury.

A crucial step in risk analysis is determining the amount of risk a company will tolerate. Obviously "high" levels of risk are not tolerable, and there is some threshold where most reasonable people can agree risk is tolerable. Figure 8.3 illustrates this concept [50, p. 42]; additional guidance is provided by the CCPS [51].

Each company must also determine what these levels of tolerability are for themselves.

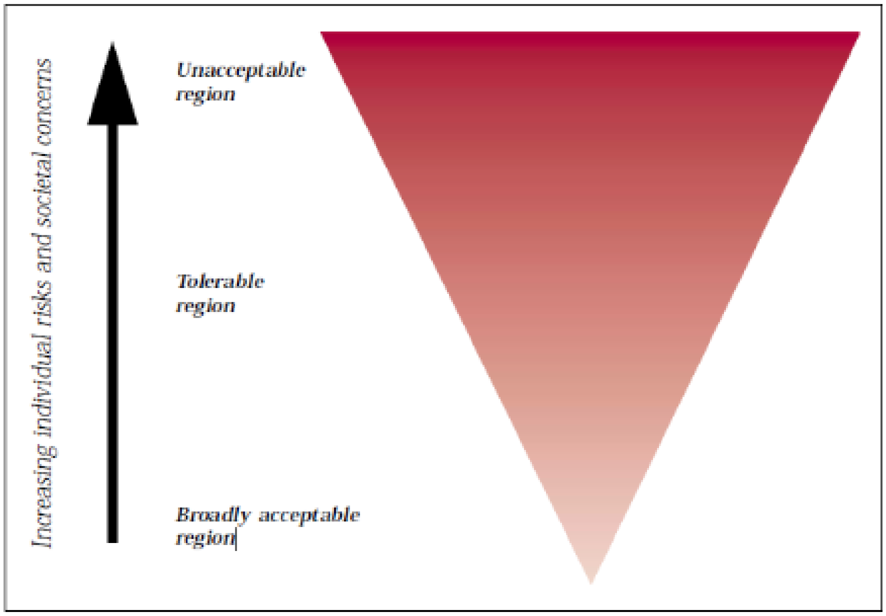


Figure 8.3 HSE Framework for the tolerability of risk [50]

Measurement of Risk

Example – the Commute to Work

Commute 10 miles (16 km) twice per work day for 200 days per year = 4000 miles (6400 km) per year.

Per National Highway Traffic Safety Administration (NHTSA), the average frequency for motor vehicle accidents in the United States during 2008 was 2.0 x 10^{-6}/vehicle mile traveled. Of total accidents, 71.3% were property damage only, 28.1% were injury related and 0.6% involved fatalities.

Several Undesired Consequences might apply for the 4000 mile/year commute:

- 5.7 X 10^{-3} Property Damage per year.
- 2.2 X 10^{-3} Injuries per year.
- 4.8 X 10^{-5} Fatalities per year.

In this example, there are three potential consequences – property damage, injury, and fatality. Risk measurement is frequency for each of these consequences.

These values represent an "average" for Individual Risk associated with the commute to work each day and is a small fraction of the total risk. Note the convention being used for risk measurement is Undesired Consequence per Year:

Presentation of Risk Results

Individual Risk is the risk to a person in the vicinity of a hazard. It includes the nature of the injury, likelihood of the injury occurring and the time period over which the injury might occur. A common form in presentation of individual risk is the risk contour where lines represent a constant likelihood of fatality for an individual (Figure 8.4). Many risk assessments are conducted on the basis of fatal effects as degree of injury is often more difficult to quantify.

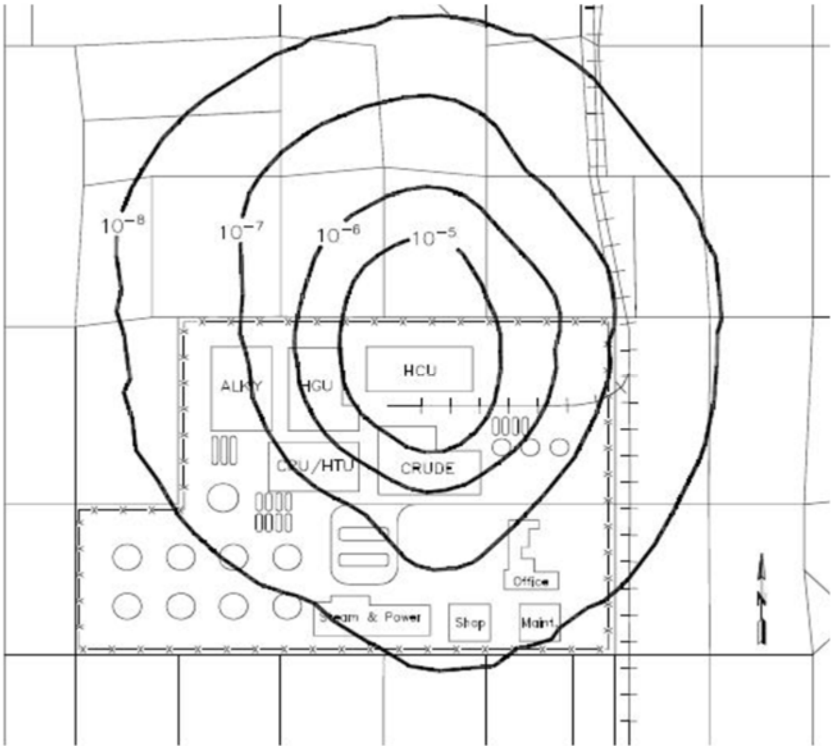


Figure 8.4 – Individual Risk Contour

Societal Risk addresses the number of people who may be affected by hazardous incidents. A common form of societal risk is the F-N (frequency-number) curve (Figure 8.5). This curve is a plot of cumulative frequency versus consequence (expressed as a number of fatalities). Many companies and regulatory agencies have specific societal risk requirements. Often these requirements are based on the summation of risks associated with all scenarios rather than risk of a single scenario.

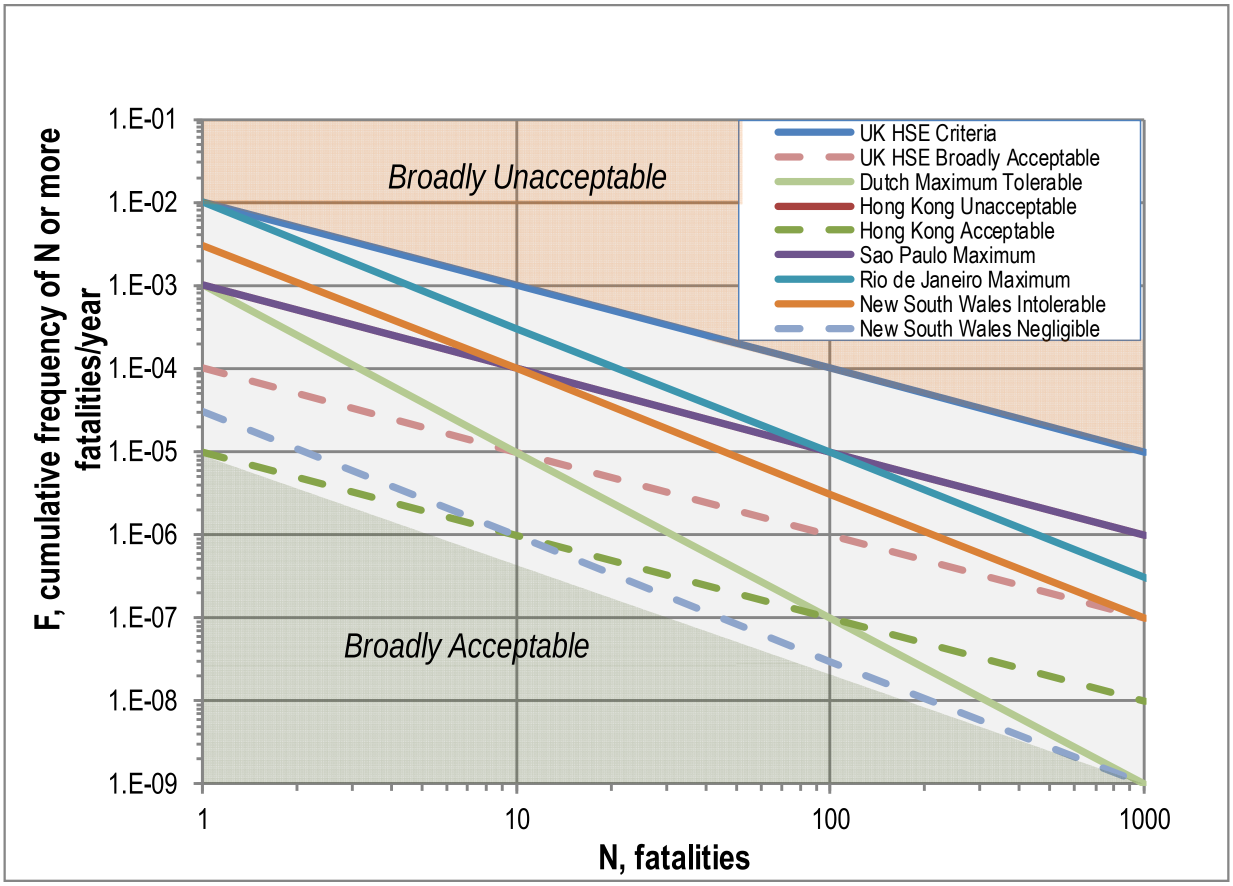


Figure 8.5 – Societal Risk Criteria [52]

In many, if not most, cases a qualitative assessment of risk (or broad categorization of simple quantitative estimates) such as a *risk matrix* (Figure 8.6) is sufficient to determine the number of protective layers needed depending on company or regulatory requirements. In the example risk matrix in Figure 8.6, green may represent acceptable, red as unacceptable while the orange or yellow may represent tolerable risk.

Example Risk Matrix: Risk = Consequency Severity times Frequency									
Severity				Frequency					
Label	People	Environment	Assets or Business	10^{-2} per year	10^{-3} per year	10^{-4} per year	10^{-5} per year	10^{-6} per year	10^{-7} per year
Severity Level-1	Minor Injury or 0.001 to 0.01 likelihood of a single fatality	<100 kg Spill of Toxic Material <1,000 kg Spill of Harmful Material *(Agency Reportable Incident)*	<$50,000 Loss	🟧	🟨	🟩	🟩	🟩	🟩
Severity Level-2	Major Injury or 0.01 to 0.1 likelihood of a single fatality	<100 kg Spill of Very Toxic Material <1,000 kg Spill of Toxic Material <10,000 kg Spill of Harmful Material *(Contamination Confined to Site)*	$50,000 to $500,000 Loss	🟥	🟧	🟨	🟩	🟩	🟩
Severity Level-3	0.1 to 1 likelihood of a single fatality	<1,000 kg Spill of Very Toxic Material <10,000 kg Spill of Toxic Material <100,000 kg Spill of Harmful Material *(Requires Significant Offsite Remediation)*	$500,000 to $5,000,000 Loss	🟥	🟥	🟧	🟨	🟩	🟩
Severity Level-4	1 to 10 fatalities	<10,000 kg Spill of Very Toxic Material <100,000 kg Spill of Toxic Material <1,000,000 kg Spill of Harmful Material *(Major Incidenet, Adverse National Media Attention)*	$5,000,000 to $50,000,000 Loss	🟥	🟥	🟥	🟧	🟨	🟩
Severity Level-5	>10 fatalities	>10,000 kg Spill of Very Toxic Material >100,000 kg Spill of Toxic Material *(Major International Incident, Class Action Lawsuit)*	> $50,000,000 Loss	🟥	🟥	🟥	🟥	🟧	🟨

Each company determines the acceptable, unacceptable and tolerable frequencies for the consequence severity adjusted to a single scenario

Legend	
Acceptable	🟩
Tolerable - Offsite	🟨
Tolerable - Onsite	🟧
Unacceptable	🟥

Figure 8.6 – Example Risk Matrix [1]

“Sharpening the Pencil”

The following sections will focus on a simplified quantitative approach to risk. There are several advantages and disadvantages to this method relative to more qualitative approaches.

Advantages:

- Improved consistency across study teams
- Provides a basis for comparison of risk across facilities
- People tend to understand consequences in terms of incident outcome (flash fire, vapor cloud explosion, etc. than attempting to express risk in terms of release size. People tend to understand consequences in terms of number of personnel impacted than incident outcome.
- A greater degree of certainty concerning the predicted consequences
- Ability for direct comparison with corporate risk criteria

Disadvantages:

- The results of real-world incident have been both significantly less or significantly more than estimated. Modeling results may be strongly influenced by exact release conditions (release orientation, weather conditions, location of personnel, etc.)
- The level of sophistication for modeling may be disproportionate to that needed in order-of-magnitude Layers of Protection Analysis (LOPA)
- The training, experience and effort may be prohibitive for low risk scenarios.

A “middle ground” may also be appropriate. An estimate initially made using simplifying assumptions such as the entire liquid release becomes airborne or all building occupants are considered severely impacted as a “worse case”. Later in the overall work process, a higher than expected result may justify updating estimations using a less conservative basis or more advanced methods.

Appropriate simplifying assumptions in Risk Analysis are those which give more conservative results. A CHEF Calculation Aid spreadsheet is provided in addition to this manual to assist participants in performing simple screening calculations for Airborne Quantity, Vapor Dispersion, and Explosions (Figure 8.7). Required inputs and the associated outputs are shaded “yellow” for various release cases.

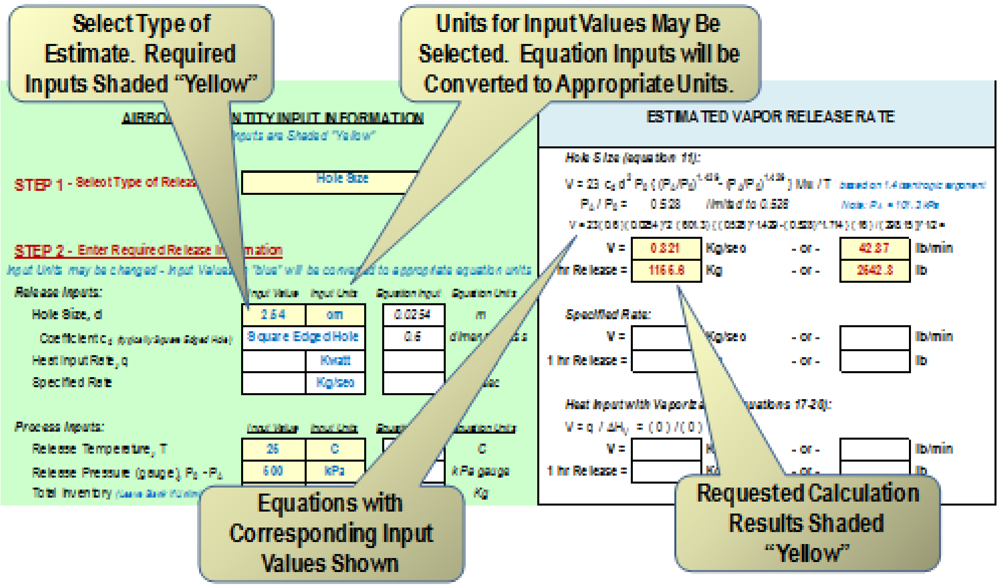


Figure 8.7 Example CHEF Calculation Aid worksheet

If greater precision is needed, various software tools are available, such as those for Dispersion Modeling, Explosion Modeling, and Fault Tree Analysis.

9. SOURCE MODELS

The Airborne Quantity for a vapor release is the flow rate calculated at the temperature and pressure conditions of the equipment when the release occurs. Liquid release requires more complex treatment. As liquid exits equipment or pipe, it may partially flash or vaporize, there is often small liquid droplets or aerosol which may be carried away with the vapor and eventually evaporate, and a liquid pool may be formed which slowly evaporates. The Airborne Quantity for a liquid release is the summation of quantity flashed and quantity evaporated from aerosol droplets and liquid pools.

Section Objectives

The following objectives are covered in this section:

- Estimation of Vapor Release Rate
    - Based on Hole Size
    - Based on Vaporization of Liquid
- Estimation of Liquid Release Rate
    - Based on Hole Size
    - Based on Catastrophic Failure
    - Based on Flashing Liquid Flow
    - Test for Two-Phase Flow
- Evaluation of Flash Fraction
- Evaluation of Aerosol Evaporation Fraction
- Estimate of Evaporation from a Liquid Pool

Several methods described in this document involve limitations relative to chemical properties, the most significant being that vapors are addressed as ideal gases and thermodynamic properties are correlated as simple linear relationship with temperature. Some source models for chemical processes operating near the critical point (critical temperature and critical pressure) will be less accurate than processes operating at or below the normal boiling point.

Flowchart for Determination of Airborne Quantity

The steps for estimating the Airborne Quantity include selection of the appropriate release model (based on a specified rate, hole size, heat balance, or catastrophic failure) as is shown in Figure 9.1.

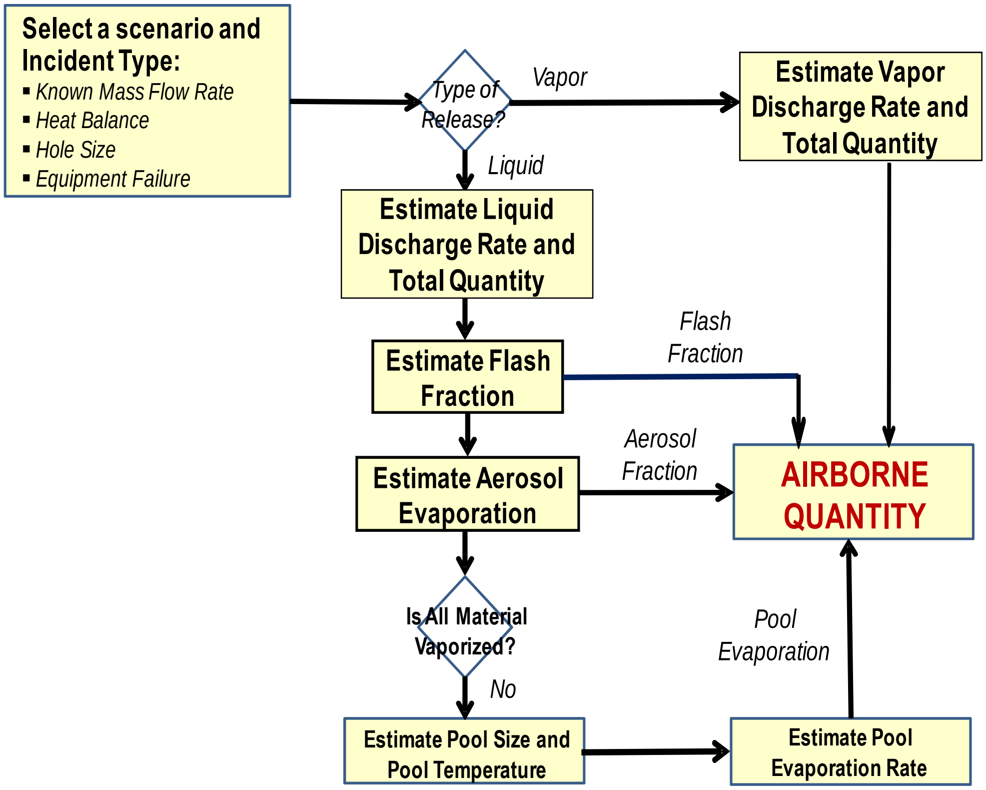


Figure 9.1 Flowchart for Estimation of Airborne Quantity

Selection of a Discharge Model

The release rate for a hazard scenario is typically determined as the *maximum feasible quantity.* There are four primary Loss Event Categories aligned to a discharge model including:

- ☐ **Hole Size** where release rate is determined by modeling the discharge from a hole of specified diameter, process pressure, and fluid density. *(Short Pipe Flashing Liquid is a special Hole Size case.)*
- ☐ **Overflow or Specified Rate** where release rate is determined from the feed or other specified release rate.
- ☐ **Excessive Heat** where release rate is determined from the rate of heat input divided by the heat of vaporization.
- ☐ **Rupture** represents a sudden release of the entire contents and may apply to both energy and hazardous chemical releases.

For loss events where the release rate may be estimated from a hole size, the general approach is to use the largest practical hole size. Hole sizes may be standardized to simplify screening evaluations. A small hole (5 to 15 mm) may represent gasket failure or leaks from mechanical pump seals. A medium (25 mm) hole may represent significant equipment or piping leaks. While a large (100 mm to full bore) hole represents hose, pipe, or equipment nozzle failure.

Hole Size Release Rate for Vapor or Subcooled Liquid

The vapor discharge rate to atmospheric pressure for a nozzle, hole, or short pipe at an average isentropic expansion coefficient of 1.4 is estimated in cgs units by Equation 9-1 [21, p. 72]:

$$\mathbf{V = 23\, c_d\, d^2\, P_0\, \{[(P_A/P_0)^{1.429} - (P_A/P_0)^{1.714}]\, Mw / T\}^{1/2}} \qquad \text{Equation 9-1}$$

The ratio, P_A/P_0, is limited to a minimum of 0.528 for sonic flow

The sub-cooled (non-flashing) liquid discharge rate to atmospheric pressure for a nozzle, hole, or short pipe at liquid head, h', may be estimated from the Bernoulli equation using cgs units in Equation 9-2 [21, p. 69]:

$$\mathbf{L = 1.2\, c_d\, d^2\, \{\, \rho_L\, [\, 1000\, (P_0 - P_A) + 9.8\, \rho_L\, h'\,]\, \}^{1/2}} \qquad \text{Equation 9-2}$$

where:

d = hole diameter (m)
Mw = vapor molecular weight
c_d = discharge coefficient
P_0 = upstream pressure (kPa)
P_A = atmospheric pressure (101.3 kPa)
L = liquid release rate (kg/sec)
V= vapor release rate (kg/sec)
h' = liquid height (m)
T = release temperature (K)
ρ_L, ρ_V = liquid or vapor density (kg/m^3)

Note that a discharge coefficient of 0.61 is typical for a hole or 1.0 for a well-rounded nozzle such as a safety valve.

Hole Size Release Rate Example-Vapor

Estimate the vapor release rate of methane (Mw = 16) from a 25 mm (0.025 m or 1 inch) hole at 500 kPa gauge (601.3 kPa absolute or 87 psia) and 25 C (287 K) using a c_d of 0.6 is:

$$P_A/P_0 = 101.3 / 601.3 = 0.169 \ \text{ limited to } 0.528$$

$$V = 23\, (0.61)\, (0.025)^2\, 601.3\, [\{ (0.528)^{1.429} - (0.528)^{1.714} \}\, 16 / 298\,]^{1/2} = 0.32 \text{ kg/sec:}$$

Hole Size Release Rate Example-Liquid

Estimate the liquid release rate of toluene from a 25 mm (0.025 m or 1 inch) hole at 55 kPa gauge (156.3 kPa absolute or 22.7 psia), 100 C (373 K), and a height of 10 meter using c_d =0.6. Use a liquid density for toluene at 100 C of 785 kg/m^3.

$$L = 1.2\, (0.61)\, (0.025)^2\, [\, 785\, \{1000\, (156.3 - 101.3) + 9.8\, (785)\, 10\}\,]^{1/2} = 4.7 \text{ kg/sec}$$

Hole or Short Pipe Size Release Rate for Flashing Liquid

The limiting liquid discharge rate for flashing liquid from a short pipe greater than 0.1 meter in length may be estimated using cgs units in Equation 9-3 [21, p. 78]:

$$\mathbf{L_F = 20\ d^2\ [\ \Delta H_V\ /\ \{\ 1/\rho_V - 1/\rho_L\ \}\ ]\ /\ [\ C_s\ \ T\ ]^{1/2}} \qquad \text{Equation 9-3}$$

where:

C_s = liquid heat capacity (J/g C)

T = temperature (K)

ΔH_V = heat of vaporization (J/g)

d = hole diameter (m)

L_F = flashing liquid release rate (kg/sec)

ρ_V, ρ_L = vapor, liquid density (kg/m^3)

A discharge length greater than 0.1 meter is required for limiting flashing flow through a short pipe. For very short discharge distances such as a hole, the **liquid does not have** sufficient time to flash during discharge and the Bernoulli equation for sub-cooled liquid is used (Equation 9-2). A discharge coefficient is not used in the above correlation for flashing liquid.

Example Hole or Short Pipe Size Release Rate for Flashing Liquid

Estimate the flashing liquid release rate of toluene (Mw=92.1) from a 25 mm (0.025 m or 1 inch) short pipe at 500 kPa gauge (601.3 kPa absolute or 87 psia), 185 C (458 K). Use a liquid density for toluene at 120 C of 695 kg/m^3, liquid heat capacity of 2.2 Joule/g C, and heat of vaporization of 310 Joule/g.

The vapor density (assuming an ideal g8s) is approximately ρ_V = 0.12 P Mw / T = 0.12 (601.3 kPa) 92.1 / 458 K = 14.5 kg/m^3

$$L_F = 20\ d^2\ [\ \Delta H_V\ /\ \{\ 1/\rho_V - 1/\rho_L\ \}\ ]\ /\ [\ Cs\ \ T\ ]^{1/2}$$

$$= 20\ (0.025)^2\ [\ 310\ /\ \{\ 1\ /\ 14.5 - 1\ /\ 695\ \}\ ]\ /\ [\ 2.2\ (\ 458\ )\ ]^{1/2} = 1.8\ \text{kg/sec}$$

Liquid Trajectory from a Hole

A stream of liquid discharging from a hole in a tank will stream out of the tank and impact the ground at some distance away from the tank (Figure 9.2).

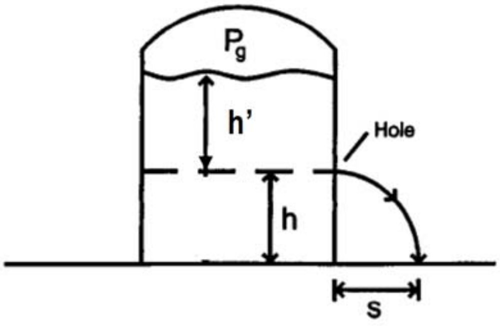


Figure 9.2 Liquid Trajectory from a Hole

The distance away from the tank the liquid stream will impact the ground, s, is given in cgs units by Equation 9-4 [21, pp. 83-85]:

$$s = v_d\, t \qquad \text{Equation 9-4}$$

and discharge velocity, given by Equation 9-5:

$$\mathbf{v_d = 4\ L\ /\ (\ \pi\ d^2\ c_d\ \rho_L\ ) = 1.27\ L\ /\ (\ d^2\ c_d\ \rho_L\ )} \qquad \text{Equation 9-5}$$

where:

L is mass release rate (kg/sec)
d is hole diameter (m)
ρ_L is the density of the discharging fluid (kg/m^3)

The time, t, for the liquid to fall the distance h, is given by simple acceleration due to gravity in Equation 9-6:

$$\mathbf{t\ = 0.45\ h^{1/2}} \qquad \text{Equation 9-6}$$

Liquid trajectory distance and time may be used to estimate duration of aerosol droplets associated with a high velocity liquid leak of estimate a distance at which personnel could be sprayed from a liquid leak. The distance may also be used to determine if a liquid stream could shoot over any dike designed to contain a spill.

Overflow or Specified Discharge Rate

For overfill scenarios, the liquid release rate is equal to the maximum fill rate.

- The liquid release rate may be estimated from the pipe size, pipe length and pressure difference to downstream equipment for backflow scenarios.
- In some cases, a control valve or other piping restriction may allow estimation of the maximum feed rate using a hole size discharge model.

Discharge Rate from Excessive Heat Input

Many loss events involve excessive heat rate where with the vapor release rate (and corresponding airborne quantity) is determined as heat rate divided by heat of vaporization. Equations for different cases are noted for fire venting (Equation 9-7), heat transfer venting (Equation 9-8), mechanical energy venting (Equation 9-9), and reaction venting (Equation 9-10):

- **Fire Venting = q_{Fire} / ΔH_V** where q_{Fire} is evaluated per NFPA 30 or other Equation 9-7
- **Heat Transfer Venting = $U\ A_{HT}\ (T_{HM} - T_R)\ /\ \Delta H_V$** *for $T_{HM} > T_R$* Equation 9-8
- **Mechanical Energy Venting = $\{\ q_{ME} - U\ A_S\ (T_R - T_A)\ \}\ /\ \Delta H_V$** *for $T_{ME} > T_R$* Equation 9-9
- **Reaction Venting = $M\ q_{RX}\ /\ \Delta H_V$** Equation 9-10

Where:

ΔH_V is heat of vaporization
U is heat transfer coefficient
A is heat transfer or surface area
q_{ME} is mechanical energy input
q_{RX} is reaction energy per mass
T_{HM} is heating media temperature
T_R is temperature at relief set pressure
T_A is ambient temperature
T_{ME} is maximum mechanical energy temperature
M is reactant mass

Example Discharge Rate from Excessive Heat Input

Estimate the average (or sizing) vapor release rate of toluene (Mw = 92) from a non-insulated vertical storage tank in a pool fire (using NFPA 30 guidance). Use: Tank dimensions of 9 m diameter by 6 m with volume of 380 m^3, "wetted" surface area of 170 m^2 , heat of vaporization of 350 Joule/g and $q_{Fire} = 630\ A_S^{0.338}$ kJoule for A_S in m^2.

$$\text{Release Rate} = q_{Fire} / \Delta H_V = 630\ A_S^{0.338} / \Delta H_V = 630\ (170)^{0.338} / 350 = 10.2\ \text{kg/sec}$$

The initial (or actual) vapor release rate may be much higher depending on the size and type of the relief device. This maximum release rate needs to be accounted for in the Risk Analysis.

Test for Two-Phase Flow

A test for two-phase flow would typically be applied to vessels or equipment exposed to fire or reactive systems where the release occurs at the top such as with relief device activation.

For a vessel at 80% full, the superficial gas velocity required for two-phase flow is roughly 0.12 m/sec (0.4 ft/sec) for "Churn-Turbulent" and 0.03 m/sec (0.09 ft/sec) for foamy or highly viscous (>100 cp at relief temperature) materials (Figure 9.3). Superficial velocity, v*, (m/sec) is determined using Equation 9-11:

$$\mathbf{v^* = 8.3\ V\ T / \{ Mw\ P\ A_{CS} \}} \qquad \text{Equation 9-11}$$

where the cross-sectional area, A_{CS}, is 0.785 D^2 for vertical tanks, 0.785 D H for horizontal tanks and 0.524 D^2 for spheres (and D is tank diameter).

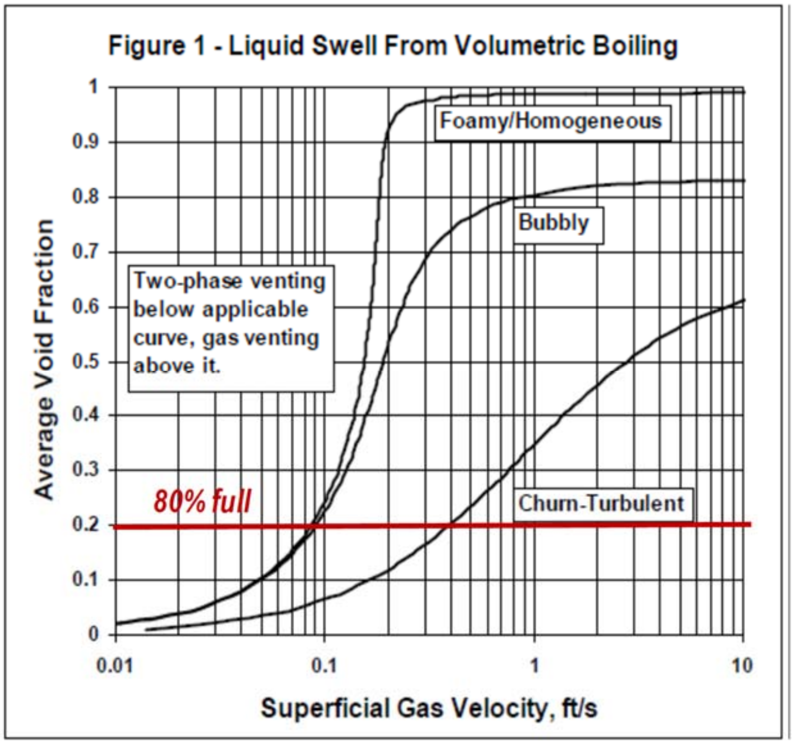


Figure 9.3 Liquid Swell from Volumetric Boiling [53, pp. Appendix 1B, 28]

A "best estimate" two-phase density (Churn-Turbulent), ρ_{TP}, is related by Equation 9-12 [53]:

$$\rho_{TP} / \rho_V = [1 + (\rho_L / \rho_V)^{1/2}] / [1 + (\rho_V / \rho_L)^{1/2}] \qquad \text{Equation 9-12}$$

The liquid portion of the two-phase release, L*, may be estimated from a "best estimate" vapor quality and vapor release rate, V, in Equation 9-13 [53]:

$$L^* = V \{\rho_{TP}/\rho_V - 1\} = V \{ [(\rho_L/\rho_V)^{1/2} - (\rho_V/\rho_L)^{1/2}] / [1 + (\rho_V/\rho_L)^{1/2}] \} \qquad \text{Equation 9-13}$$

where ρ_L, ρ_V are liquid and vapor density respectively.

The Total Airborne Quantity from a two-phase release includes Vapor plus Aerosol and Pool Evaporation of the liquid portion. Note that two-phase flow is not normally considered for external fire exposure as the heat input is only via the external surfaces.

Example Test for Two-Phase Flow

In the previous example for fire exposure to a 9 m diameter toluene storage tank, use a vapor rate of 10.2 kg/sec, relief device set pressure of 10 kPa gauge, and liquid density of 770 kg/m3. The boiling point of toluene at 10 kPa gauge (111.3 kPa absolute) is 387 K.

The superficial gas velocity for a vapor rate of 10.2 kg/sec at a pressure of 111.3 kPa absolute and temperature of 387 K is:

$$A_{CS} = 0.785\ D^2 = 0.785\ (9)2 = 63.6\ m^2$$

$$v^* = 8.3\ V\ T / \{ Mw\ P\ A_{CS} \} = 8.3\ (10.2)\ 387 / \{ 92\ (111.3)\ 63.6\ m^2 \} = 0.05\ m/sec$$

The superficial gas velocity is below that for two-phase flow at a practical maximum fill fraction of 80 to 90 % (average void fraction of 0.1 to 0.2).

The superficial velocity at the actual vapor rate or capacity of the specific relief device size also needs to be evaluated.

Equipment Rupture

For rupture of low pressure, non-volatile liquid containing vessels or equipment, the release rate is often assumed as the total contents within 10 minutes or less.

For high pressure equipment (or equipment containing volatile liquid), evaluation as an instantaneous release may be more appropriate. For an instantaneous release, the total contents are released at time equal zero. The released material undergoes flash and aerosol evaporation creating an initial total airborne quantity and any remaining liquid undergoes pool evaporation for the entire duration (typically 1 hour).

Estimation of Mixture Properties

Often, particularly for boiling liquids, the liquid composition is known and vapor composition must be estimated from a simple vapor-liquid equilibrium model (such as Raoult's Law). In this case, vapor mole fraction for any component is estimated in Equation 9-14:

$$y_i = x_i\ P_i / \Pi \qquad \text{Equation 9-14}$$

where x_i is liquid mole fraction, P_i is the component vapor pressure and Π is the total pressure which is also equal to $\Sigma\ x_i\ P_i$.

In other cases, two liquid phases may exist and vapor composition is nearly constant between the solubility limits of each liquid phase. The total vapor pressure is estimated as the sum of vapor pressures for each of the two liquid phases.

Chemical properties for mixtures are dependent on composition. The following "Mixture Rules" provide a reasonable estimate for selected chemical properties[11].

Mixture Liquid Density estimated by additive volumes using Equation 9-15:

$1/\rho_L$ mixture = sum of mass fraction times ($1/\rho_L$ component). Equation 9-15

Vapor Density estimated as an ideal gas using Equation 9-16:

$\rho_V = 0.12\ P\ Mw_{avg} / T$ where P is pressure in kPa and T in K Equation 9-16

Mixture Liquid Heat Capacity estimated by the sum of liquid mass fraction times component Heat Capacity (or mole fraction times molar Heat Capacity).

Mixture Heat of Vaporization estimated by the sum of vapor mass fraction times component Heat of Vaporization (or mole fraction times molar Heat of Vaporization).

Estimation of Flash Fraction

If a release occurs at temperature above the normal boiling point, flashing will occur. The Flash Fraction, F_V, is estimated from the change in temperature, the liquid heat capacity and the heat of vaporization using Equation 9-17:

$$F_V = (T - T_B)\ C_S / \Delta H_V \qquad \text{Equation 9-17}$$

where:

C_s = liquid heat capacity

ΔH_V = heat of vaporization

T = release temperature

T_B = normal boiling point

The contribution to Airborne Quantity from flashing liquid is the Flash Fraction times the liquid discharge rate, **$L\ F_V$**.

Flash Fraction for Chemical Mixtures

An adiabatic flash calculation for a mixture requires solving a material balance for each component using Equation 9-18 [54]:

$$z_i = (1-F_V)\ x_i + F_V\ y_i \qquad \text{Equation 9-18}$$

where x_i, y_i, and z_i is the mole fraction of component i in the liquid, vapor, and feed respectively.

The final mixture boiling point is determined as the temperature where the sum of partial pressures equals the total system pressure (typically one atmosphere). Solving a multi-component flash requires complex "trial and error" techniques found in several engineering applications such as ASPEN [55].

Aerosol Evaporation

The fraction of released liquid vaporized is a poor prediction of the total mass in the vapor cloud due to the presence of entrained liquid as droplets or aerosol. There is little information in the literature regarding aerosol formation and evaporation. Some references note multiplying the flash fraction by factors of 1 to 4 to provide a rough approximation for the impact of aerosols [56]. Another approach to determining the aerosol fraction involves estimation of droplet size and settling velocity.

Aerosol droplets are formed primarily from condensation, mechanical break-up, and/or flashing break-up of the exiting fluid. Droplets will either be carried downwind and evaporate or coalesce upon hitting the ground or other surfaces as "rainout" [21] [56]. At this time, there is not a completely acceptable method for predicting aerosol evaporation. A common practice is to assume aerosol evaporation is a multiple of the flash fraction (typically 1 to 4).

Another approach is to estimate droplet size from a critical Weber number (typically 10 to 20), duration based on release elevation and settling velocity, and evaporation rate from the droplet surface. An approximation for droplet size from mechanical and flashing break-up (based on a critical Weber number [21, pp. 98-99] of 10, typical surface tension of 0.02 N/m, assumed proportional to 1- F_V, and ambient air density of 1.18 kg/m^3) using Equation 9-19 (developed from [21] per a critical Weber number of 10-20):

$$\mathbf{d_d \sim 0.17\ (1 - F_V) / v_d^2} \qquad \text{Equation 9-19}$$

With the Critical Weber Number ~ 10 = $\rho_a v_d^2 d_d / \sigma$ and droplet diameter proportional to (1-F_V) and where d_d is droplet diameter in meter (to a maximum of 0.01 m), σ the liquid surface tension in air, and discharge velocity, $v_d = 1.27\ L / (d^2 c_d \rho')$ in m/sec. The density, ρ', is that of the discharging fluid which for <u>two-phase flow</u> is estimated as: $1/\rho' = F_V/\rho_V + (1-F_V)/\rho_L$.

A very rough approximation for the fraction evaporated from aerosol droplets for droplet diameter < 0.01 m (or v_d > 4 m/sec), F_D, is estimated from the droplet surface per mass and release elevation, h, assuming diffusion limited evaporation using Equation 9-20:

Diffusion Limited Surface Evaporation, $m = 0.0027\ Mw^{2/3}\ Psat / T$ in kg/sec m^2 [21, pp. 100-101]

Spherical Surface Area per Mass = $6 / (d_d \rho_L) = 35\ v_d^2 / [\rho_L (1-F_V)]$

Droplet Duration, $t = 0.45\ h^{1/2}$ per Equation (16) assuming horizontal release

$$\mathbf{F_D = 0.043\ v_d^2\ Mw^{2/3}\ P^{sat}\ h^{1/2} / [\ \rho_L\ T_{Aerosol}\ (1 - F_V)\ ]} \qquad \text{Equation 9-20}$$

where:

v_d = release velocity (m/sec)
h = release height (m)
Mw = molecular weight
ρ_L = liquid density (kg/m^3)
P^{sat} = vapor pressure (kPa absolute)
F_V = flash fraction
$T_{Aerosol}$ = aerosol temperature (K) limited to a maximum of the normal boiling point

The aerosol temperature, $T_{Aerosol}$, may be conservatively assumed as the release temperature to a maximum of the normal boiling point. If a more accurate pool temperature is needed, it may be estimated (iteratively) from a heat balance per mass including evaporative cooling, and heat transfer from the droplet to the air using Equation 9-21:

$$F_D\ \Delta H_V = U_D\ A_D\ t\ (T_A - T_{Aerosol}) + 2\ C_S\ (T' - T_{Aerosol}) \quad \text{for } T_{Aerosol} = (T_{Final} + T') / 2$$

Spherical Surface Area per Mass = $6 / (d_d \rho_L) = 35\ v_d^2 / [\rho_L (1-F_V)]$

Droplet Duration, $t = 0.45\ h^{1/2}$ per Equation (16) assuming horizontal release

$$\mathbf{T_{Aerosol} = \{\ 7.9\ U_D\ h^{1/2}\ v_D^2\ T_A / [\rho_L\ (1-F_V)] + C_S\ T' - F_D\ \Delta H_V / 2\ \} / \{\ 7.9\ U_D\ h^{1/2}\ v_D^2 / [\rho_L\ (1-F_V)] + C_S\ \}\ ]}$$

Equation 9-21

where:

T' = release temperature to a limit of the normal boiling point (K)
T_A = ambient temperature (K) ΔH_V = heat of vaporization (Joule/g)
m_D =droplet evaporation rate (kg/sec m^2) C_S = liquid heat capacity (Joule/g K)
U_D – heat transfer coefficient of droplet to surrounding air, typically 0.02 to 0.05 kW/m^2 K

The actual mechanism for aerosol formation is much more complex than this simple model. Very small droplets (less than 0.1 mm) may remain suspended for long periods of time and act as a mist or fog. In addition:

- The Fraction Aerosol Evaporation is limited to a maximum of 1.
- Saturation pressure, P^{sat}, is estimated at the release temperature, T', but limited to that of the normal boiling point, T_B, if the fraction vaporized is greater than zero.
- For a discharge directed downwards impinging on the ground, the equivalent release elevation and aerosol evaporation term is near zero.

The contribution to Airborne Quantity from Aerosol Evaporation is $F_D\ L\ (1 - F_V)$.

Example Aerosol Evaporation

Estimate the aerosol droplet size and fraction aerosol evaporation for a 20 m/sec release of toluene (Mw = 92) at 100 C (373 K) and height of 2 meter. The density of toluene at 100 C is 785 kg/m^3, and vapor pressure is 74 kPa. As the temperature is below the normal boiling point such that the flash fraction is zero.

The estimated average droplet diameter is:

$$d_d \sim 0.17\ (1 - F_V) / v_d^2 = 0.17\ (1 - 0) / (20)^2 = 0.00043 \text{ meter } (0.43 \text{ mm})$$

$$F_D = 0.043\ v_d^2\ Mw^{2/3}\ P^{sat}\ h^{1/2} / [\rho_L\ T'] = 0.043\ (20)^2\ (92)^{2/3}\ 74\ (2)^{1/2} / [(785)\ 373] = 0.13$$

Evaporation from a Liquid Pool

An important parameter in estimation of evaporation from a liquid pool is the pool area. If unconfined, the pool will expand during the release. The maximum pool size is attained (unless limited by a dike or bund) at the end of the leak duration. Pool size is highly dependent on the roughness of the terrain with a "smooth" surface assumed as a "worst case" resulting in the largest estimated pool size.

The area for an unconfined pool is estimated from the liquid rate and leak duration, t_L at a depth of 1 cm in Equation 9-22. The pool area is limited to the area of a dike or bund if it exists.

$$\mathbf{A_P = L' / [\ \rho_L / (100\ t_L) + m_P / 2\ ]} \quad \textit{in } m^2 \textit{ limited to the dike area} \qquad \text{Equation 9-22}$$

where:

L' = liquid spill rate to the pool = $L\ [\ 1 - F_V - (1–F_V)\ F_D\ ]$ in kg/sec
m_P = pool evaporation rate (kg/sec m^2)
t_L = liquid release duration (sec)
ρ_L = liquid density (kg/m^3)

A "first pass" estimate of maximum pool area (assuming low evaporation rate) is simply $A_P = L' / [\ \rho_L / (100\ t_L)\ ]$.

For an instantaneous release (such as equipment rupture), the pool area is estimated with Equation 9-23:

$$\mathbf{A_P = Total\ Liquid\ Released\ (\ 100\ /\ \rho_L\ )}\quad \textit{in } m^2 \textit{ limited to the dike area} \qquad \text{Equation 9-23}$$

The temperature of liquid in the pool, T_P, may be conservatively assumed as the release temperature to a maximum of the normal boiling point. For cases where the release temperature is less than ambient below the normal boiling point, it may be appropriate to assume the liquid pool approaches ambient temperature. If a more accurate pool temperature is needed, it may be estimated (iteratively) from a steady-state heat balance including solar radiation, evaporative cooling, and heat transfer from the ground using Equation 9-24:

$$m_P\ A_P\ \Delta H_V = A_P\ S + A_P\ U_{Gnd}\ (T_A - T_P) + L'\ C_S\ (T' - T_P)$$

$$\mathbf{T_P = \{T'\ L'\ C_s + A_P\ (S - m_P\ \Delta H_v + U_{Gnd}\ T_A)\}\ /\ \{L'\ C_s + U_{Gnd}\ A_P\}\ ]} \qquad \text{Equation 9-24}$$

where:

L' = liquid spill rate to the pool = $L\ (1 - F_V)\ (1 - F_D\ )$ in kg/sec
S = solar radiation input, typically 0.5 kW/m^2 for outdoor spills
T' = release temperature to a limit of the normal boiling point (K)
T_A = ambient temperature (K)
m_P = pool evaporation rate (kg/sec m^2)
ΔH_V = heat of vaporization (Joule/g)
C_S = liquid heat capacity (Joule/g K)
U_{Gnd} – heat transfer coefficient to ground, typically 0.02 kW/m^2 K to 0.2 kW/m^2 K

Evaporation rate from a liquid pool, m_p (kg/sec m^2), is evaluated as diffusion at the estimated pool temperature [57, pp. 7-10 to 7-12], T_P, using Equation 9-25:

$$\mathbf{m_P = 0.0021\ Mw^{2/3}\ u^{0.78}\ P^{sat}\ /\ T_P} \qquad \text{Equation 9-25}$$

where:

Mw = molecular weight
u = wind speed (m/sec)
P^{sat} = saturation vapor pressure (kPa)
T_P = pool temperature (K)

The pool evaporation correlation selected is from the literature [57, p. Appendix D]. This reference suggests that for indoor liquid releases, a wind speed of 0.1 m/sec (with pool temperature assuming no solar radiation) may be used.

The contribution to Airborne Quantity from Pool Evaporation is $\mathbf{m_p\ A_P}$ to a limit of entire pool evaporated or $L\ (\ 1 - F_V\ )\ (\ 1 - F_D\ )$.

Example Evaporation from a Liquid Pool

Estimate pool evaporation for a unconfined 15 minute (900 sec) liquid leak of 10 kg/sec toluene (Mw = 92) at 100 C (373 K) assuming a wind speed of 3 m/sec, a flash fraction of zero, and aerosol evaporation fraction of 0.29. The density of toluene is 785 kg/m^3 and vapor pressure is 74 kPa at 100 C.

Conservatively assuming the pool temperature as the release temperature to a maximum of the normal boiling point:

$m_P = 0.0021\ Mw^{2/3}\ u^{0.78}\ P^{sat} / T_P = 0.0021\ (92)^{2/3}\ (3)^{0.78}\ 74 / 373 = 0.020$ kg/sec m^2

$A_P = L' / [\ \rho_L / (100\ t_L) + m_P / 2\ ] = 10\ (1–0.29) / [\ 785 / (100\ \{900\}) + 0.02 / 2\ ] = 379$ m^2

And total evaporation rate = $m_p\ A_p = 379\ (0.020) = 7.6$ kg/sec limited to $10\ (1\text{-}0.29) = 7.1$ kg/sec

Example Airborne Quantity for a Flashing Liquid Release

Estimate the Airborne Quantity for failure of a 25 mm (0.025 m) diameter liquid butane hose. The location is outdoors and within a 10 m^2 diked area. Use a hose elevation of 1 meter.

Use for butane:

Molecular Weight 58.1
Release temperature of 10 C (283 K)
Normal Boiling Point of - 0.8 C (272 K)
Release Pressure of 50 kPa gauge (saturated liquid)
Liquid Heat Capacity of 2.4 Joule/g K
Heat of Vaporization of 380 Joule/g
Liquid Density of 590 kg/m^3
Vapor Density (at 10 C and 50 kPa gauge) of 3.7 kg/m^3

The liquid discharge rate for flashing liquid from a pipe or hose may be estimated as:

$L_F = 20\ d^2\ [\ \Delta H_V / \{\ 1 / \rho_V – 1 / \rho_L\ \}\ ] / [\ C_s\ \ T\ ]^{1/2}$

$= 20\ (0.025)^2\ [\ 380 / \{\ 1 / 3.7 – 1 / 590\ \}] / [\ 2.4\ (283)\ ]^{1/2} = 0.68$ kg/sec

The Flash Fraction, F_V, is estimated from the change in temperature, liquid heat capacity and heat of vaporization by:

$F_V = (\ T – T_B\ )\ C_S / \Delta H_V\ =\ (\ 283 – 272\ )\ 2.4 / 380\ = 0.07$

The two-phase release velocity,

$\rho\ ' = 1 / [\ F_V / \rho_V + (1\text{-}F_V) / \rho_L\ ] = 1 / [\ 0.07/ 3.7 + (1\text{-}0.07) / 590\ ] = 49$ kg/m^3

$v_d = 1.27\ L / (\ D^2\ c_d\ \rho'\ ) = 1.27\ (0.68) / [\ (0.025)^2\ (1.0)\ 49\ ] = 28$ m/sec

The fraction aerosol droplet evaporation, F_D, is estimated at the normal boiling point where P^{sat} is atmospheric pressure or 101.3 kPa and release elevation, h, is 1 meter.

$F_D = 0.043\ v_d^2\ Mw^{2/3}\ P^{sat}\ h^{1/2} / [\rho_L\ T'\ (1 – F_V)\ ]$

$= 0.043\ (28)^2\ 58.1^{2/3}\ (101.3)\ 1^{1/2} / [\ (590)\ 272\ (1\text{-}0.07)\ ] = 0.34$

Evaporation rate from a liquid pool, is evaluated at an estimated pool temperature (assume the normal boiling point or 272 K), wind speed of 3 m/sec and pool area of 10 m^2 as:

$m_P = 0.0021\ Mw^{2/3}\ u^{0.78}\ P^{sat} / T_P$

$= 0.0021\ (58.1)^{2/3}\ 3^{0.78}\ (101.3) / 272 = 0.028$ kg/sec m^2

The Airborne Quantity = $L\ [\ F_V + (1 – F_V\ )\ F_D\ ] + mp\ A$

$= 0.68\ \ [\ 0.07 + (1 – 0.07)\ 0.34\ ] + 0.028\ (10) = 0.54$ kg/sec

which is close to the liquid release rate of 0.68 kg/sec.

10. VAPOR DISPERSIONS

Vapor dispersion modeling is estimation of the dissipation of a toxic or flammable vapor cloud in air due to wind, thermal action, gravity spreading, and atmospheric turbulence. Estimation of the atmospheric dispersion or dissipation of vapor is a critical step in Consequence Analysis. Dispersion calculations provide an estimate of the area affected and average vapor concentration at downwind distances. The simplest models require vapor release rate (or total quantity of vapor released), wind speed and direction, atmospheric stability, surface roughness, release elevation, release velocity and density. Vapor models do not include solids deposition, mists or fog.

Section Objectives

The following objectives are covered in this section:

- Identifying the type of dispersion (jet mixing, dense gas, buoyant).
- Identifying the type of release (continuous versus instantaneous).
- Key vapor dispersion parameters.
- Estimating concentration versus distance for a simple release scenario.
- The impact of release Elevation on Ground Level Concentration.
- Relief Device Effluent Screening Process and Criteria.
- The key variables for indoor concentration estimation.
- Simplifying assumptions and limitations of simple dispersion models.

Vapor Dispersion Mechanisms

Many releases are in the form of a high velocity jet. Near the release point, the jet velocity is significantly higher than wind velocity. The jet entrains air due to shear forces, grows in size, and becomes diluted. If released vertically upward, drag forces increase with jet volume (and surface area) and eventually horizontal momentum due to wind dominates (Figure 10.1).

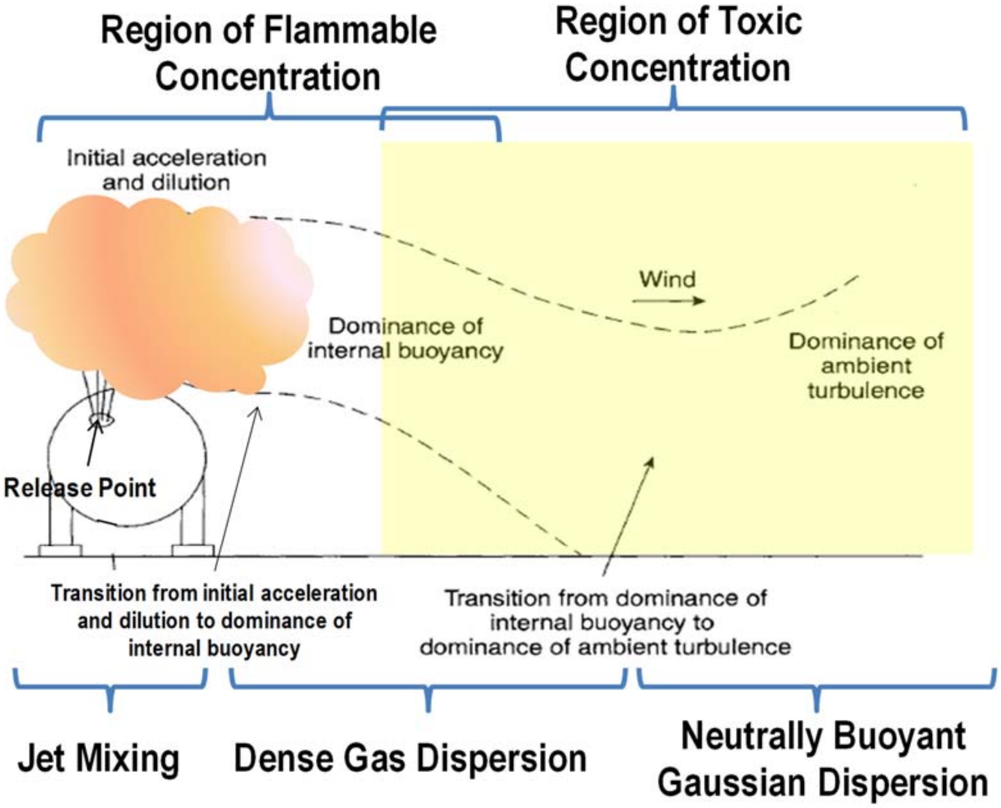


Figure 10.1 Vapor Dispersion Mechanisms

When dense gases are released, the gas travels downward and downwind while being mixed with fresh air. Considerable initial dilution occurs because of the gravity-driven intrusion of the cloud into the ambient air.

Irrespective of the initial release conditions of velocity and density, a point will eventually be reached where the gas has been diluted adequately to be considered neutrally buoyant. At this point the dispersion is dominated by ambient turbulence.

Jet Mixing

Release of flammable vapor often occurs at relatively discharge velocity. The primary dilution mechanism is entrainment of air due to shear forces. This mechanism is very important as often the initial dilution reduces concentration to below the lower flammable limit for release of a flammable vapor. A simple correlation for jet mixing of a turbulent, free (subsonic) jet (Figure 10.2) is determined using in Equation 10-1 and Equation 10-2 [58]:

$$C_0 / C = 0.32 (\rho_0 / \rho)^{1/2} X / d_0 \qquad \text{Equation 10-1}$$

$$C_0 / C_t = (\rho_0 / \rho_t) (v_0 / u) \quad at\ X = X_t \qquad \text{Equation 10-2}$$

where:

C_0 = initial volumetric concentration at exit of jet (volume fraction)
C_t = volumetric concentration at distance X_t (volume fraction)
X = distance from the release point (m)

ΔX_t = transition distance (m) or distance where jet mixing is no longer significant
d_0 = discharge pipe diameter (m)
ρ_0 , ρ_t = density of the vapor at atmospheric pressure and exit or distance X_t respectively (kg/m^3)
v_0 = initial jet velocity (m/sec) - limited to sonic velocity, v_0', of approximately 400 / $\rho_0^{1/2}$ m/sec
u = wind speed (m/sec)

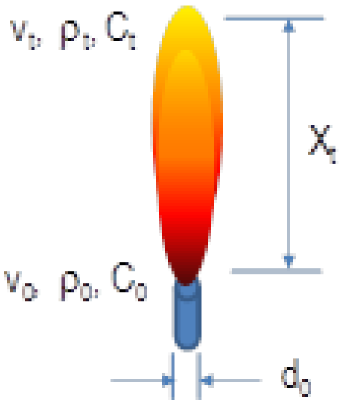


Figure 10.2 Jet Mixing

The transition distance or point where the jet velocity has diminished such that Dense Gas (or Neutrally Buoyant) Dispersion may apply using Equation 10-3:

$$\mathbf{X_t = (d_0 / 0.32) (v_0 / u) (\rho_0 / \rho_t)^{1/2}} \qquad \text{Equation 10-3}$$

Note that for sonic flow conditions, a limiting velocity $v_0' = 400 / \rho_0^{1/2}$ and "sonic equivalent" discharge diameter $d_0' = d_0 (v_0 / v_0')^{0.5}$ may be used in Equation 10-3 to provide a rough estimate of transition concentration and distance.

Jet Mixing Example

Estimate the concentration at the transition distance where jet mixing has diminished for a 1 kg/sec subsonic release of propane at 25 C through a 50 mm diameter pipe with wind speed of 3 m/sec.

Use:

ρ_t as approximately the density of air at 25 C of 1.2 kg/m3

ρ_0 of propane at 25 C and atmospheric pressure of 1.8 kg/m3

v_0 = 1.27 (1 kg/sec) / [1.8 kg/m^3 (0.05 m)^2] = 282 m/sec

$C_0 / C_t = (\rho_0 / \rho_t) (v_0 / u) = (1.8 / 1.2) (282 / 3) = 143$

C_t = 100 / 143 = 0.7 volume % (using C_0 as 100% at the release point)

The transition distance is $X_t = (d_0 / 0.32) (v_0 / u) (\rho_0 / \rho_t)^{1/2}$

$= (0.05 / 0.32) (282 / 3) (1.8 / 1.2)^{1/2} = 18$ meter

Continuous versus Instantaneous Release

Figure 10.3 depicts the plume dissipation downwind for a continuous release. However, when the release duration is very short, a "puff" or instantaneous model is more appropriate to use (Figure 10.4). An example short duration release would be catastrophic failure of a vessel.

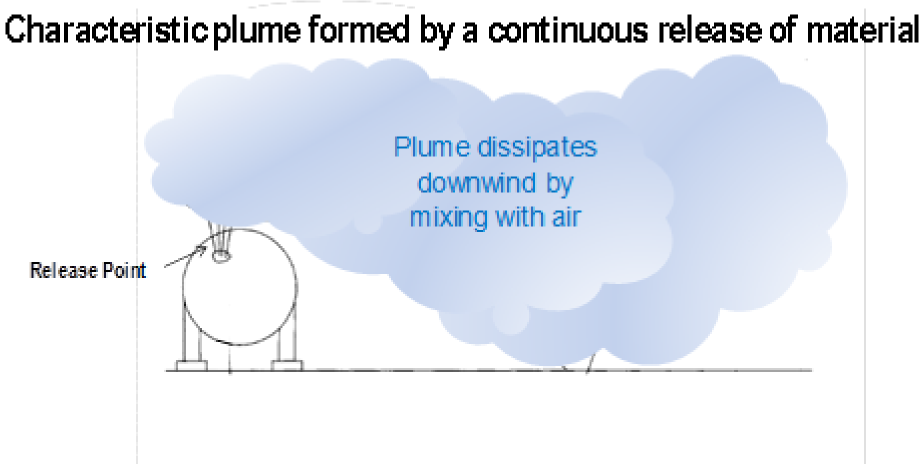


Figure 10.3 Continuous Release

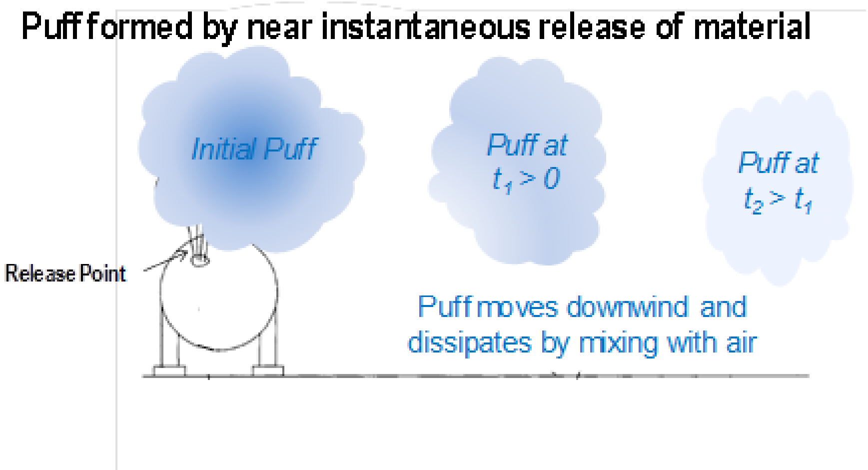


Figure 10.4 Instantaneous Release

Atmospheric Dispersion Modeling

Following initial dilution, the plume becomes longer and narrower with increasing wind speed; the release is carried downwind and diluted by diffusion and turbulence. Parameters Affecting Atmospheric Dispersion include:

- **Wind Direction** is assumed "worst case" or in the direction of the greatest number of personnel for screening of potential consequences.

- **Surface Roughness** and **Wind Speed** affect the mechanical mixing and the overall dispersion coefficient. Trees and buildings increase surface roughness which promotes mixing, whereas lakes and open areas decrease it.
- **Averaging Time** is used to quantify an average concentration which accounts for variation over time due to meandering of the vapor plume. Gaussian models are typically based on a 10 minute averaging time which is the industry standard for analysis of *toxic* cases. The industry standard for analysis of *flammable* cases utilizes a much shorter averaging time (18.75 seconds) with higher maximum concentration.
- **Release Elevation** impacts ground-level concentration. As the release height increases, ground-level concentrations are reduced because the plume must disperse a greater distance vertically.
- **Momentum and Buoyancy** of the initial material released changes the *effective* height of the release. The momentum of a high-velocity jet will carry the gas higher than the point of release, resulting in a much higher *effective* release height. If the gas has a density less than air, the released gas will initially be positively buoyant and will lift upward. If the gas has a density greater than air, then the released gas will initially be negatively buoyant and will slump toward the ground.
- **Atmospheric Stability** relates to vertical mixing of the air in neutrally buoyant models. During the day, the air temperature decreases rapidly with height, encouraging vertical motions. At night the temperature decrease is less, resulting in less vertical motion. For screening of potential consequences, Class D atmospheric conditions with a wind speed of 3 m/sec is commonly used. In more detailed Consequence Analysis, Class D at other wind speeds and “worst case” Class F at 1.5 m/sec wind speed is included.

Dense Gas Dispersion Models

A dense gas is any released vapor with a density greater than ambient air through which it is being dispersed. Most vapor releases are considered “dense gas” as either the molecular weight is greater than air or the release temperature is less than ambient.

When a dense gas is initially released, the cloud slumps toward the ground under the influence of gravity and moves both upwind and downwind. [21, pp. 119-153] [16, pp. 185-225] Dilution occurs due to gravity-driven intrusion of the cloud into ambient air. This is a different dispersion mechanism than occurs with neutrally buoyant releases. After sufficient dilution occurs, atmospheric turbulence becomes the primary mechanism. Eventually density differences become small such that the cloud may be considered neutrally buoyant.

The Britter and McQuaid model was developed using dimensional analysis and correlation of existing data on dense cloud dispersions (Figure 10.5 for dense gas plumes; Figure 10.6 for dense gas puffs; [59]). The model is best suited for ground level releases of dense gases (those of higher density than air at ambient conditions). Most of the data represents dispersion tests in remote, rural areas on mostly flat terrain. Thus, results may not be directly applicable to urban or mountainous areas. Atmospheric stability was found to have little effect on the results and is not included in this model.

Initial buoyancy is defined using Equation 10-4:

$$\mathbf{g_0 = g\,(\rho_0 - \rho_a) / \rho_a} \qquad \text{Equation 10-4}$$

where: g is the acceleration due to gravity (9.8 m/sec^2)

ρ_0 is the initial density of released material or following jet mixing and may be estimated as an ideal gas, $\rho_0 = 12.2\ Mw / T_0$ or vapor following initial dilution from jet mixing.

ρ_a is the density of air at ambient temperature and atmospheric pressure or 1.18 kg/m3
Mw is molecular weight
T_0 is the initial vapor release temperature (deg K)
T_a is the ambient temperature (deg K)

The criteria for a sufficiently dense cloud to require a dense cloud representation for a continuous release is:

$$[\, g_0\, q_0 / (\, u^3\, D_C\,)\,]^{1/3} > 0.15$$

where: q_0 is the volumetric flowrate or $0.082\ Q\ T_0 / (Ct\ Mw)$ for an ideal gas, m^3/sec
C_t is the concentration after initial dilution, volume fraction ($C_t = 1$ for little or no initial dilution)
u is the wind velocity at 10 m elevation, m/sec
D_C is a characteristic source dimension which for a continuous release is $(\, q_0 / u\,)^{1/2}$, m

Note that the buoyancy is dependent on any initial dilution of the vapor stream with air from jet mixing or other release characteristics. The initial density entering the dense cloud region in the case where jet mixing initially occurs is based on the concentration at the transition to atmospheric dispersion per equation 10-2. The initial volumetric flowrate for the dense gas region may also need to be adjusted based on the initial dilution. In this case, the initial density to be used in equation 10-4 may be estimated as:

$$\rho_0 = 12.2\ C_t\ Mw / T + (1 - C_t)\ \rho_a \quad \text{where } T \text{ may be assumed } T_a$$

Substituting for D_C yields a continuous release criterion using Equation 10-5:

$$[\, g_0^2\, q_0 / u^5\,]^{1/6} > 0.15 \qquad \text{Equation 10-5}$$

The criteria for a sufficiently dense cloud to require a dense cloud representation for an instantaneous or "puff" release is:

$$[\, g_0\, V_0 / (\, u\, D_i\,)\,]^{1/2} > 0.20$$

where: V_0 is the release volume or Q^* / ρ_0 or $0.082\ Q^*\ T_0 / Mw$ for an ideal gas

D_C is a characteristic source dimension which for a continuous release is $V_0^{1/3}$

Substituting for D_C yields an instantaneous release criteria in Equation 10-6:

$$[\, g_0\, V_0^{1/3} / u^2\,]^{1/2} > 0.20 \qquad \text{Equation 10-6}$$

The wind speed, release duration (R_d) and downwind distance may be used to estimate if a release is considered a continuous (plume) or instantaneous (puff). If $u\ R_d / X$ is greater or equal to 2.5, the release is considered continuous. If $u\ R_d / X < 0.6$, the release is considered instantaneous. Correlations for puff and plume models may also be equated to determine the downwind distance for transition from a continuous to instantaneous model.

If dense gas criteria are satisfied, then Figure 10.5 or Figure 10.6 are used to estimate the distance to a concentration.

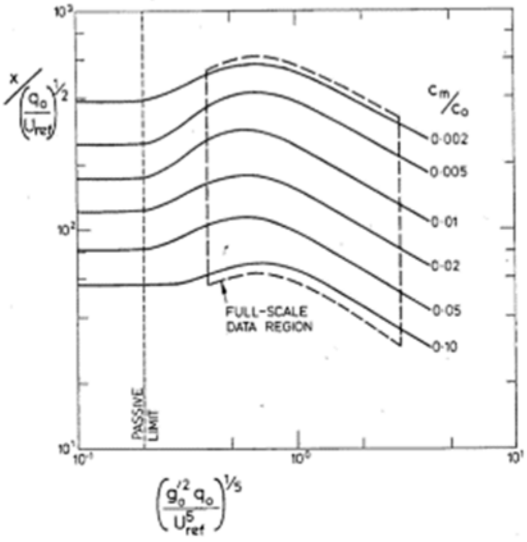


Figure 10.5. Britter-McQuaid dimensional correlation for dispersion of dense gas plumes [59].

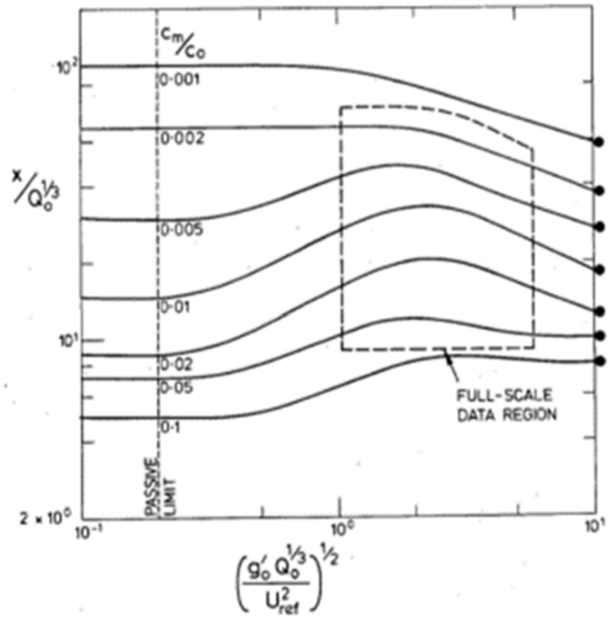


Figure 10.6. Britter-McQuaid dimensional correlation for dispersion of dense gas puffs [59].

The Britter and McQuaid model is reasonable easy to apply and results seen in good agreement with more sophisticated models. However, the model only provides an estimate of the maximum concentration at a fixed downwind distance and not any other locations.

As an example, estimate the downwind distance for the following liquified natural gas (LNG) release to the lower flammable limit of 5 volume %. Assume ambient conditions of 298 K and 1 atmosphere pressure.

Release rate: 97.8 kg/sec or 55.6 m^3/sec
Release duration: 174 sec
Release temperature: 111 K (atmospheric boiling point of LNG)
Windspeed at 10 m elevation: 10.9 m/sec
LNG vapor density at release conditions: 1.76 kg/m3
Air density at ambient conditions: 1.18 kg/m^3

The initial buoyancy parameter is:

$$g_0 = g\,(\rho_0 - \rho_a) / \rho_a = 9.8 \text{ m/sec}^2\,(1.76 - 1.18) / 1.18 = 4.82 \text{ m/sec}^2$$

For a continueous release, $u\,R_d / x > 2.5$. For a final distance less than 758 m, a continuous or plume model would be used.

The dense gas criteria for a continuous or plume release is:

$$[\, g_0^2\, q_0 / u^5 \,]^{1/6} > 0.15 \text{ or } [\,(4.82 \text{ m/sec}^2)^2\,(55.6 \text{ m}^3\text{/sec}) / (10.9 \text{ m/sec})^5\,]^{1/6} = 0.45 > 0.15$$

So a dense gas plume applies (Figure 10.5). Britter and McQuaid provide an adjustment to the concentration to account for non-isothermal release. If the original concentration is C*, the effective concentration is given by:

$$C = C^* / [\, C^* + (1-C^*)(T_a/T_0)$$

where T_a is ambient temperature and T_0 is the initial release temperature. The the required concentration of 0.05 volume fraction, the effective concentration is 0.019 volume fraction.

The dimensional correlating parameter for a dense gas plume is (Figure 10.7):

$$[\, g_0^2\, q_0 / u^5 \,]^{1/5} = [\,(4.82 \text{ m/sec}^2)^2\,(55.6 \text{ m}^3\text{/sec}) / (10.9 \text{ m/sec})^5\,]^{1/5} = 0.384$$

and $(q_0 / u)^{1/2} = (\, 55.6 \text{ m}^3\text{/sec} / 10.9 \text{ m/sec}\,)^{1/2} = 2.25$ m

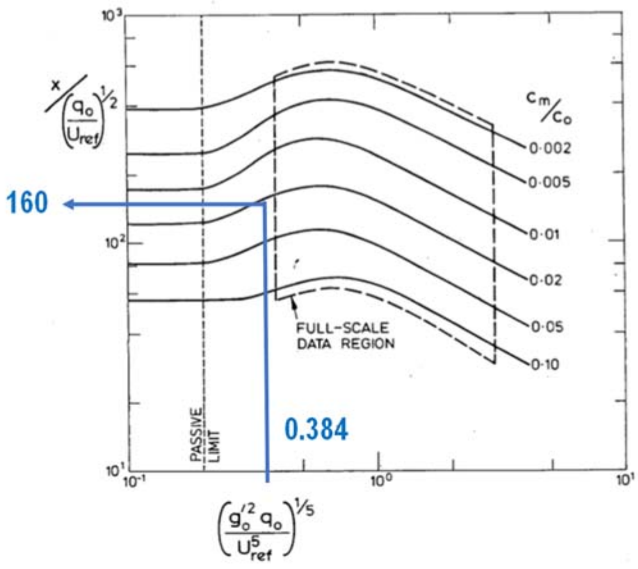


Figure 10.7 Example using Britter-McQuaid Dense Gas Plume Model

From Figure 10.7, C_m/C_0 ~ 160. The initial concentration is essentially “pure” LNG such that $C_0 = 1$ and X = 160 (2.25 m) or 360 m. This compares to an experimentally determined value of 200 m. This example illustrates that dispersion estimates may easily be off by a factor of 2.

Neutrally Buoyant Gaussian Models

Neutrally Buoyant models are based on a random mixing process driven by turbulence in the atmosphere [21, pp. 119-140] The concentration at a downwind location is approximated as a “normal” or Gaussian distribution in both the horizontal and vertical direction from the centerline of the release.

Neutrally buoyant Gaussian plume and puff models are commonly used to estimate average concentration and time profiles for flammable or toxic gas releases. The concentration estimates are time averages (typically 10-minute averages), local concentration may be greater than the average. This result is important where local concentration fluctuations have a significant impact of toxic or flammable consequences and averaging time corrections are applied. Pasquill and Gifford have recast the fundamental dispersion equations in terms of dispersion coefficients and developed correlations for these coefficients based on available data. The resulting model has become known as the Pasquill-Gifford model.

The plume model describes a continuous release of material. The solution depends on the rate of release, conditions of atmospheric stability, wind speed (typically assumed at a constant velocity in the x-direction), height of release and downwind distance as depicted in Figure 10.8.

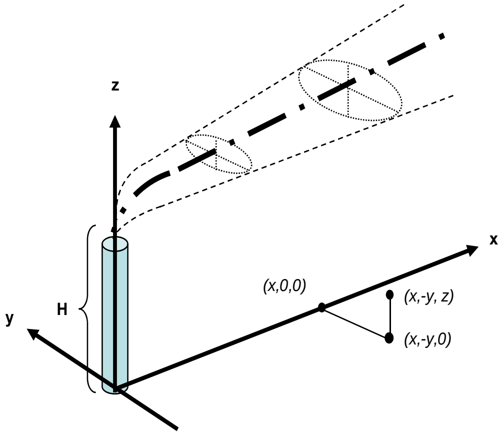


Figure 10.8 Neutrally Buoyant Model

The correlation for concentration using Equation 10-7:

$$\langle C\rangle(x,y,z)=\frac{G}{2\pi\sigma_y\sigma_z u}\exp\left[-\frac{1}{2}\left(\frac{y}{\sigma_y}\right)^2\right]\times\left\{\exp\left[-\frac{1}{2}\left(\frac{z-H}{\sigma_z}\right)^2\right]+\exp\left[-\frac{1}{2}\left(\frac{z+H}{\sigma_z}\right)^2\right]\right\}$$

Equation 10-7

where:

C is the average concentration (mass/volume)
G is the continuous release rate (mass/time)
σ_X, σ_Y, and σ_Z are the distribution coefficients in the x, y, and z directions (length)
u is the wind speed (length/time)
y is the cross-wind distance (length)
z is the distance above the ground (length)
H is the height of the release source above the ground plus any plume rise (length)

Of particular interest is the maximum or centerline concentration, C_m, at ground elevation. For this case, the cross-wind distance, y, is zero and the distance above the ground, x, is zero. The neutrally buoyant plume correlation becomes Equation 10-8:

$$\mathbf{C_m = [\ G\ /\ (\ \pi\ \sigma_Y\ \sigma_Z\ u\ )\ ]\ exp\ [\ -1/2\ (\ H\ /\ \sigma_Z\ )^2\ ]}$$

Equation 10-8

And for a ground elevation release, the plume correlation further reduces to Equation 10-9:

$$\mathbf{C_m = G\ /\ (\ \pi\ \sigma_Y\ \sigma_Z\ u\ )}$$

Equation 10-9

The puff model describes near instantaneous release of material. The solution depends on the total vapor released, , conditions of atmospheric stability, height of release and downwind distance. In the puff model, wind speed does not appear explicitly in the correlation. The center of the cloud is located at downwind distance x = u t where t is the time duration since the release has occurred. The overall puff or instantaneous correlation is shown in Equation 10-10:

$$\langle C\rangle(x,y,z,t)=\frac{G^*}{(2\pi)^{3/2}\sigma_x\sigma_y\sigma_z}\exp\left[-\frac{1}{2}\left(\frac{y}{\sigma_y}\right)^2\right]\times\left\{\exp\left[-\frac{1}{2}\left(\frac{z-H}{\sigma_z}\right)^2\right]+\exp\left[-\frac{1}{2}\left(\frac{z+H}{\sigma_z}\right)^2\right]\right\}$$

Equation 10-10

where:

C is the average concentration (mass/volume)
G* is the total vapor released (mass)
σ_X, σ_Y, and σ_Z are the distribution coefficients in the x, y, and z directions (length)
y is the cross-wind distance (length)

z is the distance above the ground (length)
H is the height of the release source above the ground plus any plume rise (length)

If the coordinate system is fixed at the release point, Equation 10-10 is multiplied by the factor for concentration at any downwind location in Equation 10-11:

$$\exp [-1/2 (x - u t / \sigma_X)^2] \quad \text{Equation 10-11}$$

Of particular interest is the maximum or centerline concentration, C_m, at ground elevation. For this case, the cross-wind distance, y, is zero and the distance above the ground, x, is zero and at the center of the cloud, x – ut is zero. The neutrally buoyant plume correlation becomes Equation 10-12:

$$C_m = [2 G^* / \{ (2 \pi \; \sigma_X \sigma_Y \sigma_Z \}] \exp [-1/2 (H / \sigma_Z)^2] \quad \text{Equation 10-12}$$

And for a ground elevation release, the plume correlation further reduces to Equation 10-13:

$$C_m = 2 G^* / \{ (2 \pi)^{3/2} \sigma_X \sigma_Y \sigma_Z \}. \quad \text{Equation 10-13}$$

Predictive formulas for distribution coefficients σ_X, σ_Y, and σ_Z are available in the literature from different sources. For the plume model, a simple power law relationship has been created from literature [21, pp. 121-123] information for the distribution coefficients shown in Table 10.1 and Table 10.2:

$\sigma_Y = a \; X^b$

and, $\sigma_Z = c' \; X^{d'}$

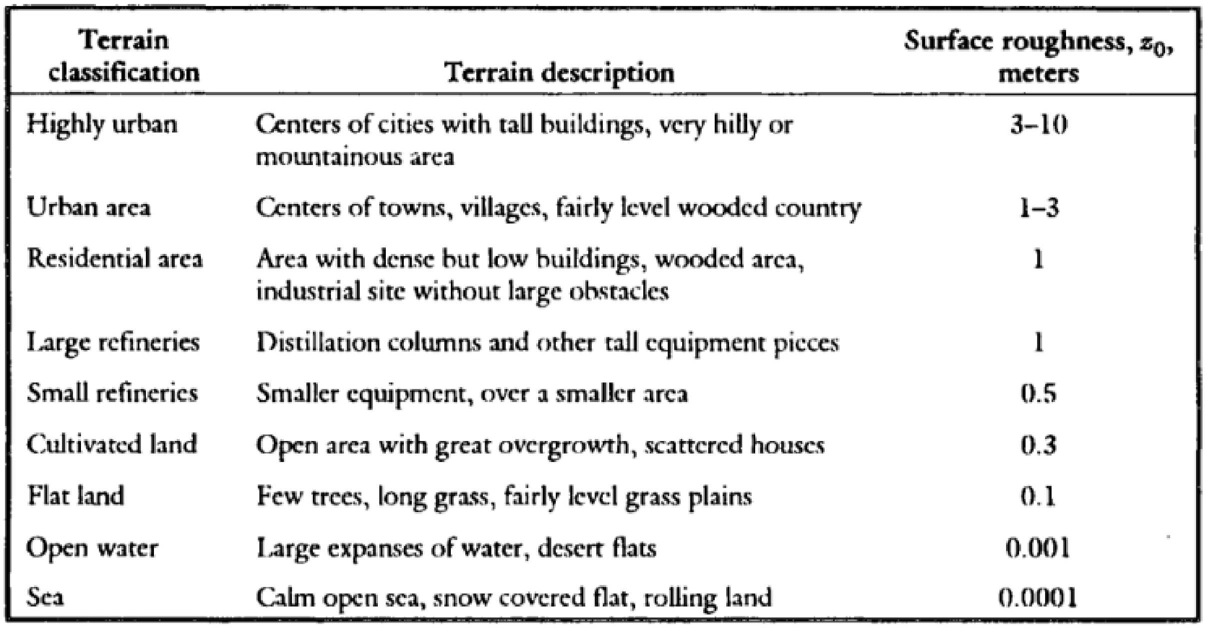
Stability Class	σ_Y		σ_Z	
	a	b	c	d
A	0.32	0.93	0.2	1
B	0.23	0.93	0.12	1
C	0.16	0.93	0.14	0.89
D	0.12	0.93	0.25	0.71
E	0.087	0.93	0.13	0.72
F	0.058	0.93	0.071	0.72

Table 10.1 Plume Distribution Parameters for Calculation of σ_Y and σ_Z at Rural Surface Roughness

Stability Class	σ_Y		σ_Z	
	a	b	c	d
A-B	0.76	0.83	0.069	1.25
C	0.52	0.83	0.2	1
D	0.38	0.83	0.71	0.65
E-F	0.26	0.83	0.33	0.71

Table 10.2 Plume Distribution Parameters for Calculation of σ_Y and σ_Z at Urban Surface Roughness

Surface roughness impacts the distribution coefficients and overall concentration at a downwind distance [21, p. 116] (Table 10.3).



Terrain classification	Terrain description	Surface roughness, z_0, meters
Highly urban	Centers of cities with tall buildings, very hilly or mountainous area	3–10
Urban area	Centers of towns, villages, fairly level wooded country	1–3
Residential area	Area with dense but low buildings, wooded area, industrial site without large obstacles	1
Large refineries	Distillation columns and other tall equipment pieces	1
Small refineries	Smaller equipment, over a smaller area	0.5
Cultivated land	Open area with great overgrowth, scattered houses	0.3
Flat land	Few trees, long grass, fairly level grass plains	0.1
Open water	Large expanses of water, desert flats	0.001
Sea	Calm open sea, snow covered flat, rolling land	0.0001

Table 10.3 Surface Roughness Descriptions at various Surface Roughness Length Parameter, z_0

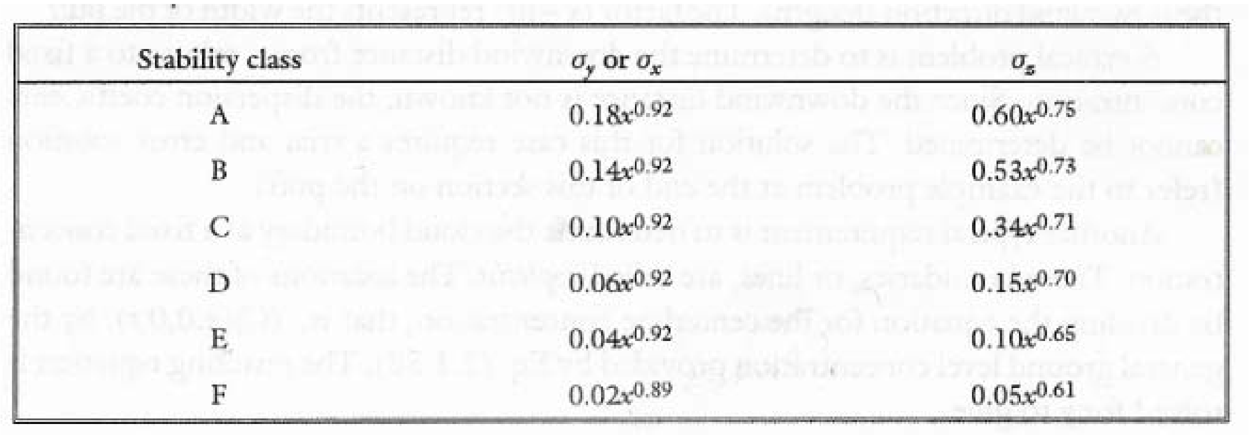
Of particular interest is Residential or Industrial Surface Roughness (z_0 ~ 0.5 to 1.0) as this likely represents surface conditions within plant site or surrounding populated areas. Values have interpolated to represent Residential or Industrial Surface Roughness in Table 10.4.

Stability Class	σ_Y		σ_Z	
	a	b	c	d
A-B	0.56	0.85	0.068	1.22
C	0.39	0.85	0.17	0.98
D	0.28	0.85	0.41	0.73
E-F	0.19	0.85	0.24	0.71

Table 10.4 Plume Distribution Parameters for Calculation of σ_Y and σ_Z at Residential Surface Roughness

As an approximate correction for surface roughness to Rural conditions, the ratio of σ_Z to the correlation at $z_0 = 0.1$ may be utilized. The correction from Rural to Residential or Industrial surface conditions are estimated as the ratio of parameters from these tables σ_Y at desired surface roughness to σ_Y at rural conditions.

Distribution coefficients for Neutrally Buoyant Puff models may also be correlated by a simple power law [21, p. 123] (Table 10.5).



Stability class	σ_y or σ_x	σ_z
A	$0.18x^{0.92}$	$0.60x^{0.75}$
B	$0.14x^{0.92}$	$0.53x^{0.73}$
C	$0.10x^{0.92}$	$0.34x^{0.71}$
D	$0.06x^{0.92}$	$0.15x^{0.70}$
E	$0.04x^{0.92}$	$0.10x^{0.65}$
F	$0.02x^{0.89}$	$0.05x^{0.61}$

Table 10.5 Neutrally Buoyant Puff Distribution Parameters for Calculation of σ_X, σ_Y, and σ_Z

Incorporating these distribution coefficients into the Neutrally Buoyant plume correlation for maximum ground level concentration for a ground elevation release yields for Class D atmospheric stability and Residential or Industrial surface roughness ($z_0 = 1.0$) yields Equation 10-14:

$$\sigma_Y = a\ X^b = 0.128\ X^{0.905} \text{ and } \sigma_Z = c'\ X^{d'} = 0.395\ X^{0.701}$$

$$\mathbf{C_m = G / (\pi\ \sigma_Y\ \sigma_Z\ u) = 6.3\ G / (u\ X^{1.61})\ \ kg/m^3 = 1.54 \times 10^8\ G / (Mw\ u\ X^{1.61})\ ppm\ by\ volume}$$

Equation 10-14

Assuming an ideal gas at atmospheric pressure and temperature approaching ambient at the downwind location, concentration may be multiplied by $24.45 \times 10^6 / Mw$ to convert from kg/m^3 to ppm by volume.

Incorporating these distribution coefficients into the Neutrally Buoyant puff correlation for maximum ground level concentration for a ground elevation release yields for Class D atmospheric stability and Residential or Industrial surface roughness ($z_0 = 1.0$, note that coefficients for the puff model are only reported for Rural surface conditions) yields Equation 10-15:

$$\sigma_X = \sigma_Y = 0.06\ X^{0.92}$$
$$\text{and } \sigma_Z = 0.15\ X^{0.7} \text{ times surface roughness correction } 1.98\ X^{-0.059} = 0.297\ X^{0.641}$$

$$\mathbf{C_m = 2\ G^* / \{ (2\ \pi)^{3/2}\ \sigma_X\ \sigma_Y\ \sigma_Z \}.= 119\ G^* / X^{2.48}\ \ kg/m^3 = 2.91 \times 10^9\ G / (Mw\ X^{2.48})\ ppm\ by\ volume}$$

Equation 10-15

Neutrally Buoyant Vapor Dispersion Model Example

Estimate the maximum concentration at a downwind distance of 500 m for a continuous ground elevation release of 1 kg/sec Mw=30 material under Class D atmospheric stability at 25 C (298 K) with wind of 3 m/sec. Assume a very low release velocity such that the initial dilution is zero and an averaging time of 10 minute applies.

$$C_m = 1.54 \times 10^8\, Q / [\, Mw\ \ X^{1.61}\,] = 1.54 \times 10^8\, (\, 1\ kg/sec\,) / [\, 30\, (\, 3\ m/sec\,)\, (500\ m)^{1.61}\,]$$

$$= 77 \text{ ppm by volume}$$

Combined Dense Gas and Neutrally Buoyant Vapor Dispersion

The transition from dense gas to neutrally buoyant dispersion is discussed in Crowl and Louvar [16, pp. 219-225]. For a dense gas plume (Figure 10.5), the criteria for the Britter and McQuaid dense gas model was noted earlier in the section as $[\, g_0^2\, q_0 / u^5\,]^{1/6} > 0.15$. To locate the transition point, x_t for a continuous release, the density downwind of the release is:

$$\rho_x = \rho_0\, (C_x / C_0) + \rho_0\, (1 - C_x / C_0)$$

A simple material balance between concentration and flow based on the original volume being diluted with entrain air is:

$$q_x\, C_x = q_0\, C_0$$

The dense to neutrally buoyant transition is determined in Equation 10-16:

$$(C_t / C_0)^{1/6}\, [\, g_0^2\, q_0 / u^5\,]^{1/6} = 0.15$$

and,

$$\mathbf{C_t = C_0\, 0.15^6 / [\, g_0^2\, q_0 / u^5\,]} \qquad \text{Equation 10-16}$$

Similarly, for a dense gas puff (Figure 10.6), the criteria for a sufficiently dense cloud to require a dense cloud representation for an instantaneous or “puff” release is $[\, g_0\, V_0^{1/3} / u^2\,]^{1/2} > 0.20$. The dense to neutrally buoyant transition is determined in Equation 10-17:

$$(C_x / C_0)^{1/3}\, [\, g_0\, V_0^{1/3} / u^2\,]^{1/2} = 0.20$$

and,

$$\mathbf{C_x = C_0\, 0.20^3 / [\, g_0\, V_0^{1/3} / u^2\,]^{3/2}} \qquad \text{Equation 10-17}$$

At a concentration less than the transition concentration or distance greater than that estimated for the dense gas puff model at the transition concentration, the vapor dispersion is considered neutrally buoyant and the Pasquill-Gifford puff model is used with a “virtual distance” correction. The virtual distance is the downwind distance estimated from the neutrally buoyant model at the dense gas transition concentration. The distance used to estimate concentration in the neutrally buoyant region is represented by Equation 10-18:

$$\mathbf{x_b = x - x_t + x_v} \qquad \text{Equation 10-18}$$

where: x is the downwind distance of interest
x_t is the dense gas model distance where transition to neutrally buoyant dispersion occurs
x_v is a virtual distance estimated from the neutrally buoyant model at the transition concentration
x_{nb} is the corrected distance for estimating concentration beyond the transition to neutrally buoyant

Transition from Dense Gas to Neutrally Buoyant Vapor Dispersion Model Example

Estimate the maximum concentration at 200 m downwind distance for a continuous ground elevation release of 0.1 kg/sec chlorine under Class D atmospheric stability at 25 C (298 K), Residential surface roughness, with wind of 3 m/sec. Assume a very low release velocity such that the initial dilution is zero ($C_0 = 1$) and an averaging time of 10 minute applies. Use a vapor density of 2.89 kg/m^3 for chlorine.

Initial buoyancy is: $g_0 = g\ (\rho_0 - \rho_a) / \rho_a = 9.8\ (\ 2.89 - 1.18\ )\ /\ 1.18 = 14.2$ m/sec^2

Initial voluimetric release rate is: $q_0 = Q^* / \rho_0 = 0.1$ kg/sec / 2.89 kg/m^3 = 0.035 m^3/sec

$[\ g_0^2\ q_0 / u^5\ ]^{1/6} = [\ (14.2 \text{ m/sec}^2)^2\ 0.035 \text{ m}^3\text{/sec} / (3 \text{ m/sec})^5\ ]^{1/6} = 0.55 > 0.15$, dense gas applies

The transition concentration is:

$C_t = C_0\ 0.15^6 / [\ g_0^2\ q_0 / u^5\ ] = (1.0)\ 0.15^6 / [\ (14.2 \text{ m/sec}^2)^2\ 0.035 \text{ m}^3\text{/sec} / (3 \text{ m/sec})^5\ ]$

= 0.00039 vol fraction or 390 ppm by volume.

The dimensionless dense gas correlating parameter is (Figure 10.9):

$[\ g_0^2\ q_0 / u^5\ ]^{1/5} = [\ (14.2 \text{ m/sec}^2)^2\ 0.035 \text{ m}^3\text{/sec} / (3 \text{ m/sec})^5\ ]^{1/5} = 0.49$

The distance dense gas correlating parameter for plumes is:

$(\ q_0 / u\ )^{1/2} = (\ 0.035 \text{ m}^3\text{/sec} / 3 \text{ m/sec}\ )^{1/2} = 0.108$

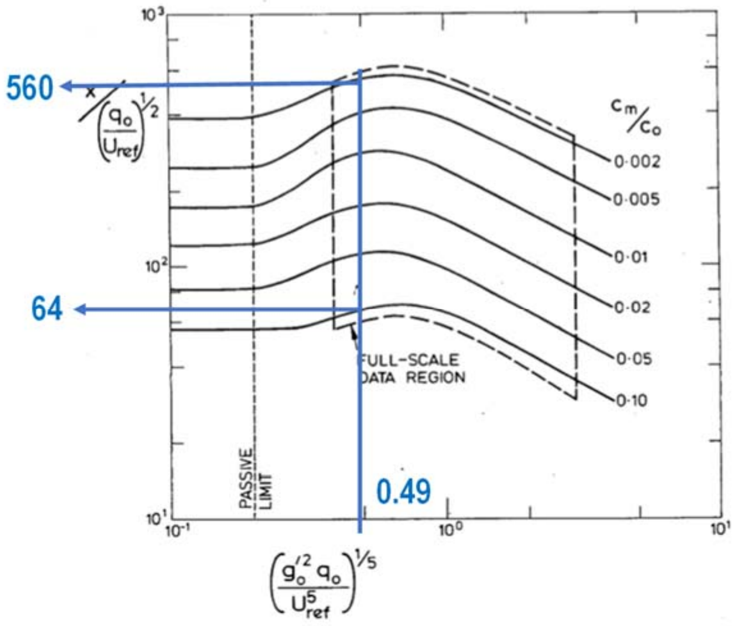


Figure 10.9 Example using Britter-McQuaid for the Transition Between Gas Phase Models

From the Britter and McQuaid graphical correlation for dense gas plumes at Rural surface roughness, the estimated distance to a dimensionless concentration $C_m/C_0=0.1$ is 64 (0.108) = 6.9 m and the estimated distance to a dimensionless concentration $C_m/C_0=0.002$ is 560 (0.108) = 60.5 m. Extrapolation to a concentration C_m/C_0 corresponding to the transition of 0.00039 volume fraction may be estimated as a simple power law relationship, $C_m/C_0 = a\ X^b$.

$b = \ln(0.002 / 0.1) / \ln(60.5 / 6.9) = -1.80$ and $a = 0.1 / 6.9^{-1.80} = 3.24$

or $\quad C_m / C_0 = 3.24\ X^{-1.80}$

Correcting this correlation for Residential or Industrial surface roughness yields:

$C_m = C_0\ 3.24\ X^{-1.80} / 1.98\ X^{-0.059} = 1.64\ X^{-1.741}$

The dense gas model distance to the transition concentration is approximately:

$(0.00039 \text{ volume fraction} / 1.64)^{(-1 / 1.741)} = 120.6 \text{ m}$

The transition from dense to neutrally buoyant dispersion occurs at 120.6 m which is less than the 200 m distance. Therefore, concentration at the distance of interest is in the neutrally buoyant region.

The correlation for the Pasquill-Gifford neutrally bouyant model for Class D weather and Residential surface roughness is $C_m = 154 \, G / (M_w \, u \, X^{1.61})$ for C_m in volume fraction.

or $C_m = 154 \; (0.1 \text{ kg/sec}) / [70.9 (3 \text{ m/sec}) X^{1.61}] = 0.0724 \, X^{-1.61}$

The virtual distance or neutrally buoyant model distance to the transition concentration is:

$(0.00039 \text{ volume fraction} / 0.0724)^{(-1 / 1.61)} = 25.7 \text{ m}$

The estimated concentration at 200 m will utilize the neutrally buoyant correlation at a equivalent distance of:

$x_b = x – x_t + x_v = 200 – 120.6 + 25.7 = 105.1 \text{ m}$

$C_m = 0.0724 \, (105.1 \text{ m})^{-1.61} = 105.1 \text{ m} = 0.0000403$ volume fraction or 40.3 ppm by volume

Note that this estimated concentration at 200 m downwind distance is significantly less than predicted by only the dense gas model (162 ppmv) and significantly more than predicted by only the neutrally buoyant model (14.3 ppmv).

Concentration may be estimated at various distances using a combined Britter and McQuaid dense gas and Pasquill-Gifford neutrally buoyant models to obtain a “power law” fit representing a broad range of concentration versus distance (Figure 10.10).

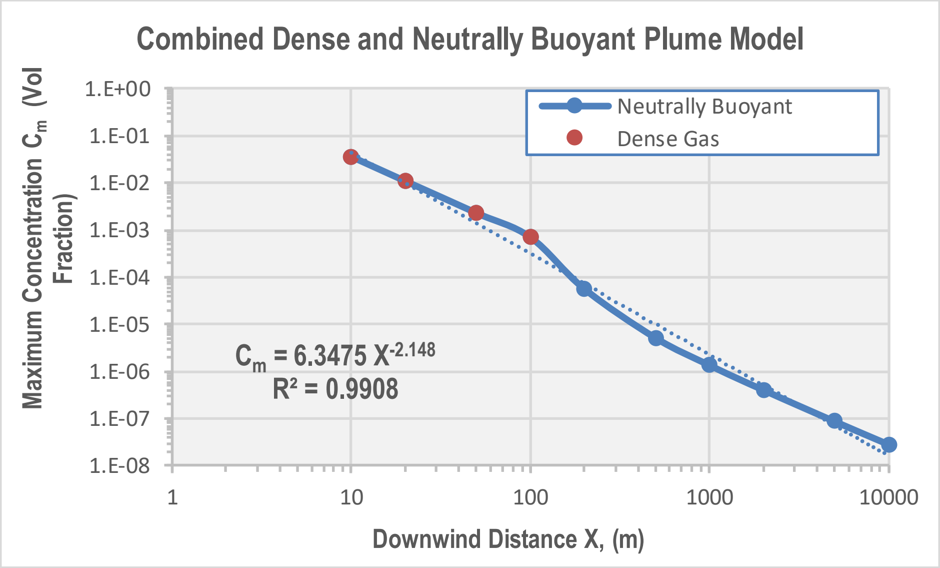


Figure 10.10 Concentration versus Distance for 0.1 kg/sec ground elevation chlorine release for 3 m/sec wind, Class D atmospheric stability and Residential surface roughness.

Distance Correction for Initial Dilution

The vapor dispersion correlations noted in this section are applicable to an ideal point source from which the vapor is released. At the source, the simple point-source models have concentration values of infinity and will overpredict concentration in the near field. These simple dispersion model may also require a “virtual” distance correction to improve accuracy *for downwind distance much less than 100 m*. For many situations, this correction is small and can be ignored.

For correlations of the form Concentration = a X^b, the correction, x_0, is estimated as the upwind virtual distance that matches the initial concentration, C_0, Equation 10-19.

$$x_0 = (C_0 / a)^{1/b} \qquad \text{Equation 10-19}$$

The correction, x_0, is added to the actual distance when evaluating concentration relatively close to the release location.

As an example, in the previous example, concentration versus distance for a 0.1 kg/sec ground elevation chlorine release at 3 m/sec wind with Class D atmospheric stability and Residential surface roughness is $C_m = 6.35\ X^{-2.148}$ volume fraction. The concentration at the release location (X=0) is infinity. If chlorine is released as a pure vapor, the initial concentration C_0 = 1 volume fraction. The distance correction becomes:

$$x_0 = (C_0 / a)^{1/b} = (1.0 / 6.35)^{-1/2.148} = 2.4 \text{ m}$$

Averaging Time Correction Factor

Concentration at a specified distance fluctuate over time. For plume models, an averaging time of 10 minutes is common. For situations where maximum concentration is needed over a much shorter time interval (such as when evaluating the maximum concentration for a flammable release), a correction is needed. The correction factor for concentration assuming a very short averaging time to a 10-minute average is approximately 2 [21, p. 140].

Evaluation of Short Duration Release

For a short duration release, one needs to determine if a Continuous or Instantaneous dispersion model should be used. For the Britter and McQuaid dense gas model, it is suggested that if the dimensionless group $u\ t_d / X_{Ref} > 2.5$, the continuous model is appropriate and that if $u\ t_d / X_{Ref} < 0.6$, an instantaneous puff model is appropriate. The vapor rate, Q, where transition occurs may be estimated by equating the continuous and instantaneous models for the same concentration at the distance of interest.

If a continuous plume dispersion is correlated by $C_m = a\ Q / u\ (X_{Ref}^b)$ and an instantaneous puff is correlated by $C_m = a'\ Q^*\ X_{Ref}^{b'}$, then the release rate where a transition from plume to puff occurs can be estimated using Equation 10-20:

$$Q > (a' / a)\ Q^*\ u\ X_{Ref}^{b'-b} \qquad \text{Equation 10-20}$$

where:

t_D is vapor release duration or exposure duration (sec)

Q = airborne rate (kg/sec)

Q* = total airborne quantity (kg)

u = wind speed (m/sec)

X_{Ref} = reference downwind distance (m)

For Equipment Rupture, the Airborne Rate is extremely large and use of an Instantaneous Model may be appropriate.

Estimation of Toxic Exposure Duration

Often exposure duration less than one hour will be used in estimating toxic dose or time-scaled ERPG values. The exposure duration, t_D, for a continuous vapor release can be estimated from the total airborne quantity, Q*, divided by the vapor rate, Q, using Equation 10-21:

$$t_D = Q^* / Q \qquad \text{Equation 10-21}$$

For a liquid release, one might conservatively estimate dose based on the total vapor quantity divided by the maximum vapor rate. This will result in the maximum concentration at any distance (from the maximum vapor rate) in combination with a minimum exposure duration yielding a conservative estimate of dose if n is 1 or greater for the relationship toxic Dose = $C^n t_D$.

For instantaneous release, the dose relationship is much more complex and based on the width of the cloud in the downwind or x direction and time for the cloud to pass by For a specified concentration of interested (such as ERPG-3), the maximum cloud width is found at a distance of approximately ½ the distance to the concentration of interest.

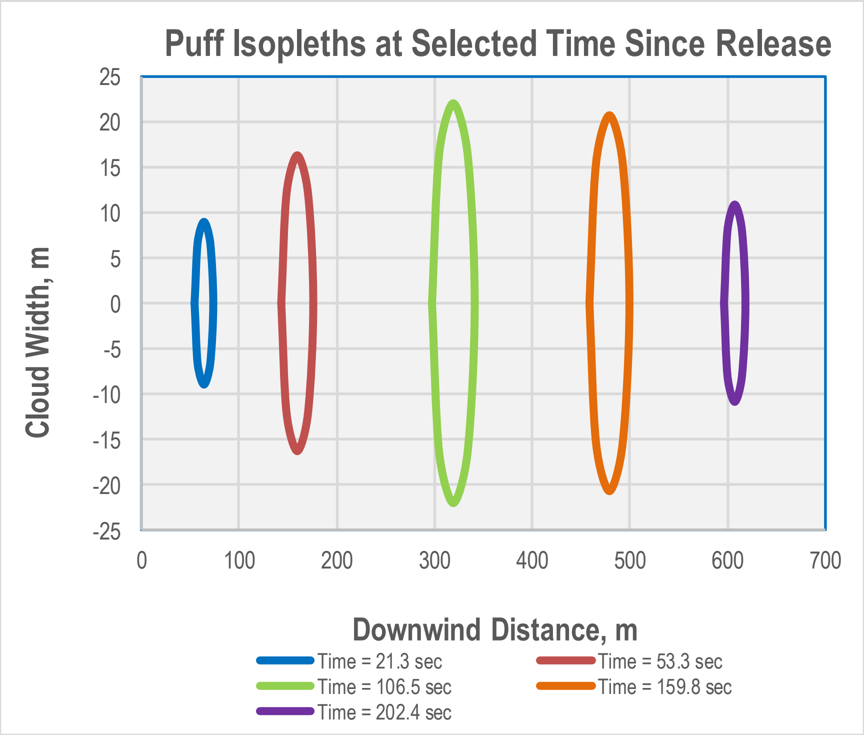


Figure 10.11 - Estimated 'Puff" Cloud of 100 ppm concentration isopheth at various time after release for 10 kg molecular weight 30 material at 3 m/sec wind speed, and Class D atmospheric stability.

The cloud width at this point is estimated using Equation 10-22 and Equation 10-23:

Cloud width in x direction = $\boldsymbol{\sigma_X (-2 \ln(C_i / C_{m\ at\ X_i}))^{0.5}}$ Equation 10-22

and **$\boldsymbol{t_D}$ = 2 max width / u** Equation 10-23

where:

t_D = estimated exposure duration (sec)
u = wind speed (m/sec)
Ci = isopleth concentration of interest
Xi = distance to concentration of interest

As an example, consider the 10 kg instantaneous release of molecular weight 30 material at 3 m/sec wind speed, Residential surface roughness and Class D atmospheric stability shown in Figure 10.11. If the overall concentration with distance is correlated as $C_m = 9.7 \times 10^8 X^{-2.48}$, then:

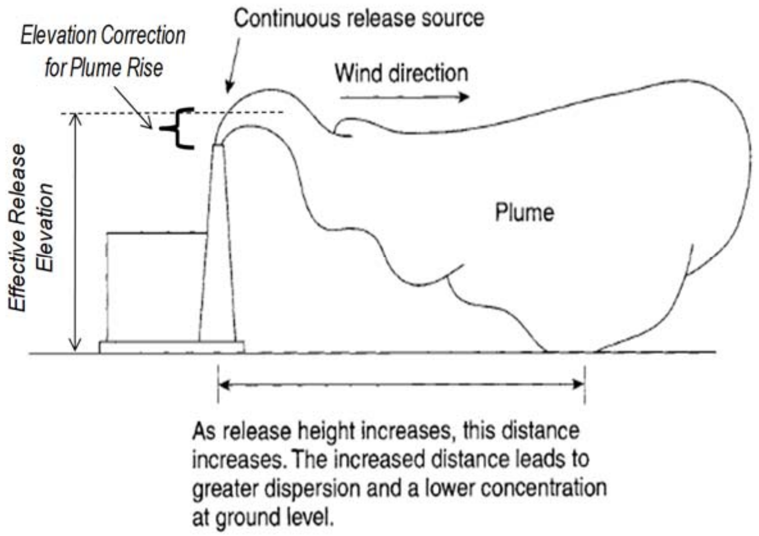
½ Distance to concentration of interest (100 ppm) = $0.5 (100 \text{ ppm} / 9.7 \times 10^8)^{(-1/2.48)}$ = 328 m

Maximum (or centerline) concentration at 328 m, $C_m = 9.7 \times 10^8 (328 \text{ m})^{-2.48}$ = 559 ppm

σ_X is downwind distance = $0.06 X^{0.92}$ = 12.4 m
Cloud width in x-direction = $\sigma_X (-2 \ln(C_i / C_{m\ at\ X_i}))^{0.5} = 12.4 (-2 \ln(100/559))^{0.5}$ = 23 m
Exposure duration (or time for cloud to pass by) = 2 (23 m) / 3 m/sec = 15.3 sec

Correction for Elevation in Simple Vapor Dispersion Model

The release height significantly affects ground-level concentrations (Figure 10.12).



As release height increases, this distance increases. The increased distance leads to greater dispersion and a lower concentration at ground level.

Figure 10.12 Elevated Vapor Release

Correction for release elevation due to vapor momentum and density may be approximated using the Holland plume rise correlation shown in Equation 10-24 [16] [60]:

$$\mathbf{H = H' + 1.5\ (v_0 / u)\ d_0\ [\sin \Theta + 1.8\ d_0\ (1 - \rho_0 / \rho_{air})]} \qquad \text{Equation 10-24}$$

where:

$\sin\Theta$ is 1 for a vertically upward release and 0 for a horizontal release
H' is the release elevation (or stack height)
v_0 = gas exit velocity
u = wind speed
d_0 = discharge pipe diameter (m)
ρ_0 = exit gas density
ρ_{air} = density of ambient air

For Class D weather, "industrial" surface roughness, and a Gaussian distribution; the ratio of concentration at a vertical distance from the center of the cloud to the ground is estimated by Equation 10-25:

$$\mathbf{C / C_m = \exp[-0.5\ (H / \sigma_Z)^2] = \exp[-0.5\ (H / \{\ 0.41\ (X + \Delta X_0)^{0.73} \})^2]} \qquad \text{Equation 10-25}$$

where:

H = effective release elevation minus reference or receptor elevation (m)
X = downwind distance (m)

Example Correction for Elevation

Estimate the ground level concentration at 100 m downwind for a continuous plume with wind of 3 m/sec, Class D atmospheric stability and 10 meter effective elevation. Assume a maximum concentration at the is zero.

H = 10 – 1.2 = 8.8 meter using 4 ft or 1.2 m for "ground"

$C = C_m \exp[-0.5\ (8.8\text{ m} / \{ 0.395\ X^{0.701} \})^2] = 500\text{ ppm} \exp[-0.390] = 339\text{ ppm}$

Note that the reference elevation for "ground" level is typically assumed as 1.2 m (or 4 ft).

Estimation of Maximum Ground Level Concentration

For a ground elevation release, the maximum ground level concentration is the concentration at the release location. For an elevated plume release, the location of the maximum concentration is found using Equation 10-26:

$$\mathbf{\sigma_Z = H / 2^{1/2}} \qquad \text{Equation 10-26}$$

And the maximum ground elevation concentration is determined using Equation 10-27:

$$\mathbf{C_{max} \sim\ 2\ G\ (}\ \sigma_Z / \sigma_Y\ )\ 2.45 \times 10^7 / (\ e\ \pi\ Mw\ u\ H^2\ ) \qquad \text{Equation 10-27}$$

where:

AQ = airborne quantity (kg/sec)
ΔH = effective release elevation minus reference elevation (m)
Mw = molecular weight of released vapor
C_{max} = max ground level concentration (ppm)

For release from an elevated location, the maximum ground concentration (neutrally buoyant, Residential surface roughness and Class D atmospheric stability) may be estimated using Equation 10-28 [21, p. 125]:

$$C_{max} \sim 1.5 \times 10^{7} / (Mw\ u\ H^{2.29}) \quad \text{at a downwind distance of } 2.26\ H^{1.43}\ \text{m} \qquad \text{Equation 10-28}$$

Relief Device Effluent Screening

Overpressure scenarios represent a significant portion of potential releases in a typical facility risk analysis. These will often represent the design scenarios for pressure relief devices. Common scenarios include:

- Heat from fire exposure
- Closed outlet with heat source on – external heat input (vaporization)
- Thermal expansion of liquid – may be an issue if gasket or piping/equipment failure is not discovered before next use of piping or equipment.
- Loss of cooling
- Over pumping of liquid (overfill and back flow)
- Control valve / pressure regulator failure
- Heat exchanger tube failure (for heat exchangers)
- User provided Relief Rate (Relief Duty needed by customer)
- Pumping liquid in plus thermal breathing-API (vapor from liquid displacement)
- Pumping liquid out plus thermal breathing-API (potential vacuum condition)
- Runaway Reaction

A hazard screening and analysis process determines when pressure relief devices can be safely vented to the atmosphere and under what conditions (proximity, direction, etc.). Cases that fail the screening hazard assessment must be designed to minimize risk using the results of a Layers of Protection Analysis (LOPA) and / or vapor cloud dispersion model. *If dispersion modeling shows the pressure relief device can not be safely vented to the atmosphere, or LOPA shows that the risk is too high for atmospheric venting, then the effluent should be routed to a treatment system. High Integrity Protection Systems (HIPS)* can also be used to eliminate relief scenarios that have unacceptable effluent consequences.

Simplified Relief Effluent Screening Process

The Relief Effluent Screening involves several key steps (Figure 10.13):

- Is the released material considered hazardous?
- Is the release all vapor? (Liquid and Two-Phase release requires a more detailed analysis and is excluded from this screening at this time.)
- 1st Pass Screening using simple modeling methods to determine if routed to a safe location
- 2nd Pass Screening using advanced modeling – or – performing a simplified Risk Analysis (using Layers of Protection Analysis) based on venting to atmosphere

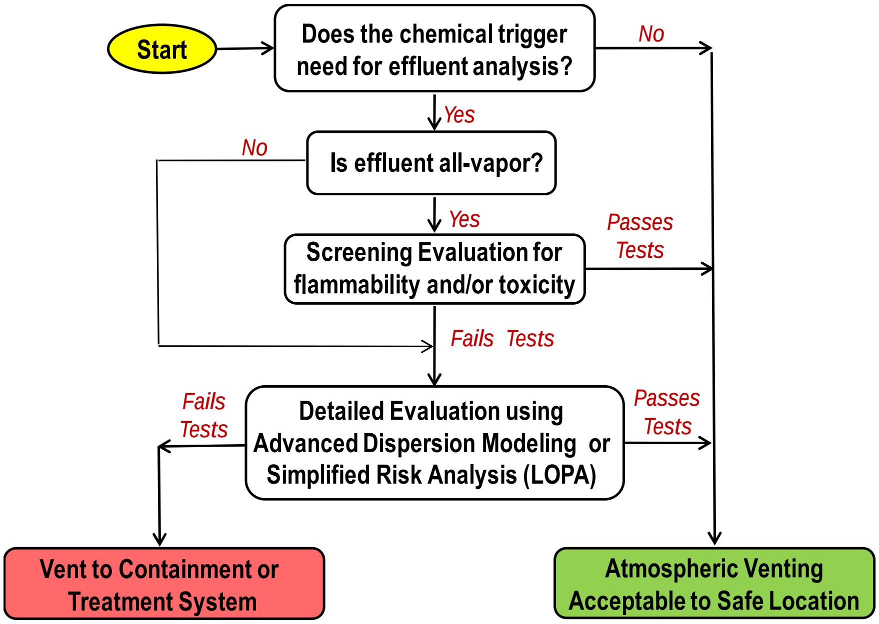


Figure 10.13 Example Relief Effluent Screening Flowchart

Relief Effluent Screening Criteria

Relief Effluent Screening addresses if onsite personnel could be exposed to flammable or toxic cloud or if the cloud potentially exceeds the distance to plant's property limit (Figure 10.14).

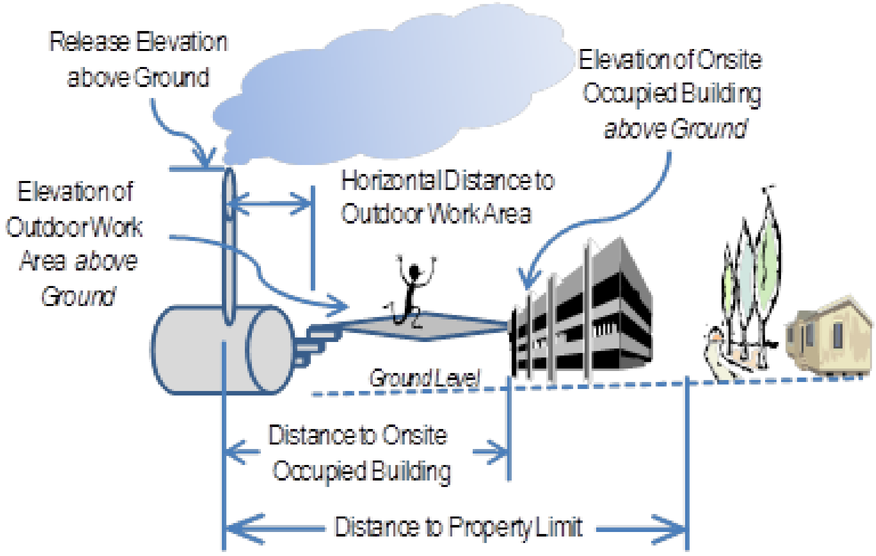


Figure 10.14 Depiction of Relief Device Effluent

Here are some example screening criteria:

- Offsite concentration less than ERPG-2 (at ≤ 4 ft elevation)
- Onsite concentration less then ½ the Lower Flammable Limit at distance and elevation of nearest unrestricted work area
- Onsite concentration less then time-scaled ERPG-3 at distance and elevation of nearest unrestricted work area
- Onsite concentration less than ERPG-3 (scaled to 1 hour) at the distance and elevation of the nearest occupied building is noted in the screening

Relief Effluent Screening Tool and Additional Information

A Relief Effluent Screening Tool has been developed for vapor releases which uses a simple dispersion method and addresses time varying release rates as discussed in the Toxicity training section. The tool, available in RAST, also:

- Adresses chemical mixtures
- Accounts for release elevation and direction of discharge
- Accounts for release *duration* in estimation of equivalent toxic dose
- Provides information as input for detailed modeling if additional screening is needed.

Releases Impacting Personnel Located Indoors

There are two special cases where indoor personnel may be impacted from a hazardous release – those within an enclosed process area and those in a nearby occupied building. Each of these cases depends on ventilation rate. For those within an enclosed area, high ventilation rate will more quickly exhaust hazardous material and draw in fresh air. For those in a nearby occupied building, high ventilation will initially draw hazardous material into the building more quickly.

Releases within an Enclosed Process Area

The overall *average* concentration within an enclosed process area depends on the airborne leak rate (AQ) building volume (V_B) and ventilation rate (VR) and in indoor concentration can be estimated using Equation 10-29.

$$\mathbf{C_{Indoor} = 8.8 \times 10^{10} \; (AQ / Mw) / (VR \; V_B + 88020 \; AQ / Mw)} \qquad \text{Equation 10-29}$$

The average indoor concentration is limited to the total airborne release divided by the building volume for short duration releases, as shown in Equation 10-30:

$$\mathbf{C_{Limit} = 2.45 \times 10^{7} \; (Total \; AQ) / (V_B \; Mw) \; in \; ppm} \qquad \text{Equation 10-30}$$

where:

AQ = airborne quantity (kg/sec)
C = concentration (ppm by volume)
Mw = molecular weight
Total AQ_T = total release quantity (kg)
V_B = building volume (m^3)
VR = ventilation rate (air changes/hour)

A typcial ventilation rate of 1 air change per hour is often used to estimate average concentration of an enclosed process area. Concentration within the building will be significantly higher near the leak source than the overall average.

Toxic Infiltration from an Outdoor Release

Air will typically enter occupied buildings through open windows and doors, unsealed wall penetrations, and through the ventilation system. For screening analysis, the concentration indoors is typically assumed at ½ the concentration outside the building (Figure 10.15). If greater precision is needed, the indoor concentration may be estimated as a fraction of outdoor concentration at a specified ventilation rate, VR, in air changes per time, at time, t, using Equation 10-31:

$$C_{Indoor}/C_{Outdoor} = 1 - e^{-VR\,t} \qquad \text{Equation 10-31}$$

Equation 10-31 is based on good mixing of air inside the building. At a typical 3 air changes per hour, the indoor concentration reaches 50% of the outdoor concentration within 15 minutes. For a release duration less than 1 hour, concentration will fall off once the release has stopped as fresh air is drawn into the building.

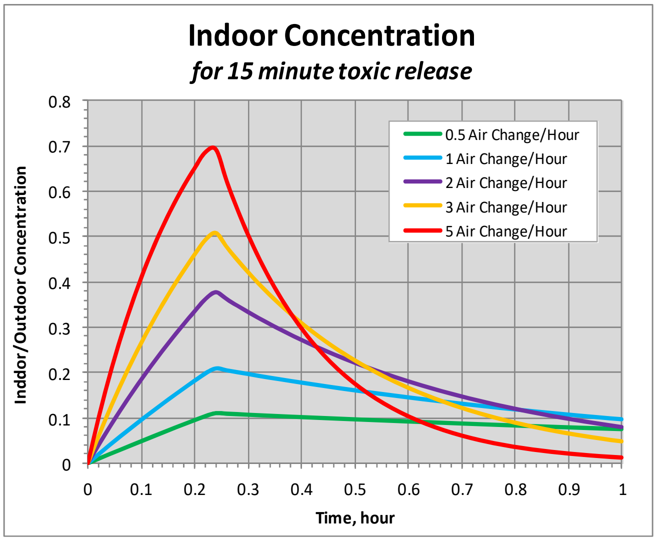


Figure 10.15 Ratio of Indoor to Outdoor Concentration vs Time

For very short duration releases within the typical range of ventilation rate, a practical upper limit for indoor concentration is $C_{Indoor}/C_{Outdoor} = 2\,t'$ where t' is the release duration in hours.

Typical Ventilation Rates

The ventilation rate for occupied buildings is typically (per industry resources) designed for 2 air changes per hour for office areas, 6 for kitchens and restrooms, and higher for laboratories or process areas with possible toxic gas leaks. These or other design rates may be required by local permitting agencies.

Ventilation rate also depends on construction type, outdoor wind speed and degree of mechanical ventilation. A practical upper limit for enclosed process areas without mechanical ventilation is 2 air changes per hour with a range of 0.1 to 2 depending on outdoor wind speed. For screening analysis, a typical value of 1 air change per hour for an enclosed process area may be appropriate if the actual ventilation rate is not known. Typical ventilation rate for residential in estimation of offsite toxic impacts is shown in Table 10.6.

Typical Ventilation Rate for Houses in an Urban Area

Construction Level	Air Exchanges per Hour
Tight	0.25
Average	0.50
Leaky	1.0
Very Leaky	2.0

Table 10.6 Typical Ventillation Rate for Houses

11. EXPLOSIONS

An explosion results from the rapid release of energy, often expansion of gases resulting in a rapidly moving pressure or shock wave. The damage depends on whether the propagation rate (detonation or deflagration) and level of confinement or congestion.

Section Objectives

The following objectives are covered in this section:

- Types of explosion – vapor cloud explosion, building or equipment explosion, and physical explosion.
- Key parameters for Estimation of Explosion Energy including typical Heat of Combustion per cloud volume, Fuel Reactivity, and Level of Equipment Congestion.
- Estimation of blast overpressure versus distance for Physical Explosion using a simple TNT model.
- Estimation of blast overpressure versus distance for a Building Explosion using a simple Baker-Strehlow-Tang model.
- Estimation of blast overpressure versus distance for a Vapor Cloud Explosion using a simple Baker-Strehlow-Tang model.
- Limitations of simple blast models.

Explosion Definitions

Common terms associated with explosion are:

Detonation – A release of energy caused by the propagation of a chemical reaction in which the reaction front advances into the unreacted substance at greater than sonic velocity in the unreacted material.

Deflagration - A combustion that propagates by heat and mass transfer through the un-reacted medium at a velocity less than the speed of sound.

Boiling-Liquid Expanding-Vapor Explosion (BLEVE) – A type of rapid phase transition in which a liquid contained above its atmospheric boiling point is rapidly depressurized, causing a nearly instantaneous transition from liquid to vapor with a corresponding energy release. A BLEVE of flammable material is often accompanied by a large aerosol fireball, since an external fire impinging on the vapor space of a pressure vessel is a common cause. However, it is not necessary for the liquid to be flammable to have a BLEVE occur.

Dust Explosion – an explosion resulting from rapid combustion of fine solid particles.

Potential Explosion Site (PES) - A volume within a plant with sufficient congestion and/or confinement that a flammable vapor cloud ignited there could likely develop into an explosion.

Damage and Blast Overpressure

The maximum pressure resulting from blast or shock wave is the Peak Overpressure which is correlated to damage. Some typical examples of the damage associated with this overpressure is shown in Table 12.1.

Overpressure *(PSI)*	**Damage per NFPA-921**
0.3	**"Safe distance" (95% probability of no serious damage)**
0.5	**Shattering of glass windows**
1	**Partial demolition of houses**
2	**Partial collapse of walls and roofs of houses**
5	**Wooden utility poles snapped/Flying glass serious injury**
10	**Total destruction of buildings/Heavy machine damage**
15	**Severe Injury/some fatalities (eardrum rupture/lung damage)**
30	**Near 100% Fatality from direct blast effects**

Table 12.1 Blast Overpressure vs Damage [61]

Overpressure is the pressure caused by a blast wave over and above normal atmospheric pressure. The duration of the blast wave is the **Impulse**. Simple damage models are based on correlation of damage to peak overpressure assuming a relatively long duration impulse.

Physical Explosion Using Simple TNT Model

The TNT equivalency model has been used for many years and is based on an assumption of "equivalence" between flammable materials and TNT. This simple model may be used for estimating damage distance for equipment rupture or sudden release of stored chemical energy. Stored pressure-volume energy may be estimated as the energy of expansion of an ideal gas using Equation 11-1 [16, p. 299] and Equation 11-2:

$$Q_{PV} = V^* P_B \left[\ln (P_B/P_A) + (P_A/P_B) - 1 \right] \qquad \text{Equation 11-1}$$

$$V^* = V_V + V_L\, f\, (\rho_L / \rho_V) \qquad \text{Equation 11-2}$$

where:

V^* is the vapor volume in the vessel plus the volume (at the pressure inside the vessel) of vapor generated from instantaneous vaporization (m^3)

V_V is the initial vapor volume (m^3)

V_L is the initial liquid volume (m^3)

f is the fraction liquid vaporized

ρ_L / ρ_V Is the ratio of liquid to vapor density at the initial pressure and temperature (before burst)

Q_{PV} = explosion energy (kJoule)

P_A, P_B = atmospheric and burst pressure (kPa) respectively.

Note that the vapor generated from instantaneous vaporization is based on a maximum initial temperature less than the superheat critical limit (roughly 90% of the critical temperature)

The TNT equivalent, kg_{TNTeq}, is the explosion energy divided by 4600 kJoule per kg_{TNTeq}.

The TNT model is an empirical correlation of Scaled Pressure versus Scaled Distance (Figure 11.1). The scaled pressure is can be estimated using the blast overpressure divided by atmospheric pressure. Scaled Distance, Z, is distance from the vessel or equipment divided by TNT equivalent raised to the 1/3 power [21, pp. 160-161].

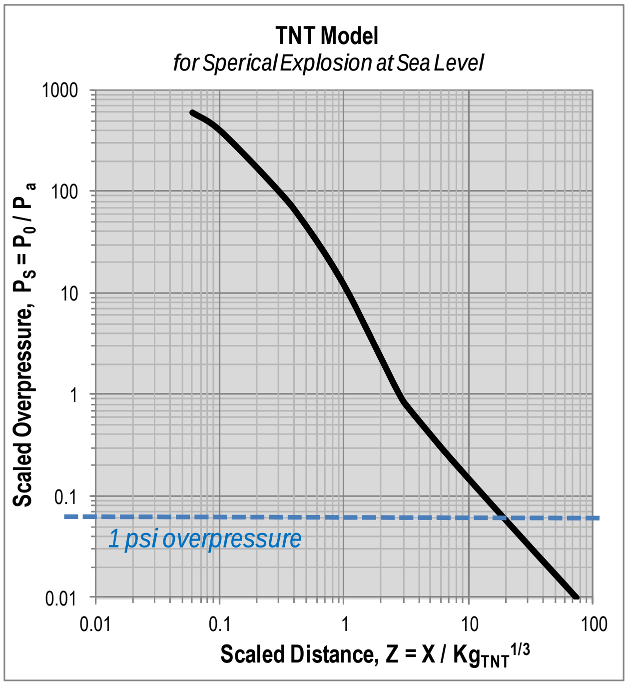


Figure 11.1 Scaled Overpressure vs Scaled Distance – TNT Model

For pressure vessels (design of greater than 1 atmosphere gauge), failure is assumed to occur between 2 and 4 times the design pressure. For screening evaluation, 100% of the energy at the minimum failure pressure is assumed for the blast wave (ignoring the portion energy that may be consumed by the equipment failure). Explosion distance to a specific Scaled Overpressure is estimated from Scaled Distance on the TNT Model graph shown in Figure 11.1.

TNT Model Example

Estimate the distance to 1 psi overpressure for rupture of a vapor filled 10 m^3 (2640 gal) vessel at 1000 kPa (145 psia).

$Q_{PV} = V\,P_B\,[\,\ln(P_B/P_A) + (P_A/P_B) – 1\,]$

$= 10\,(1000)\,[\,\ln(1000/101.3) + 101.3/1000 – 1] = 1.39 \times 10^4$ kJoule

$kg_{TNTeq} = 1.39 \text{ X } 10^4 / 4600 = 3.0$ kg

From the TNT graph at 1 psi overpressure, Scaled Distance, $Z = 18 = X / 3.0^{1/3}$

$X = 18\,(3.0^{1/3}) = 26$ m

Baker-Strehlow-Tang Explosion Model

Blast modeling for flammable vapor or dust explosion is based on rapid combustion. Correlation of Blast Overpressure for combustion related explosions requires a more complex model than the simple TNT Model. Blast energy for the Baker-Strehlow-Tang Model[4] is correlated to flame speed (expressed in Mach number units) and related to:

- **Fuel Reactivity** (categorized as high, medium or low)
- **Obstacle Density or Congestion** (categorized as high, medium or low).
- **Degree of Confinement** (categorized as 1D, 2D, or 3D)

Fuel Reactivity is based on fundamental burning velocity. A measure for the fuel reactivity is depicted in Table 12.2.

Table 12.2 Fuel Reactivity

High	**Medium**	**Low**
Fundamental Burning Velocity > 75 cm/s	*Fundamental Burning Velocity 45-75 cm/s*	*Fundamental Burning Velocity <45 cm/s*
Acetylene, vinyl acetylene, methyl acetylene, ethylene, ethylene oxide, propylene oxide, hydrogen (indoors), cryogenic hydrogen, carbon disulfide, propyne, propadiene and hydrocarbon mixtures with more than 33% hydrogen (molar basis)	Chemicals not listed as high or low reactivity. **Most hydrocarbons are medium reactivity.**	Methane, ammonia, some chlorinated hydrocarbons Class I Dusts

The presence of obstacles within a flammable cloud generates turbulence and accelerates the flame front. Low, medium, and high congestion examples are shown in Figure 11.2.

Low Congestion represents only 1-2 layers of obstacles. One can easily walk through the area relatively unimpeded.

Medium Congestion represents 2-4 layers of obstacles. One can walk through an area, but it is cumbersome to do so. Medium Congestion is common for most of our manufacturing facilities.

High Congestion represents many layers of repeated obstacles. One could not possibly walk through the area and little light penetrates the equipment or piping congestion.

Figure 11.2 Examples of Low, Medium and High Congestion

Degree of Confinement is the presence of surfaces that prevent flame propagation in any one or more of three directions (Figure 11.3).

3D Confinement indicates the flame front is free to expand in any direction.

2D Confinement indicates the flame front is free to expand in only two of three directions such as the space beneath platforms, between closely spaced vessels, or between closely spaced cars in a parking lot.

1D Confinement indicates the flame front is free to expand in only one direction such as within a tunnel.

Figure 11.3 Examples of 1D, 2D, and 3D Confinement

Although many combinations of *Fuel Reactivity*, *Obstacle Density or Congestion, and Degree of Confinement are possible,* only the 3-5 most common Flame Speed Mach Numbers are used for simple screening. These MACH numbers are shown in Table 12.3.

Table 12.3 BST Mach Number at Common Congestion and Fuel Reactivity Combination [62]

Fuel Reactivity	Obstacle Density or Congestion		
	Low	Medium	High
High	0.5	>1	>1
Low-Medium	0.35	0.5	1
Class I Dust		0.35	0.5

Table 12.3 is based on 2.5 D Confinement. 1D Confinement addressed as Mach >1 as transition to detonation is assumed to occur. Note that detonation is also assumed to occur for High Fuel Reactivity and Medium or High Obstacle Density (or congestion).

The Baker-Strehlow-Tang (BST) model is also a correlation of Scaled Pressure versus Scaled Distance (Figure 11.4). The Scaled Distance, R, is the distance from the Potential Explosion Site divided by (2 X Explosion Energy in kJoule / 101.3 kPa)$^{1/3}$.

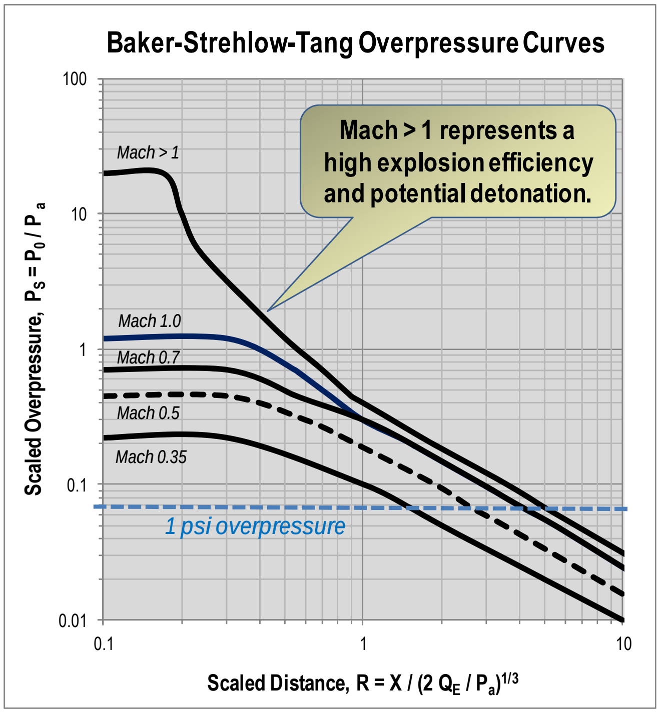


Figure 11.4 Scaled Overpressure vs Scaled Distance – BST Model

Potential Explosion Site (PES)

A Potential Explosion Site (PES) represents a congested or confined volume that can be occupied by a flammable vapor or dust cloud (Figure 11.5).

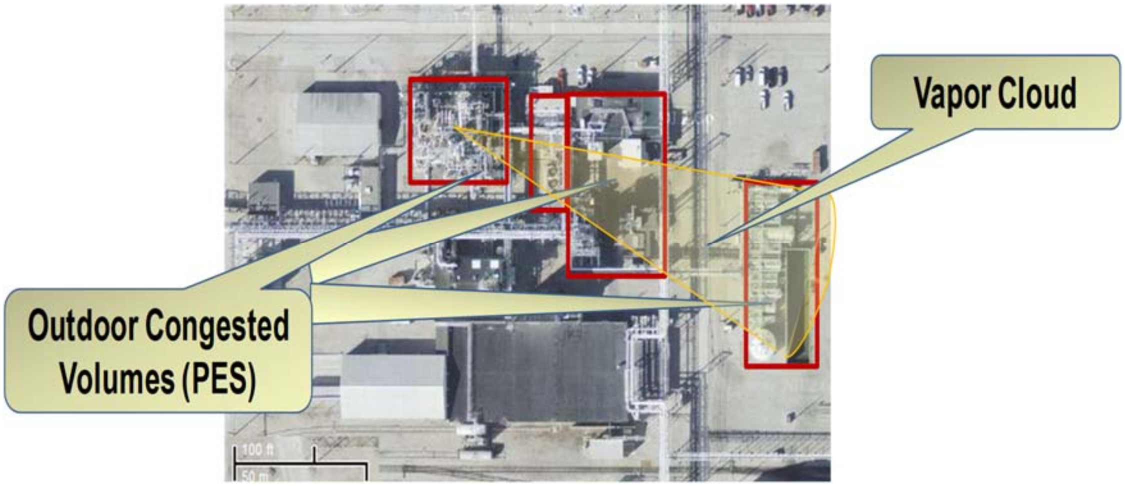


Figure 11.5 Potential Explosion Site

- An indoor PES is the confined area, building or portion of a building in which a flammable release occurs.
- Outdoor congested volumes act as independent PES's if separated from adjacent congested volumes by at least 15 ft (5 m) of open space.
- Multiple blast sources can emanate from a single outdoor release.

The Explosion Energy is estimated from a stoichiometric concentration of air and fuel in Equation 11-3 [21, p. 166]:

$$\mathbf{Q_E = 3500\ V_{PES}} \qquad \text{Equation 11-3}$$

where Q_{VCE} is explosion energy in kJoule and V_{PES} is the Potential Explosion Site volume in m^3. The factor 3500 kJoule/m^3 represents a typical heat of combustion for a stoichiometric hydrocarbon-air mixture.

Building Explosion and Equipment Deflagration

Explosion within a building or low design pressure equipment represents unique confinement situation which changes during the event (the walls fails). Typically 2 D or 2.5 D is assumed. The volume of confined area within a building or equipment head space is a well-defined single Potential Explosion Site. Other considerations include:

- Consider the combustion chamber of a Fire Tube Boiler as 1D as typically only the heads or ends of the tube fail.
- Consider a dust collector as medium to high obstacle density.
- Consider vessel head space, solids hopper, or silo as low obstacle density.

The location of the PES epicenter is the center of the Building or Equipment Head Space.

Building Explosion Example

Estimate the distance to 1 psi (6.9 kPa) blast overpressure from explosion of a 7580 m^3 low-congestion process building using medium fuel reactivity.

Explosion Energy is estimated as:

$$Q_E = 3500\ V_{PES} = 3500\ (7580\ m^3) = 2.65 \times 10^7 \text{ kJoule}$$

The scaled pressure is 1 psi / 14.7 psi = 0.068. At Mach 0.35 for low-congestion and medium reactivity fuel, the Scaled Distance, R = 1.5.

$$X_E = 1.5\ [2 \times 2.65 \times 10^7/101.3]^{1/3} = 121 \text{ meter to blast overpressure of 1 psi}$$

Vapor Cloud Explosion Using Simplified Baker-Strehlow-Tang Model

An outdoor release of flammable material may result in a Vapor Cloud Explosion. The outdoor Potential Explosion Site (PES) volume is more difficult to define than that for a building or equipment headspace. A reasonable simplification for screening Vapor Cloud Explosion damage is an assumed single outdoor PES equal to the vapor cloud volume that can be represented by an average level of confinement and obstacle density or congestion (Figure 11.6).

The entire vapor cloud is considered a Potential Explosion Site with the epicenter of the explosion at the center of the cloud (0.5 X_{LFL}). All wind directions are considered to determine an overpressure contour.

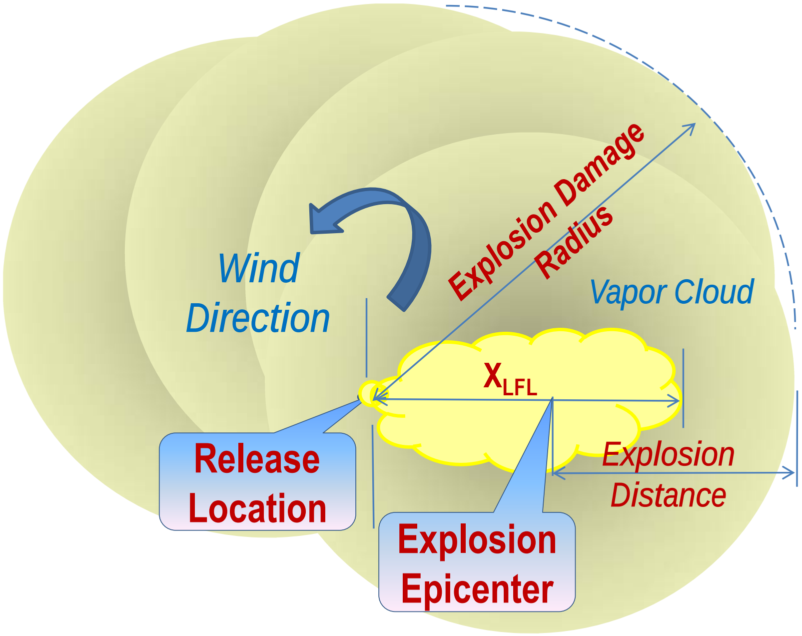


Figure 11.6 Simple Depiction of Vapor Cloud Explosion

The Potential Explosion Site volume is the expanded Cloud Volume *to a maximum or limit of 30000 m³* which accounts for decreased explosion efficient with increasing cloud volume. The vapor cloud volume is estimated using Equation 11-4:

$$\mathbf{V_C \sim 2440\ Q\ X_{LFL} / (\phi\ u\ Mw\ C_{LFL})} \qquad \text{Equation 11-4}$$

where:

Q is the release rate (kg/sec)	Wind is wind speed (m/sec)
X_{LFL} is distance to LFL (m)	Mw is molecular weight
C_{LFL} is the LFL Concentration (vol %)	ϕ is average concentration / C_{LFL} *(typically a value of 2)*

Note that damage distance is estimated *from the release point to the impacted building* rather than from the Potential Explosion Site to the impacted building. All distances closer to the release point than the epicenter (0.5 X_{LFL}) are assumed at the maximum explosion pressure.

Vapor Cloud Explosion Example

Estimate the distance to 1 psi (6.9 kPa) blast overpressure from a 400 kg/sec isopropyl amine (molecular weight 59.1, medium reactivity fuel) airborne rate into a medium congestion process area. The distance to the lower flammable limit of 2 volume % is estimated as 468 meter with a wind speed of 3 m/sec and averaging time of 19 seconds. The cloud volume estimated as $V_C = 2440\ Q\ X_{LFL} / (\phi\ u\ Mw\ C_{LFL}) = 435{,}000\ m^3$. The suggested Baker-Strehlow-Tang Flame Speed is Mach 0.5

The PES volume is estimated as V_C limited to a maximum of 30000 m³.

The explosion energy is roughly:

$$Q_E = 3500\ V_C = 3500\ (30000\ m^3) = 1.05 \times 10^8\ \text{kJoule}$$

The scaled pressure is 1 psi / 14.7 psi = 0.068 where the Scaled Distance, R = 2.5 at Mach 0.5.

$$X_E = R\ [2\ Q_E / 101.3]^{1/3} = 2.5\ (2 \times 1.05 \times 10^8 / 101.3)^{1/3} = 319\ m$$

The epicenter is assumed at 0.5 X_{LFL} or 234 m such that the total distance is 319 + 234 or 553 meter from the release point.

Class Exercise

Estimate the distance to 1 psi (6.9 kPa) blast overpressure from a 15 kg/sec butadiene (molecular weight 54.1 and medium reactivity fuel) leak into a low congestion outdoor process area. Use a lower flammable limit of 2 volume % and wind speed of 3 m/sec. The distance to the lower flammable limit from dispersion modeling at an averaging time of 19 seconds is estimated as 91 meter.

____

Share this estimate and any simplifying assumptions used.

Limitations of Simple Explosion Models

Simple models do not account for blast impulse and are treated as high impulse/long duration events. Results of these simple models may underestimate distance to overpressure greater than 3 to 5 psi and *should not be used to estimate damage to blast resistant buildings*. In addition:

- Vapor Cloud Explosion overpressure contours may be conservative as they are estimated as circular which does not account for regions within the LFL cloud that does not contain congested or confined areas (Potential Explosion Sites).
- The overpressure contour may be underestimated if there is a region of higher than average congestion near the furthest distance of the LFL cloud.

Physical Explosion and Confined Explosion 1 psi overpressure contours match closely with more advanced models as these are nearly “point sources”. Distance to higher overpressure may be underestimated with these simple models.

12. IMPACT ASSESSMENT

Source models generate a variety of feasible Incident Outcomes that are caused by release of hazardous material or energy. The next step in the Overall Work Process is selection of a specific Outcome and assessment of Consequences (Figure 12.1; refer to Figure 8.2). In assessing effects on people, consequences may be expressed as number of serious injuries or potential fatalities. In assessing physical damage, consequences may be expressed as business loss. Environmental effects may be more complex to quantify.

It must be noted that **estimating the number of people impacted for a scenario is extremely inaccurate**. Often consequence severity is predicted significantly higher or significantly less than actual historical incidents. It is the intent of this manual to provide estimates primarily for consistency among Hazard Identification and Risk Analysis studies and for comparison.

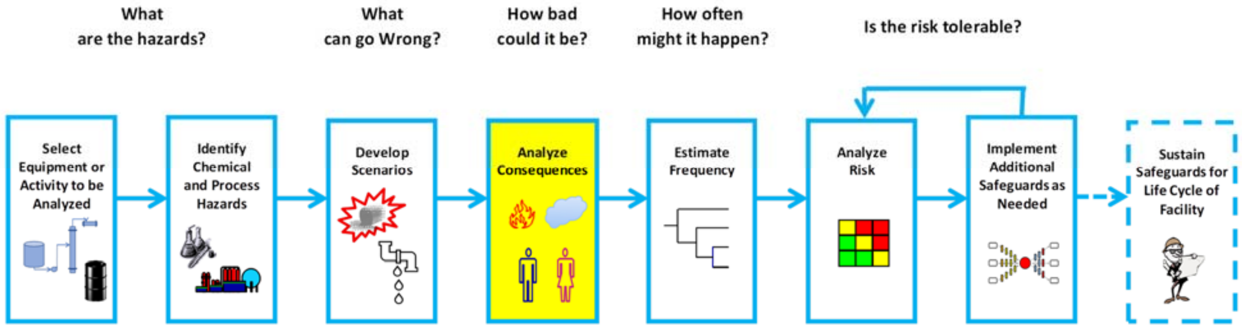


Figure 12.1 The Impact Analysis Step in the HIRA Workflow Process

Section Objectives

The following objectives are covered in this section:

- Be able to select applicable Incident Outcome for a scenario.
- Estimation of an Effect Zone and number of people impacted for on-site toxic, flammable, and explosion scenarios.
- Screening Criteria for Levels of Concern associated with the various Outcome.
- Estimation of an Effect Zone for Thermal Radiation or Fireball exposure.
- Estimation of toxic or explosion vulnerability within Occupied Buildings.
- Be able to estimate the number of people potential impacted for a simple scenario case:

Incident Outcome

Flash Fire is the non-explosive combustion of a vapor cloud in air. The primary hazards associated with flash fires are thermal burns and direct flame contact.

Building Explosion is feasible if the *indoor chemical concentration exceeds its lower flammability limit*. Building explosion for a combustible dust is feasible if the particle size is less than 420 mm and a concentration greater than 0.3 gram per cubic meter can be achieved from a fluidized release or dispersion of accumulated dust from floors, beams and rafters. Relatively small quantities of fuel are generally involved in building explosions and projectiles represent the major threats.

Vapor Cloud Explosion requires that a flammable cloud of sufficient size be formed prior to ignition and sufficient confinement or turbulent mixing must be present. Buildings located at a distance corresponding to less than 6.9 kPa (1 psi) overpressure would not be expected to sustain damage sufficient for occupants to be severely injured. (Low strength or portable buildings may be an exception and sustain significant damage at this overpressure).

Physical Explosion and BLEVE can produce a shock wave and/or eject equipment fragments from the sudden release of pressure-volume energy. Burst pressure of 1.1 times design pressure for low pressure tanks to 3 times design pressure for carbon steel pressure vessels may be appropriate for screening purposes to account for variability in design codes.

Toxic Release effects are based on short duration rather than chronic inhalation exposure. Off-site represents a distance beyond the property line and includes areas normally populated by members of the public. On-site personnel may tolerate exposure to higher concentrations without serious effect as this group would not include the most susceptible people (elderly, infants, those with cardio-vascular illness, etc.) and be well trained in emergency response.

Generalized Outcome Event Tree

A single loss event may have several outcomes (Figure 12.2). A release of flammable material may result in a jet or flash fire, an outdoor vapor cloud explosion, or a non-ignited vapor cloud. A release of toxic material may result in an indoor toxic environment for those in an occupied building or an outdoor toxic impact. A sudden release of pressure-volume energy (such as from an equipment rupture) may result in a physical explosion.

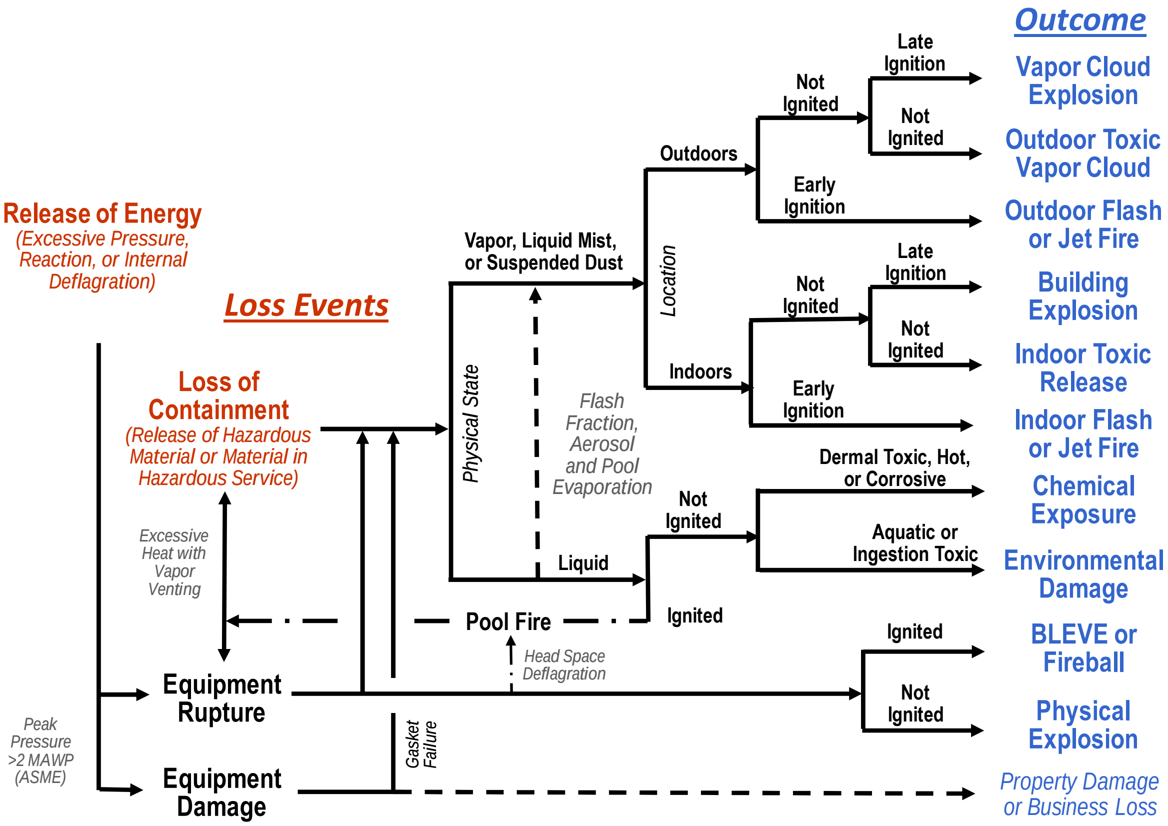


Figure 12.2 Generalized Outcome Event Tree

Incident Outcome Selection Criteria

Following determination of Release Rate and Airborne Quantity, models are used to determine downwind concentrations and overpressure versus distance for explosions. Various Outcome screening criteria are used to determine which are feasible.

- **Flash (or Jet) Fire**: the distance of a flammable cloud to a multiple of LFL concentration exceeds a de minimis value.
- **Vapor Cloud Explosion**: Greater than 1000 kg flammable (100 kg for high flame speed) released within 5 minutes.
- **Building Explosion:** Indoor average concentration exceeds a multiple of LFL concentration
- **Physical Explosion**: Blast Overpressure exceeds a Threshold Distance
- **Toxic Vapor Release** (Indoor, Outdoor)
  - Off-site exposure to > ERPG-2 concentration
  - On-site exposure to > LC-50 concentration
  - On-site exposure to > ERPG-3 concentration within an occupied building

On-Site Consequence Severity

A simple *Impact Analysis* is based on Hazards originating from a point source such that the effect zone is estimated in terms of radial distance from the source[2]. Personnel within the effect zone are assumed severely impacted while those outside of this area are assumed not affected.

Using a simple point source method is a simplification necessary to evaluate common consequences of an outdoor “on-site” incident. A more detailed analysis would look at many other variables such as wind direction, wind speed, weather, release impingement, terrain, etc. for *each* incident. In addition, a lethality for personnel at multiple locations would be summed versus simplification to zero and 100 % lethality regions.

An effect zone (or impact area) may be estimated in terms of radial distance from the source. The consequence within a particular impact area is assumed constant (such as serious impact to personnel including fatality). Generally, the probability of the consequence is assumed unity for any location within the impact area and zero for any location outside the impact area. For scenarios such as explosion or thermal radiation, the impact area (or “footprint”) is estimated as a circle at typically ground level elevation. For flammable or toxic releases impacted by wind, the impact area is estimated as a circle segment.

For Outcome Affected by Wind Direction (Outdoor Toxic and Flammable Releases) – the Effect Zone is Conical Plume estimated as a Pie Shaped Segment at Ground Level (Figure 12.3).

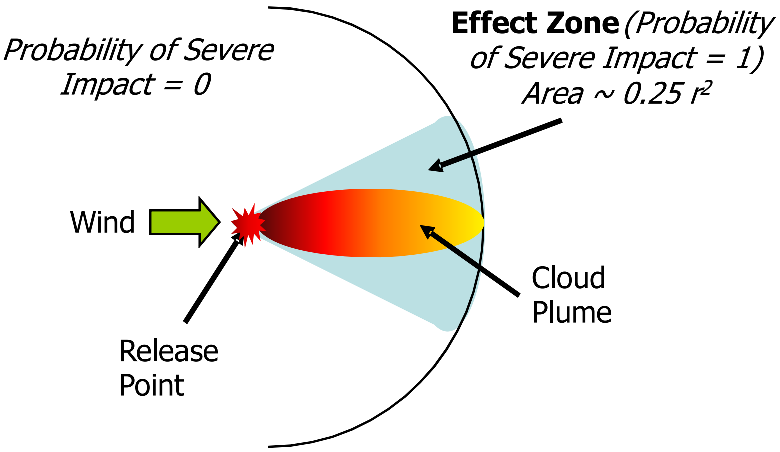


Figure 12.3 Example Outdoor Effect Zone

The impact area for an outdoor release is determined using Equation 12-1

Impact Area = 0.25 radius^2 *(for Class D weather)* Equation 12-1

For Outcome resulting from Release within an Enclosed Process Area (or Process Building) – the Effect Zone is estimated as *the fraction of building* above the severe impact concentration using Equation 12-2 for flammable releases or Equation 12-3 for toxic releases (Figure 12.4).

Impact Area = $V_B^{2/3}$ C_{indoor} / LFL *for flammable release* Equation 12-2

Impact Area = $V_B^{2/3}$ C_{indoor} / LC-50 *for toxic release* Equation 12-3

Where V_B is the volume of the Enclosed Process Area and C_{Indoor} is the average indoor concentration.

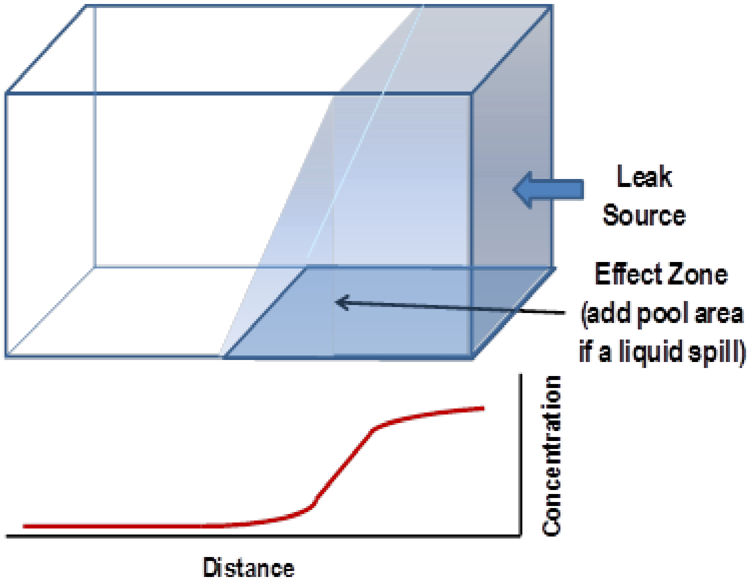


Figure 12.4 Indoor Effect Zone

For Explosions – the Impact Area (for Overpressure or Projectiles) a Hemispherical Effect Zone (Figure 12.5).

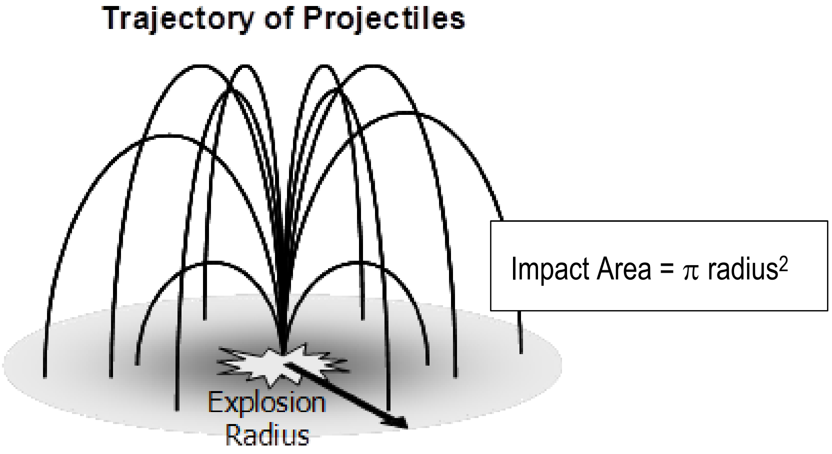


Figure 12.5 Projectile Effect Zone

Estimation of fragment effects may be important as significant personal injury and domino damage are attributable to fragments. Typically a small number of large fragments (between 2 and 10) are produced upon pressure vessel failure so the likelihood of being struck is very small.

De Minimis Consequence

If the hazard distance or impact area is extremely small, a potential fatality or severe injury is nearly impossible. The cross-sectional area of a toxic cloud less than a few meters distance to LC-50 concentration is so small that a person would not be able to take a few breaths while remaining within the cloud. The cross-sectional area of a flammable cloud less than a few meters distance to ½ LFL is so small that burns could not cover a sufficient fraction of body area to be a fatality or severe consequence. If the distance to 10 psi overpressure from a physical explosion (with no fragments) is less than one meter, a fatality or severe injury is not feasible.

Example Screening Criteria for Consequence Severity sufficient to warrant further Risk Analysis

- **Flash (or Jet) Fire**: personnel exposure to a flammable cloud greater than 3 m to ½ LFL concentration
- **Direct Explosion Impacts**: personnel exposure to blast wave of distance to 10 psi overpressure greater than 1 m (excluding projectiles or fragments).
- **Building Damage:** Blast overpressure greater than 1 psi at distance to occupied building for typical construction or greater than 0.5 psi at distance to occupied building for low strength construction
- **Thermal Radiation**: personnel exposure to fireball with distance to severe burns from thermal radiation greater than 3 m
- **Toxic Vapor Release** (Indoor, Outdoor):
    - Off-site personnel exposure to greater than ERPG-2 concentration
    - On-site personnel exposure to toxic cloud greater than 3 m to LC-50 concentration
      Indoor personnel exposure to average concentration greater than ERPG-3

Chemical Exposure Example Criteria

Exposure to dermal toxic chemicals, chemical corrosive to human tissue, or high/low temperature fluids may cause serious injury. A potential fatality is considered if the release quantity and rate are sufficient to expose greater than 25% of body area to:

- Liquids considered “toxic in contact with skin”
- Liquids considered “corrosive”
- Liquids hotter than 60 C or colder than -23 C
- Vapors hotter than 93 C

Thermal Radiation Example Criteria

Thermal radiation from a BLEVE or fireball is a significant cause for damage or injury (Figure 12.6). The distance to a specific thermal radiation level may be estimated using Equation 12-4 [21, p. 209]:

$$X_{ThemRad} = \{ 828\ M^{0.771} / E_r - 18.9\ M^{2/3} \}^{1/2} \qquad \text{Equation 12-4}$$

A hazard distance and related impact area for severe burns from a fireball or BLEVE may be approximated using Equation 12-5 [21, p. 207]:

$$X_{Thermal} = 2.64\ t^{0.379}\ M^{0.307} \qquad \text{Equation 12-5}$$

where M is the total flammable mass in the fireball (kg) and hazard distance, t is t is the fireball duration (sec) estimated as 0.45 $M^{1/3}$ for M<30,000 kg or 2.6 $M^{1/6}$ for M>30,000 kg. E_r is radiation flux (Kw/m^2), at distance, $X_{Thermal}$, in meter.

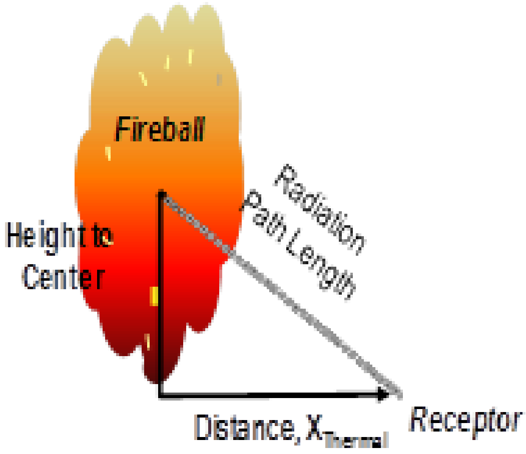


Figure 12.6 Radiation Fireball

A Boiling-Liquid Expanding-Vapor Explosion (BLEVE) may occur if a vessel containing liquid above its normal boiling point ruptures. This outcome is typically based on external fire heating the vessel contents and weakening the structural integrity. The sudden vaporization of a large fraction of the vessel contents, possibly followed by intense combustion or explosion of the vaporized cloud is a very high energy release event. In addition to damage from the resulting blast overpressure wave, thermal radiation from the fireball is a very significant cause for human injury. When estimating the number of people impacted, however, consideration of personnel who have taken shelter due to the fire prior to occurrence of the BLEVE may be appropriate.

Fireball distance resulting from a vented internal explosion or deflagration from flammable vapor may be estimated using Equation 12-6 [18]:

$$\textbf{Fireball Distance} = \textbf{3.1 Equipment Volume}^{0.402} \qquad \text{Equation 12-6}$$

Fireball distance resulting from a vented internal explosion or deflagration from dust may be estimated using Equation 12-7 [18]:

$$\textbf{Fireball Distance} = \textbf{10 Equipment Volume}^{1/3} \qquad \text{Equation 12-7}$$

Estimating Number of People Impacted for On-site Incident

Onsite Outdoor Population Density accounts for maintenance and other personnel who may occasionally be in a nearby outdoor process area. A typical value is 0.0002 people/m^2 *for a large, well-automated facility*.

Personnel in the Immediate Vicinity include those associated with procedures requiring operator attendance such as unloading a tank truck, sampling, etc. in addition to personnel using nearby walkways, at a nearby elevated work area, etc. Personnel in the Immediate Vicinity are considered:

Estimating the On-site Probability of Exposure

When the Effect Zone is small such that the number of people impacted is less than 1, the value representing a "random" probability of a single severe impact or fatality is used. These simplifying assumptions that are used in CHEF for small on-site exposure probabilities are depicted in Table 11.1.

Table 11.1 Probability of Exposure

Number Impacted	Probability of Exposure
0.1 to 1	1
< 0.1	0.1

If Personnel are in the Immediate Area, then the Probability of Exposure may be based on Time at Risk or the fraction time the hazard exists that a person could be present. Time at Risk depends on the time window that the hazard exists. If the Initiating Event for the hazard scenario is caused by the operator or other person in the immediate area, than Time at Risk may be nearly 100% (a probability of 1).

Example Impact Assessment for Outdoor Release

Estimate the number of people impacted from an outdoor release of acrylonitrile. The distance to the LC-50 concentration is 100 meter. The distance to a multiple of LFL is 25 meter. Use an outdoor population density of 0.0002 people/m^2 and no people in the immediate vicinity of the release. Assume 3 m/sec wind and Class D Atmospheric stability.

For a release impacted by wind direction, the effect zone is 0.25 X^2 in m^2.

Toxic Impact: 0.25 (100 m)^2 (0.0002 people/m^2) = 0.5 people rounded to 1

Flammable Impact: 0.25 (25 m)^2 (0.0002 people/m^2) = 0.03 people

Considered as 0.1 probability of 1 person

Note that example assumes a random probability of people being sufficiently close to the release to be impacted. If personnel could be in the immediate area, they would be added to the total estimated in the example.

Also note that the average outdoor population density is 0.0002 people/m^2. For a "typical" facility covering 20000 m^2, this represents 4 people within the plant's outdoor process area at any time. A higher population density should be used for locations where a higher number of personnel could be in the specific area near the release location.

Estimating Number of People Impacted within Occupied Buildings

A simple Effect Zone approach is not effective for Occupied Buildings as not all personnel within a building are typically impacted to the same extent. In these cases, the fraction of people impacted or "vulnerability" is estimated from inhalation of toxic chemicals or level of explosion damage. The estimated number of people seriously impacted is the maximum number of occupants times the estimated fraction vulnerability.

A one hour exposure is assumed for Building Occupants in estimated toxic impacts. For a release duration less than 1 hour, concentration will fall off once the release has stopped as fresh air is drawn into the building. For screening assessment, using an indoor dose of ½ the dose at the building ventilation inlet may be appropriate. The Probability of Severe Impact discussed in the Toxicity section - Multiple of ERPG-3 Concentration versus Vulnerability Models may be used to estimate the fraction of total Building Occupants impacted (Figure 12.7).

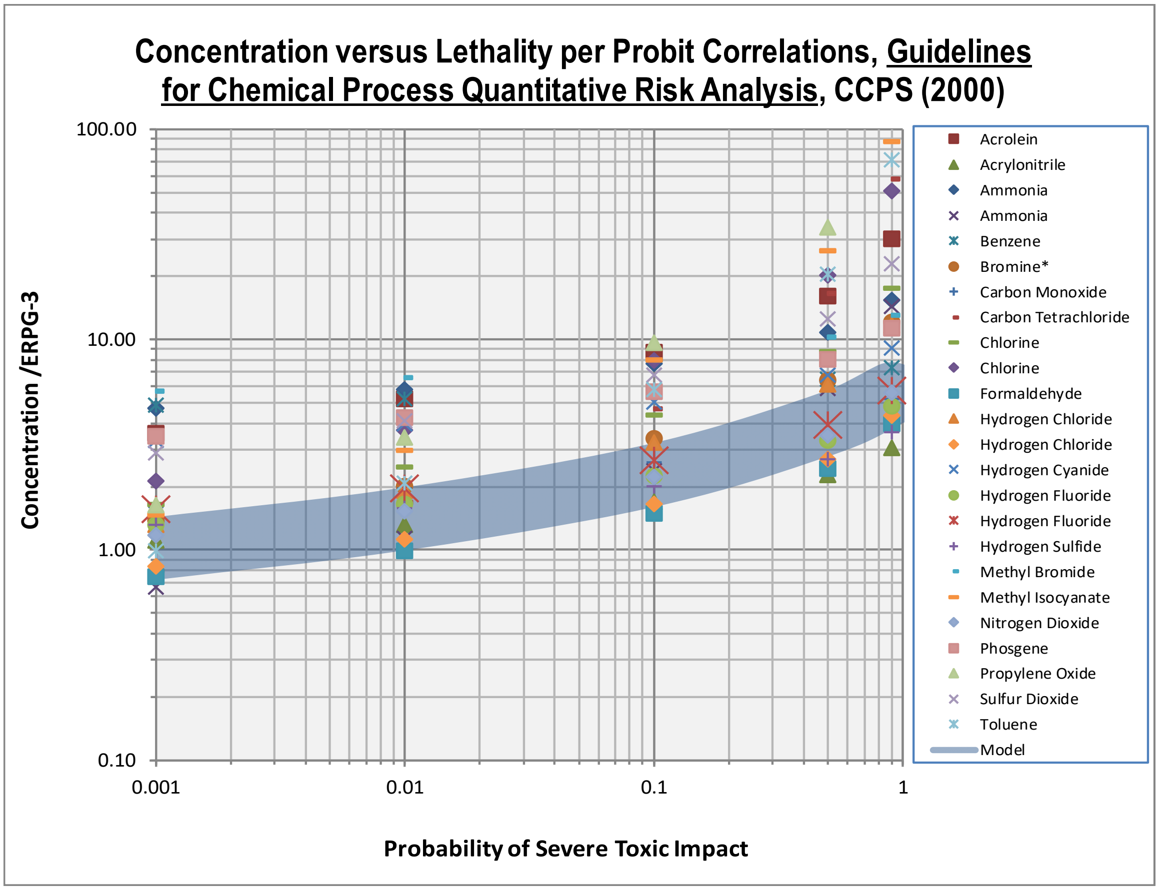


Figure 12.7 Toxic Vulnerability at One-Hour Explosure Duration

It is generally believed that the primary cause of injury within buildings subject to blast effects is due to building collapse and blunt force trauma. The threshold overpressure for significant building damage is assumed 9 kPa (1.3 psi) for typical construction or 4 kPa (0.6 psi) for low strength or portable buildings (Figure 12.8). Damage to blast resistant buildings are not well correlated by simple methods.

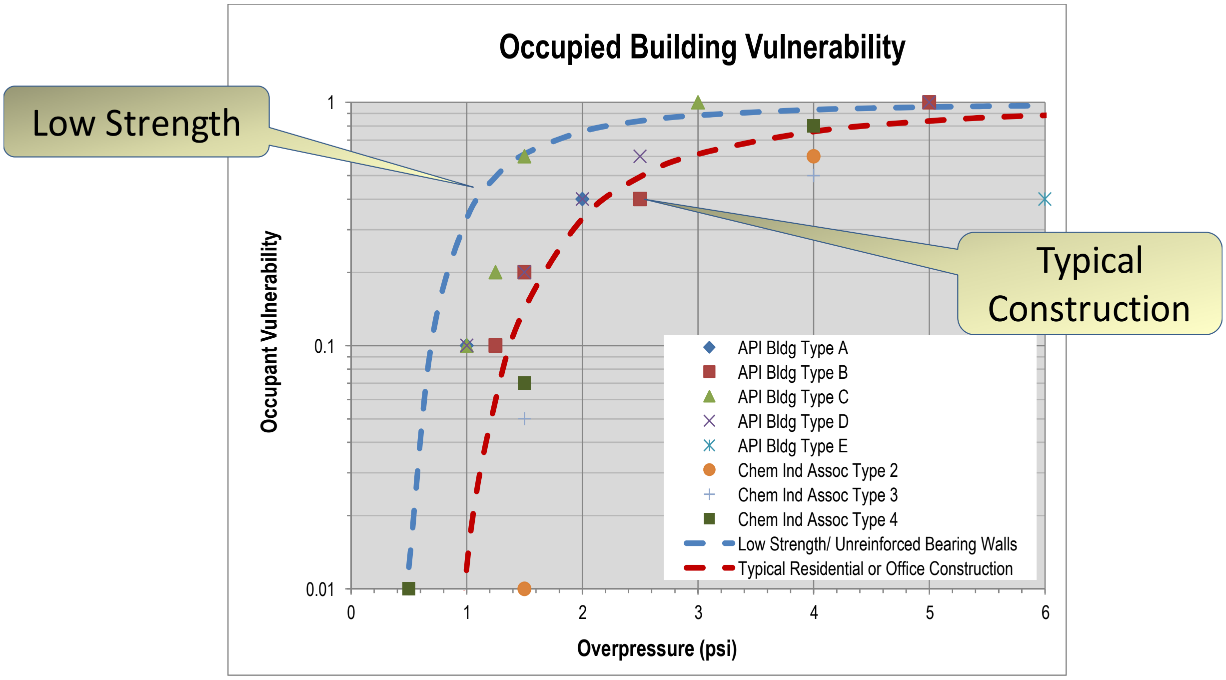


Figure 12.8 Occupied Building Vulnerability (specific to 1996 edition [63])

Note that for physical explosions of small volume equipment; the section of building wall exposed to overpressure greater than 9 kPa may be small, resulting in cosmetic damage to a building rather than structural damage. If the overpressure at the distance to the nearest edge of the building exceeds 9 kPa (1.3 psi) for typical construction, (4 kPa or 0.6 psi for low strength or portable buildings) but overpressure at the distance to the center is less than 9 kPa psi for typical construction (4 kPa for low strength or portable buildings), partial damage may be assumed with a 1-2 people seriously impacted.

Example Impact Assessment for an Occupied Building Example

Estimate the number of people within an Occupied Building impacted from a 1 hour outdoor release of acrylonitrile. The outdoor concentration at the building is 4 times the ERPG-3 value or 300 ppm. Use a maximum daytime occupancy of 20 people in the building.

An indoor concentration of ½ that outside of the building is assumed or 2 times ERPG-3 (150 ppm).

> From the graph on the previous slide, the Vulnerability at 2 times ERPG-3 is 0.15.
>
> Number of People Impacted = 0.15 (20) = 3 people

Estimate the number of people severely impacted within a typical construction occupied building exposed to 2 psi (14 kPa) overpressure if there are 10 building occupants.

> From the Vulnerability Curve for typical construction building at 2 psi, the Vulnerability is roughly 0.4.
>
> Number of People Impacted = 0.4 (10) = 4 people

Offsite Toxic Impacts

Equation 12-8, a simple exponential function, may be used to relate toxic vulnerability.

$$\ln(\text{toxic } vulnerability) = c + d / C^m \quad \text{or} \quad vulnerability = e^{c + d / C^{\wedge}m} \qquad \text{Equation 12-8}$$

where

c and d are evaluated at 2 points from a probit model (proposed as 1 and 50% lethality)

a **specific exposure duration** using an assumed value of m = 2 b.

b is the exponent of the Simple Dispersion Model.

The value of m is selected such that lethality is proportional to distance. This simplifying assumption to a gaussian response is used in CHEF (Figure 12.9). The simple correlation compared to the gaussian correlated Probit value has a maximum error is less than 20% (the simplification shows 100% lethality where gaussian would be 83%, Figuire 12.9).

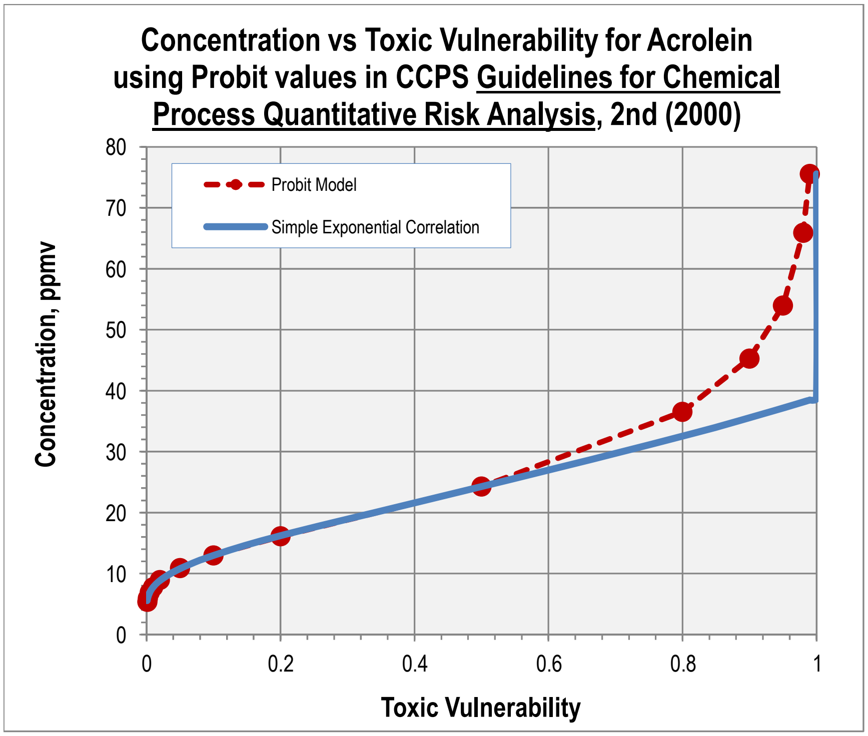


Figure 12.9 Approximate Concentration versus Toxic Vulnerability

By combining the simple Lethality (lethality versus concentration) and simple Dispersion (concentration versus distance) models, the lethality as a function of distance may be estimated using Equation 12-9 for continuous releases and Equation 12-10 for instantaneous releases.

Continuous Release:

$\ln(\text{Lethality}) = c + d / C^{m}$ where $m = 2\,b$

$\text{Concentration, } C = (a / X)^{1/b}\, Q / (Mw\,u) = a^{1/b}\,[\,Q / (Mw\,u)\,] / X^{1/b}$

$\ln(\text{Lethality}) = c + d\,[\,X^{2}\,\{(Mw\,u) / Q\}^{2b} / a^{2}\,]$

$$\textbf{Lethality} = e^{c+d\,[\,X^{2}\,\{(Mw\,u)/Q\}^{2b}/a^{2}\,]} \qquad \text{Equation 12-9}$$

Instantaneous Release:

$\ln(\text{Lethality}) = c + d / C^{m}$ where $m = 2\,b$

$\text{Concentration, } C = (a / X)^{1/b}\,(Q^{*} / Mw)^{1/(3\,b)} = [\,a^{1/b}\,(Q^{*} / Mw)^{1/(3\,b)}\,] / X^{1/b}$

$\ln(\text{Lethality}) = c + d\,[\,X^{2}\,(Mw / Q^{*})^{2/3} / a^{2}\,]$

$$\textbf{Lethality} = e^{c+d\,[\,X^{2}\,(Mw/Q^{*})^{2/3}/a^{2}\,]} \qquad \text{Equation 12-10}$$

where:

C = concentration

Mw = Molecular Weight

Q = release rate (mass/time)

Q^{*} = release quantity (mass)

u = wind speed (distance/time)

X = downwind distance (including any correction for initial dilution)

a, b, c, d, m = correlation coefficients

For a constant population density in the region of interest, P_D, the number of people impacted are simply the integral of lethality times the change in impact area with distance times a constant population density. Since the Impact Area may be simply correlated by $A = f\,X^{2}$, the change in impact area with distance, $dA / dX = 2\,f\,X\,dX$, as shown in Equation 12-11.

$$\textbf{Number Impacted} = 2\,\eta\,P_D\,f \int_{X0}^{X} X\, e^{c+d\,[\,X^{2}\,\{(Mw\,u)/Q\}^{2b}/a^{2}\,]}\, dX$$

$$= \eta\,P_D\,f\,a^{2}\,\{Q/(Mw\,u)\}^{2b}\,\{\,e^{c+d\,[\,X^{2}\,\{(Mw\,u)/Q\}^{2b}/a^{2}\,]} - e^{c+d\,[\,X0^{2}\,\{(Mw\,u)/Q\}^{2b}/a^{2}\,]}\,\} / d \qquad \text{Equation 12-11}$$

The lethality integral may also be written utilizing X_{Ref} as the distance to a concentration, C_{ref}, by substituting, resulting in Equation 12-12:

$[\,Q / (Mw\,u)\,]^{2b}\,a^{2} = C_{Ref}^{2b}\,X_{Ref}^{2}$ for a continuous release

$[\,Q / (Mw\,u)\,]^{2/3}\,a^{2} = C_{Ref}^{2b}\,X_{Ref}^{2}$ for an instantaneous release

$$\textbf{Number Impacted} = 2\,\eta\,P_D\,f \int_{X_0}^{X} X\, e^{c+d\,[\,X^{2}/(C_{Ref}^{2b}\,X_{Ref}^{2})\,]}\, dX$$

$$= \eta\,P_D\,f\,C_{Ref}^{2b}\,X_{Ref}^{2}\,\{\,e^{c+d\,[\,X^{2}/(C_{Ref}^{2b}\,X_{Ref}^{2})\,]} - e^{c+d\,[\,X_0^{2}/(C_{Ref}^{2b}\,X_{Ref}^{2})\,]}\,]\,\} / d \qquad \text{Equation 12-12}$$

The factor η corrects for average lethality at a distance to the lethality at the centerline concentration. Typical values would be 0.5 to 1.

Note that this integral applies in the region where lethality < 1. For lethality > 1, it is estimated by the multiple of the population density times the Impact Area.

Personnel may be located outdoors or within buildings (or homes) and weather conditions may be different between day and night. The correlation for the number of people impacted may be repeated for people within buildings where the concentration may be a fraction of the outdoor concentration. In addition, the correlation for number of people impacted may be repeated for night weather conditions if different from day conditions of wind speed and atmospheric stability. The total estimate becomes the sum of fraction of time times the estimated number of people impacted for each condition.

Summary of Key Consequence Analysis Steps

The key steps in analysis of Consequences are:

- Estimate Airborne Quantity (per Airborne Quantity discussion)
    - Perform flash calculations, aerosol and pool evaporation
- Evaluate Hazard Distances (per Vapor Dispersions or Explosion discussion)
    - Distance (and Elevation) for Flash Fire
    - Distance (and Elevation) and Cloud Volume for Vapor Cloud Explosion
    - Distance for On-Site Toxic Impact
    - Distance for Direct Explosion Impact
    - Distance needed for Off-Site Toxic Impact
    - Concentration at Distance to Occupied Building for Toxic Infiltration
    - Overpressure at Distance to Occupied Building for Building Damage
- Estimate Impact Area for On-Site incident outcome. Personnel Impact determined from Area of Effect Zone and On-Site Outdoor Population Density (including personnel in immediate area)
- Estimate “Vulnerability” for Occupied Buildings. Personnel Impact determined from “vulnerability” times number of occupants.

13. LIKELIHOOD EVALUATION

Likelihood Evaluation is the methodology used to estimate the frequency and/or probability of occurrence of an event sequence leading to an incident. Estimates are based on historical data or from failure sequence models such as Fault Tree or Event Tree. Estimating requires consideration of factors such as common-cause failures (a single factor leading to simultaneous failures – such a power failure), human reliability, and frequency (as well as applicability) of external events.

Likelihood Evaluation is not always preceded by Consequence Analysis (Figure 13.1). In some cases, an estimated likelihood for a scenario may indicate such a low frequency that evaluation of risk is not needed. For existing facilities, the likelihood (frequency or probability) component of risk is often the easiest (or most cost effective) to change.

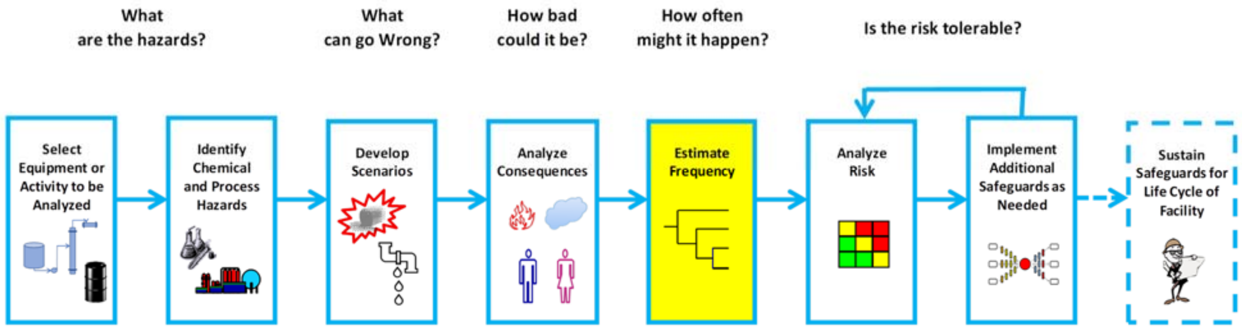


Figure 13.1 The Frequency Estimating Step in the HIRA Workflow Process

Section Objectives

The following objectives are covered in this section:

- Reliability and Failure Probability
- System and Component Interactions
- Probability of Failure on Demand
- Estimating Failure Frequencies from Historical Data
- Human Reliability
- Frequency Modeling Techniques including Fault Tree and Event Tree

Definition of Terms

Terms commonly encountered in Frequency Evaluation include:

- **Likelihood** – a measure of the expected frequency or probability of occurrence of an event. It may be expressed as a frequency or as a probability of occurrence during a time interval.
- **Frequency** – number of occurrences of an event per unit time.
- **Probability** – the likelihood of occurrence of an event or event sequence during an interval of time – or – likelihood of the success or failure of an event on test or demand. Probability is expressed as a number between 0 and 1.
- **Reliability** – the probability that an item is able to perform a required function for a stated period of time.

Failure Frequency

Many components exhibit a typical “bathtub” failure rate. The failure rate is highest when the component is new (infant mortality) and when it is old (old age (Figure 13.2). Between these two periods, the failure rate is reasonably constant for most components.

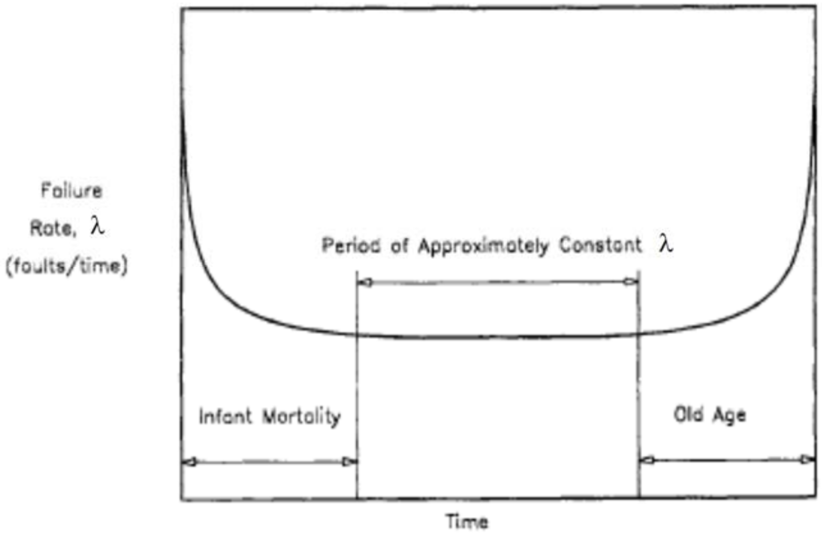


Figure 13.2 Failure Rate vs Time

Reliability and Failure Probability

Equipment failures in a process occur as a result of complex interactions of the individual components. The Probability that a particular hardware component will not fail during the time interval, t, for a constant failure rate, λ, is estimated using Equation 13-1 [16, pp. 550-558]:

$$R(t) = e^{-\lambda t} \qquad \text{Equation 13-1}$$

where R is reliability over the time interval

The Failure Probability over this time interval, $P(t)$, *assuming zero time for repair,* is calculated using Equation 13-2:

$$P(t) = 1 - R(t) = 1 - e^{-\lambda t} \qquad \text{Equation 13-2}$$

The Mean Time Between Failure (MTBF) for constant failure rate is estimated by Equation 13-3:

$$\mathrm{MTBF} = 1 / \lambda \qquad \text{Equation 13-3}$$

The Mean Time to Repair (MTTR) is the mean time to restore a failed component or system to operation.:

Interactions Between Hardware or System Components

Process components interact in two different fashions. In some cases a process failure requires the simultaneous failure of a number of independent components in parallel. This parallel structure is represented by a logical "AND" function which means that the failure probabilities for the individual components must be multiplied.

$$P = \Pi P_i = P_1 P_2 P_3 \ldots$$

Process components also interact in series. This means that a failure of any single component in the series of components will result in failure of the process. The logical OR function represents this case. For series components the overall failure probabilities is approximately the summation of failure probabilities for the individual components (which assumes an interaction probability - or both components in series fail – is small).

$$P = \Sigma P_i = P_1 + P_2 + P_3 \ldots$$

A Common Cause Failure is a single event that affects a number of systems simultaneously and may significantly increase overall failure probability. Common cause failures include events such as loss of utilities such as electricity or instrument air. These failure probabilities are typically addressed via OR logic within a summation of component failure probabilities. One needs to deliberately design systems to minimum common cause failures.

Probability of Failure on Demand

Simple failure probability correlations assumed failures are immediately obvious and corrected in a negligible amount of time. For many components (particularly emergency interlocks), failure may not be obvious without regular and reliable testing.

For an *unrevealed* failure, the failure becomes obvious only upon regular inspection. For example (Figure 13.3): a flat tire on a car is immediately obvious to the driver (revealed failure). However, the spare tire may also be flat without the driver being aware until the spare is needed (unrevealed failure).

Figure 13.3 Changing a Tire

The Probability of Failure on Demand (PFD) for an unrevealed failure is based on the fraction of time that a system or component is unavailable and may be estimated Equation 13-4 [21, pp. 558-562]:

$$\mathbf{PFD_{average}} \textit{ for Unrevealed Failures} = \tfrac{1}{2} \lambda \tau \qquad \text{Equation 13-4}$$

where

τ = the inspection interval

λ = the average failure rate (or $1/\lambda$ is the Mean Time Between Failures).

The average PFD for a revealed or obvious failure may be estimated using Equation 13-5:

$$\mathbf{PFD} \textit{ for Revealed Failures} = 1 - e^{-\lambda \tau} \qquad \text{Equation 13-5}$$

The PFD for revealed failures that can be repaired may be estimated using Equation 13-6:

$$\mathbf{PFD = MTTR / (MTTR + MTBF)} \qquad \text{Equation 13-6}$$

Note that mean time to repair (MTTR) above includes the time to detect, diagnose and repair the revealed failure.

A decrease in the Inspection Interval relative to the Mean Time Between Failures (MTBF) significantly improves the failure probability.

Failure Frequency from Historical Data

Failures of industrial equipment are usually reported in terms of a *Failure Rate or a Mean Time Between Failures.* These failures are not often presented in terms of probability of failure on demand for a number of reasons. First, the probability of failure on demand is only of interest when the piece of equipment is a protection layer whose failure will not be detected until it needs to act. When the failure initiates a chain of events that leads to a loss event or a nuisance shutdown, failure rate is a more appropriate measurement. Second, the probability of failure of a piece of equipment that does not initiate a loss event, or a shutdown, will depend on how often the equipment is tested. Test frequency becomes quite important when one is designing a system to meet a specific SIL requirement.

Much of the existing data failure resulting in leaks is from hydrocarbon facilities which likely represent clean, non-corrosive service. In general, large leaks have occurred, historically, less frequently than small leaks with only a small fraction of piping leaks are “full bore” (Figure 13.4).

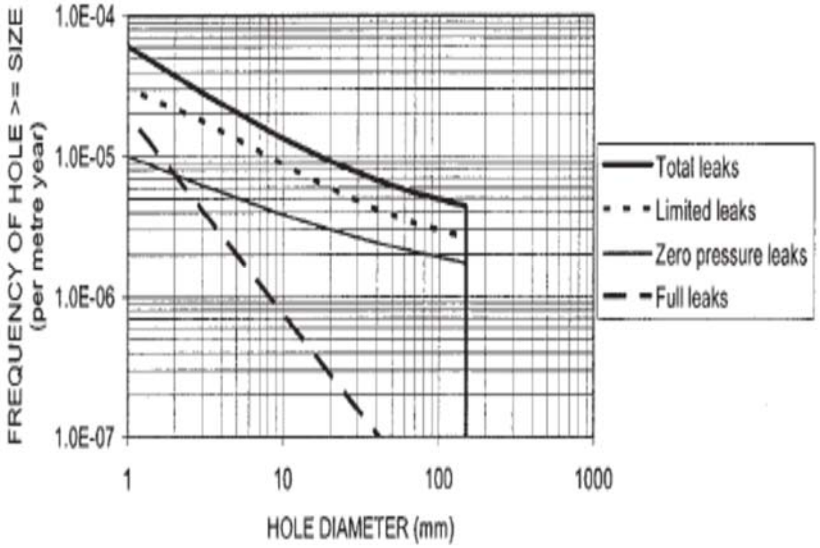


Figure 13.4 Leak frequencies for 150 mm diameter pipe - HSE offshore data

In many cases, the failure frequency is determined as the number of reported loss events divided by the exposure period. The number of failures per time is usually well defined, however, failure frequency requires an accurate estimate of the total number equipment items in the population (including those that did not fail). In addition, frequency is often based on a specific failure mode (such as fail open, fail closed, etc.). For example, the failure rate for pipeline requires a good estimation of the total length of piping for the study. Finally, design practices, inspection and maintenance programs, and protective layers may already be in place and thus incorporated into the failure frequency.

An example of published Frequency Data found in the literature is tabulated in Table 13.1 [6]:

Table 13.1 Common Initiating Event Frequencies [Adapted from [6, p. 71]

Initiating Event	Frequency Range from Literature (per year)
Basic process control system failure	1 to 10^{-2}
Pressure regulator failure	1 to 10^{-1}
Gasket or packing blowout	10^{-2} to 10^{-6}
Cooling water failure	1 to 10^{-2}
Pump seal failure	10^{-1} to 10^{-2}
Unloading hose failure	1 to 10^{-2}
Safety valve opens spuriously	10^{-2} to 10^{-4}
Piping leak per 100 m pipe length (20% leak)	10^{-3} to 10^{-5}
Piping leak per 100 m pipe length (full breach)	10^{-5} to 10^{-6}
Large external fire (aggregate causes)	10^{-2} to 10^{-3}
Lightning strike	10^{-3} to 10^{-4}
Third party intervention (impact by vehicle)	10^{-2} to 10^{-4}
Human error (routine procedure, unstressed)	10^{-1} to 10^{-3} *per opportunity*

Likelihood Modeling

When the failure rate for a system or group of components (such as a process control loop) is not available from plant history, an estimate may be needed. Fault Tree modeling is commonly used to estimate failure frequency or Probability of Failure on Demand. Event Tree modeling is used to evaluate all outcomes from an undesired event or loss event.

Fault Tree Likelihood Modeling

Fault-tree is a technique that allows failure analysis teams to identify all potential causes of an undesired event (Figure 13.5).

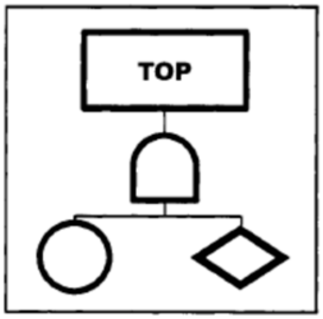


Figure 13.5 Depiction of a Fault Tree Analysis Chart

- A Fault Tree model illustrates the combinations of failures causing one specific failure of interest, the Top Event.
- It is a deductive technique that uses Boolean logic (AND gates, OR gates, etc.) to break down the causes of the Top Event into basic equipment failures and human errors.
- Each of the intermediate causes is further examined for the basic causes of each intermediate event until the boundary of the analysis is reached**.**

The undesired event is the problem the failure analysis team is going to solve. When preparing a fault-tree analysis, the failure analysis team should, from a diagram of the process, mentally place themselves at the point where the failure manifested itself and ask, "What is in me or immediately adjacent to me that can induce this condition?" After answering this question, the events and conditions that can induce the failure are further developed, navigating through the system in a point-to-point manner. If any of the hypothesized causes of a command event could induce the condition, an OR gate should be used. If all of the hypothesized causes going into a command event are required, an AND gate should be used.

There are three categories of symbols used in Fault Tree Analysis: events, gates, and transfer symbols. Events are things that can happen and, either in isolation or in combination with other events, inducing an undesired or loss event. Gates show the relationship between events (if an event can induce an undesired condition by itself or if it must be combined with other events or conditions).

Advanced software is available to aid in performing Fault Tree Analysis.

Example Fault Tree Analysis

Consider a simple system failure analysis for failure of a porch light (Figure 13.6). The top undesired event in the fault tree is that the porch is dark.

The immediate causes of the "Porch is dark" are: loss of electrical supply, both porch bulbs burnt out, failure to turn on switch, and a fuse failure in the porch electric circuit. Wire failures and other causes are much less likely, so they are not included in the fault tree model.

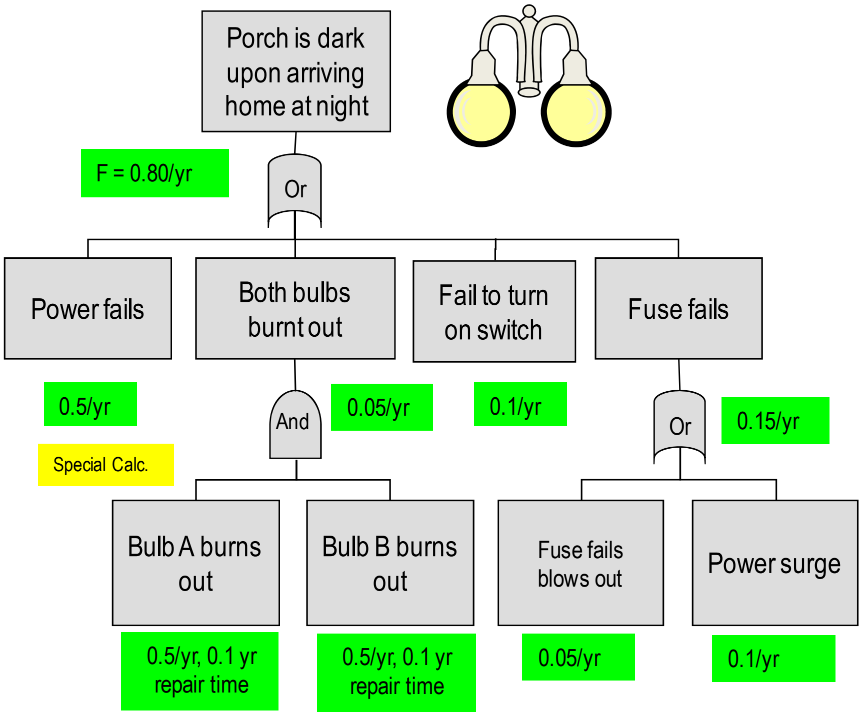


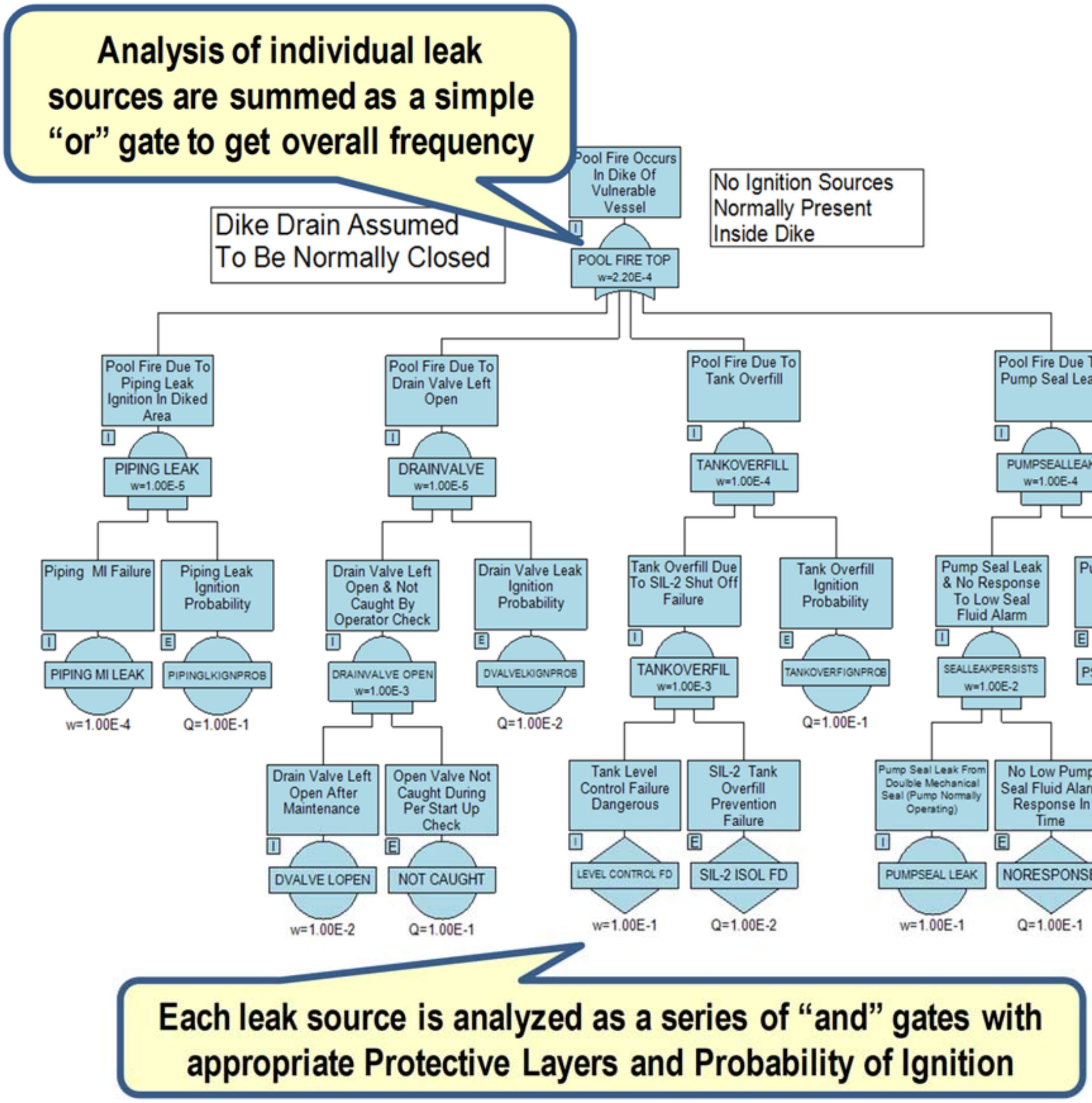
Figure 13.6 Example Fault Tree

The Fault Tree Models the logic that will capture the credible relevant ways the top event can occur. After identifying the immediate causes or events of the top event, the causes for each immediate event are then developed. This process continues until desired stopping point or basic event level is achieved.

Pool Fire Frequency Analysis using Simplified Fault Tree

There are typically many sources for leaks or spills that could ignite and cause a pool fire within the area (or nearby) where the equipment being analyzed is located (Figure 13.7). An estimate of the quantity of fuel present should be made to determine if heat up of vessel contents can occur in a reasonable time period. This time will be different for different vessel fill levels. For Reactive Cases, low Temperature of No Return (TNR) means a smaller, shorter fire could create a problem. Next, fire scenarios for nearby equipment based on the leak sources and ignition probabilities are performed. To determine the overall frequency, each source must be identified and its contribution to the overall frequency for pool fire estimated and summed to a total.

In a simple Fault Tree analysis, each leak scenario is analyzed as a series of “and” gates and the total frequency is estimated by the summation of all scenarios. As a simplification, common-cause failures are not included, so the final result for low frequency scenarios (less than 0.0001/year) may be overly optimistic and should utilize more advance Fault Tree software. Common-cause failures are a single event that may affect several branches in the Fault Tree. Examples of common-cause failure would include power loss disabling several electrical systems simultaneously or a maintenance error resulting in mis-calibration of multiple sensors.


Analysis of individual leak sources are summed as a simple "or" gate to get overall frequency

Each leak source is analyzed as a series of "and" gates with appropriate Protective Layers and Probability of Ignition

Figure 13.7 Example Fault Tree for Pool Fire Exposure to Equipment

Event Tree Likelihood Modeling

The event tree is used to trace the initiating event through its various hazardous consequences (Figure 13.8). It will be simplest for loss events that have few possible outcomes (e.g., toxic releases or internal explosions). Releases that are both flammable and toxic may have many possible outcomes.

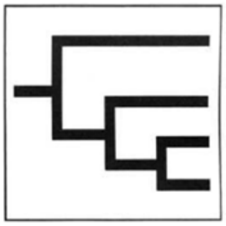


Figure 13.8 Depiction of an Event Tree

- An event tree is a logic model that identifies possible Outcomes following an event.
- An event tree may also be used to evaluate the range of consequences possible (a post loss event application) where loss of containment has occurred.
- An event tree will have only one event that leads to many possible outcomes while a fault tree may have many initiating events that lead to the single top event.

The construction of an event tree is sequential and left-right in the usual convention. The construction begins with an event, and the temporal sequences of occurrence of all relevant safety functions or events are entered. Each branch of the event tree represents a separate outcome or event sequence.

Example Event Tree Analysis for Series of Protective Layers

One initiating event leads to many branches based on success/failure options of each Protective Layer (Figure 13.9). If any Protective function is successfully executed then the ultimate unsafe outcome will not occur (this time). The overall frequency of the undesired Consequence is estimated from the Initiating Event (or sometimes the "Top Event") frequency times the Probability of Failure on Demand for each of the Protective Layers (assuming each is independent).

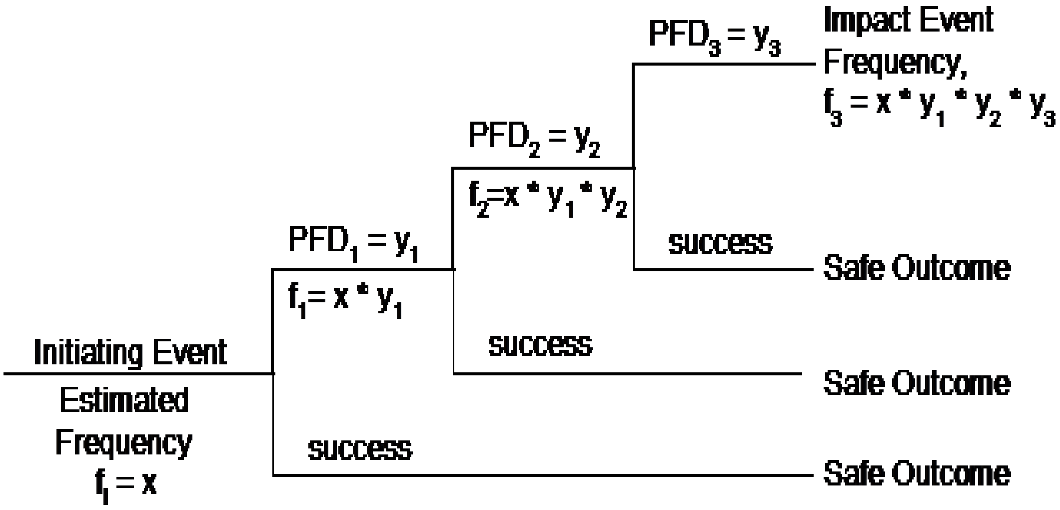


Figure 13.9 Example Event Tree

14. LAYER OF PROTECTION ANALYSIS (LOPA)

Introduction

One method used to determine the tolerable risk is the Layer Of Protection Analysis (LOPA), the Risk Tolerance Step shown in Figure 14.1. A LOPA is a simplified method of risk analysis that provides the middle ground between a qualitative process hazard analysis and a traditional, expensive quantitative risk analysis. The approach analyzes one incident scenario (cause-consequence pair) at a time, using simplifying rules to evaluate initiating event frequency, independent layers of protection failure probabilities, and consequence severity to provide an order-of-magnitude estimate of risk that may be compared to a company's tolerable risk criteria. The primary purpose of LOPA is to determine if there are sufficient layers of protection against an incident scenario. LOPA can be useful in the process development, process design, operational, maintenance, modification and decommissioning life cycle phases.

LOPA builds on qualitative hazard evaluations (such as HAZOP or scenarios gathered from any source, such as historical performance or incident investigation) for identification of scenarios. By analyzing selected scenarios in detail, effective application of LOPA can determine whether the risk posed by each analyzed scenario has been reduced to be within a tolerable risk range. However, if the analyst or team can make a reasonable risk decision using only qualitative methods, then LOPA may not be warranted (see Section 7.2). Qualitative hazard evaluation methods (such as HAZOP) are intended to identify a comprehensive set of incident scenarios and qualitatively analyze those scenarios for the adequacy of safeguards using engineering judgement. This approach is satisfactory for most scenarios. By contrast, LOPA might be used to analyze 10 to 30% of the incident scenarios, and Chemical Process Quantitative Risk Analysis (CPQRA) might be employed to study only 1% of the scenarios in detail. An exception to this is for a facility in a locality or country that requires a QRA.

LOPA assumes all events and protective layers are independent such that frequencies and probabilities are multiplied to obtain an overall frequency which is compared to a Tolerable Frequency to determine if sufficient protective layers are present. Order of magnitude categories for the Initiating Event frequency, Consequence Severity (tolerable frequency), and Probability of Failure on Demand for protective layers are typically used.

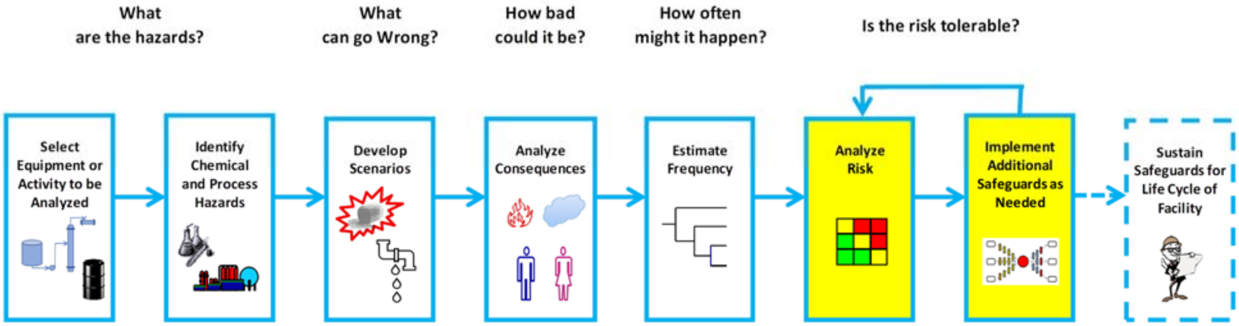


Figure 14.1 The Risk Tolerance Estimation Step in the HIRA Workflow Process

Section Objectives

The following objectives are covered in this section:

- Steps in performing a Layers of Protection Analysis
- LOPA Simplifying Assumptions
- Criteria for Enabling Condition/Conditional Modifiers and Independent Protective Layers
- Determine Scenario Frequency
- Documentation of analysis results

Steps in Performing Layers of Protection Analysis

Figure 14.2 shows the steps n performing a LOPA. The steps are shown as a circle. The process continues as each scenario of concern is analyzed, and because the LOPA may need to be updated as part of the management of change program, or as the initial scenario identification method is revalidated.

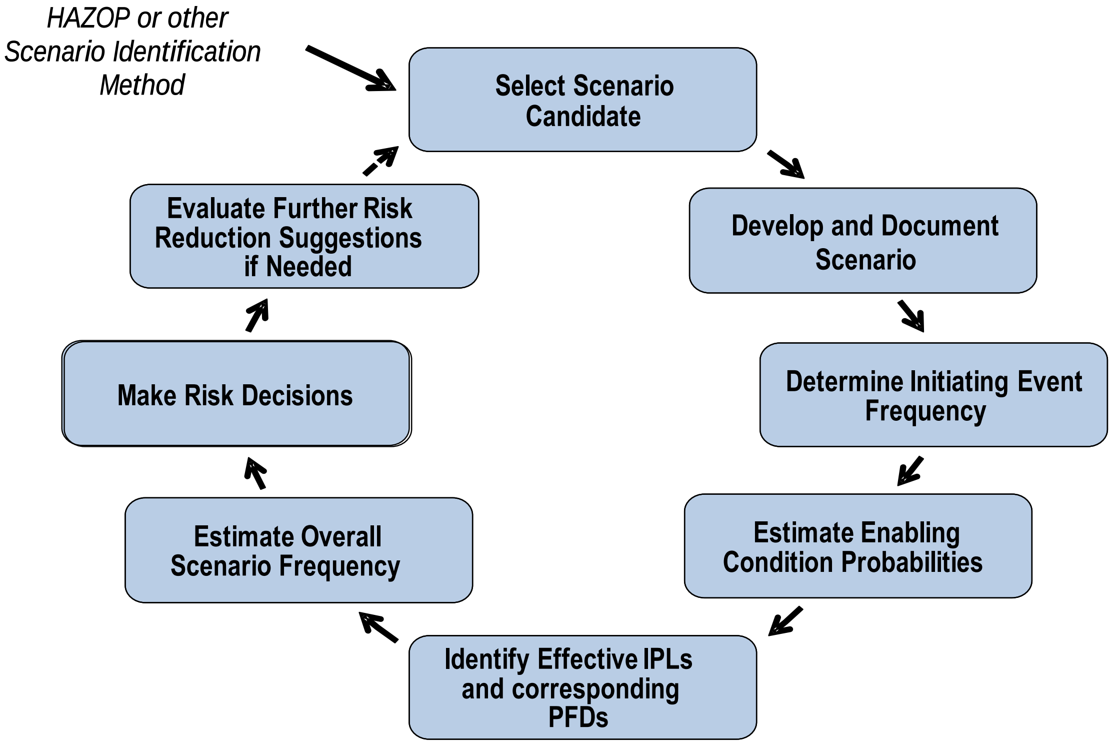


Figure 14.2 Steps in Performing Layers of Protection Analysis

Step 1: Select Scenario Candidate. LOPA scenarios are typically identified during a qualitative Process Hazard Analysis (PHA) but may include scenarios identified from any source including design options or incident evaluations. The LOPA analyst or team screens these scenarios to determine which to include in the analysis. The most common screening method is based on consequence.

Step 2: Develop Scenario. LOPA is applied to one scenario at a time. Once a candidate scenario has been selected, it must be developed to the level where a basic understanding of the events is achieved.

Step 3: Identify Initiating Event Frequency. The Initiating Event must ultimately lead to the Incident given failure of all safeguards and protective layers.

Step 4: Estimate Enabling Condition or Conditional Modifier Probabilities. Background aspects, such as the probability that the process is in a certain mode of operation at the time another failure occurs, are not initiating events but *enabling conditions*. Under LOPA, their probabilities modify the initiating event frequency.

Step 5: Identify Effective Independent Protective Layers (IPLs) and corresponding Probability of Failure on Demand. A scenario may require one or many independent protection layers (IPLs) depending on the severity of the consequence. Only one layer must work successfully for the scenario consequence to be prevented. However, since no layer is perfectly effective, sufficient layers must be provided to render the incident risk as tolerable. During this step effective Safety Instrumented Systems can be identified with their preliminary design specifications and validation methods. Details for determining the PFD, special considerations and validation methods for IPLs are beyond the scope of this Manual.

Step 6: Estimate Overall Scenario Frequency. Combine the Initiating Event frequency times any Enabling Condition or Conditional Modifier probability times the probabilities of failure on demand (PFD) for existing Independent Protection Layers to estimate the overall scenario frequency.

Step 7: Compare Estimated Scenario Frequency to Company Tolerable Frequency. This comparison will help in reaching a decision if scenario risk is adequately managed, a more detailed risk evaluation should be performed, or if additional protective layers should be considered.

Step 8: Evaluate Further Risk Reduction Suggestions as Needed. Determine if there are additional cost-effective Protective Layers that may be appropriate in further reducing process risk.

Selection of LOPA Scenario Candidates.

The analysis team must screen for which scenarios to include in the LOPA analysis. The most common basis is by consequence severity although other criteria may be used depending on a specific company or business requirement. There are several approaches that may be used for evaluation of consequence severity depending on the risk methodology adopted by the organization (company, regulatory agency, etc.). Each approach has advantages and disadvantages.

Release Size/Characterization (example 1500 kg toxic release)

- Simple and easy to use
- Avoids overt appearance that injuries and fatalities are tolerable
- May introduce inconsistency in interpretation and inconsistency of results

Simplified Injury/Fatality Estimates (uses human harm as the consequence of interest)

- People tend to understand consequence in terms of harm rather than release size
- Consequences may be compared directly with corporate risk criteria
- Qualitative estimates of human harm may introduce inconsistencies depending on analysist level of experience

Detailed Injury/Fatality Estimates

- More accurate predicted consequences and comparison to company risk criteria
- Modeling consequences are strongly influenced by exact release conditions
- Complex and time-consuming

Previous sections in this manual describe simplified consequence analysis techniques including methods for estimation of release size, effect zone, building damage and number of people impacted.

Estimation of Consequence Severity

After a Scenario candidate has been selected for LOPA analysis, it must be developed and documented. All important steps for an event sequence to progress from the Initiating Event to an Outcome with undesired Consequence should be documented (Figure 14.3). Companies will often have a specific protocol or format for LOPA documentation.

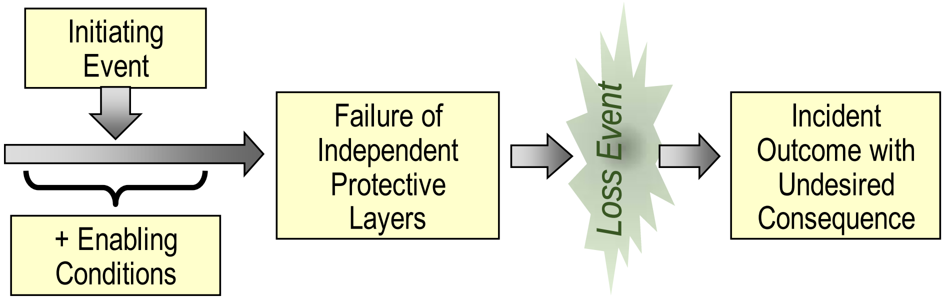
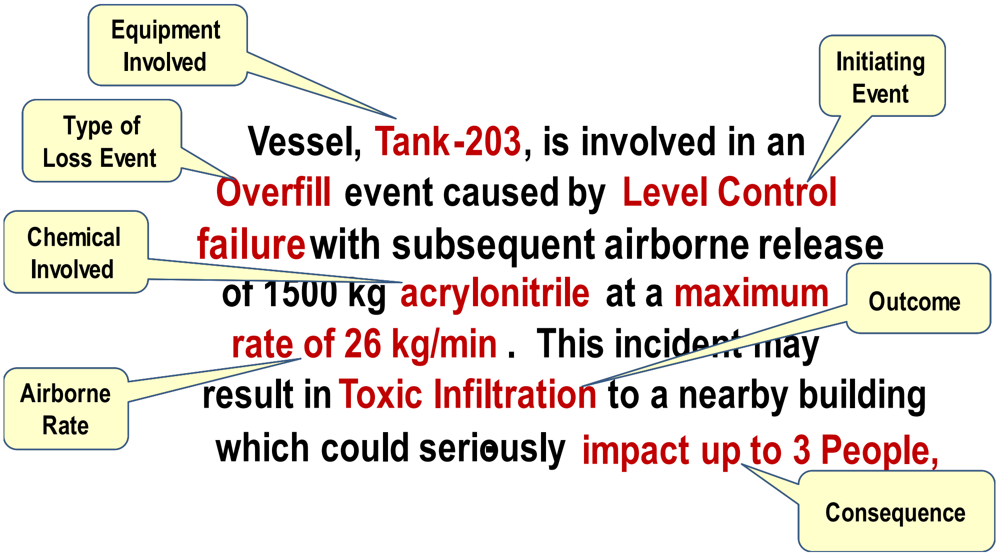


Figure 14.3 Depiction of Typical LOPA Scenario

A well-developed LOPA scenario description should contain information regarding the Initiating Event, Loss Event, and Outcome. Often the equipment involved, chemical, or energy released will be noted. In addition, the consequence severity may be noted. Figure 14.4 provides an example scenario description.



Vessel, Tank-203, is involved in an Overfill event caused by Level Control failure with subsequent airborne release of 1500 kg acrylonitrile at a maximum rate of 26 kg/min. This incident may result in Toxic Infiltration to a nearby building which could seriously impact up to 3 People,

Figure 14.4 – Example LOPA Scenario Description

Initiating Event Frequency

In the context of hazard evaluation procedures, the operational error, mechanical failure, or external event that is the first event in an incident sequence and marks the transition from a normal situation to an abnormal situation. Synonymous with initiating cause.

Initiating Events typically fall into broad categories:

- **External event** including natural phenomena such as earthquakes or lightning strike, and third-party intervention such as impact damage from collision. An external event may also relate to major incidents in adjacent equipment or facilities which may indirectly cause damage or unintended release of hazardous material or energy from the equipment or facility being analyzed.
- **Equipment related failure** includes failure of Basic Process Control, and Equipment or Mechanical Integrity failure due to wear, fatigue, corrosion, or improper maintenance.
- **Human error** including error of omission (something not done) and error of commission (something done wrong).

Management system failures, such as faulty design or inadequate training, often lead to an unsafe acts or conditions that are root causes of an incident. If the root causes were removed, the particular incident would not occur. Root Causes are not typically Initiating Events but may contribute to the frequency by which an Initiating Event occurs. Equipment or Mechanical Integrity failures are sometimes considered as Initiating Events. These situations typically involve chronic issues rather than a short duration process upset. The frequency of integrity failures often depends on the effectiveness of management systems such as maintenance or Mechanical Integrity programs.

Often discrete initiating event frequencies are grouped into a representative set. For control system failures, the overall loop failure rate includes failure of any of several components (the sensor, the control element such as a valve, and the logic solver) and may include other factors such as improper set points, mis-calibration, or operation in manual mode. This simplifies the analysis and improves consistency of risk estimates across the company or business.

Individual companies typically choose initiating event frequency values consistent with the company methods for making risk-based decisions and operating experience. The failure rate selected should be representative of the industry. Where sufficient data does not exist, engineering judgment is often used. Typical initiating event frequency for use in LOPA evaluation are shown in Table 14-1. Note that failure rate is normally assumed constant and “order of magnitude” values are common for LOPA evaluation. Detailed guidance including special conditions for use, quality assurance, and generic validation methods is available in the literature [64].

TABLE 14-1 Typical Frequency Values Assigned to Initiating Events

Initiating event	**Frequency range from literature (per year)**	**Example of a value chosen by a company for use in LOPA (per year)**
Pressure vessel residual failure	10^{-5} to 10^{-7}	1 x 10^{-6}
Piping residual failure, 100 m, full breach	10^{-5} to 10^{-6}	1 x 10^{-5}
Piping leak (10% section), 100 m	10^{-3} to 10^{-4}	1 x 10^{-3}
Atmospheric tank failure	10^{-3} to 10^{-5}	1 x 10^{-3}
Gasket/packing blowout	10^{-2} to 10^{-6}	1 x 10^{-2}
Turbine/diesel engine overspeed with casing breach	10^{-3} to 10^{-4}	1 x 10^{-4}
Third-party intervention (external impact by back-how, vehicle, etc.)	10^{-2} to 10^{-4}	1 x 10^{-2}
Crane load drop	10^{-3} to 10^{-4} per lift	1 x 10^{-4} per lift
Lightning strike	10^{-3} to 10^{-4}	1 x 10^{-3}
Safety valve opens spuriously	10^{-2} to 10^{-4}	1 x 10^{-2}
Cooling water failure	1 to 10^{-2}	1 x10^{-1}
Pump seal failure	$10^{-1}$to 10^{-2}	1 x10^{-1}
Unloading/loading hose failure	1 to 10^{-2}	1 x10^{-1}
BPCS instrument loop failure	1 to 10^{-2}	1 x10^{-1}
Regulator failure	1 to 10^{-2}	1 x10^{-1}
Small external fire (aggregate causes)	10^{-1} to 10^{-2}	1 x10^{-1}
Large external fire (aggregate causes)	10^{-2} to 10^{-3}	1 x 10^{-2}
LOTO (lock-out tag-out) procedure failure (overall failure of a multiple element process)	10^{-3} to 10^{-4} per opportunity	1 x 10^{-3} per opportunity
Operator failure (to execute routine procedure; well trained, unstressed, not fatigued)	10^{-1} to 10^{-3} per opportunity	1 x 10^{-2} per opportunity

Note that Initiating Event frequency is expressed as failures “per year”. For frequencies expressed a failure “per opportunity” or “per lift”, values must be multiplied by opportunities per year or lifts per year to obtain the proper frequency. This may be as simple as counting the number of opportunities per year. Or, it may require more complex techniques as Fault Tree of Event Tree.

Human Reliability

A human error is an action that fails to meet a criteria of acceptability defined for a system. The error may be a physical action (such as closing a valve) or a cognitive action (such as problem diagnosis or decision making). Human error is either a cause or a contributor in virtually every process incident. It can occur at any stage in the chemical manufacturing process; research, design, construction, commissioning, operating or demolition. The human error can cause the incident immediately (active error) or exist for many years before causing the incident (latent error).

Factors impacting Human Reliability include:

- Familiarity with the task
- Complexity of the task (including problem diagnosis and decision making)
- Time to complete
- Human – Machine Interface
- Work Environment – stress, fatigue, training, etc.

If these items are clearly defined and well documented, identification of appropriate controls and mitigations (existing or proposed to be added as an upgrade to close the gap), as well as subsequent reviews, of the case will be easier.

Enabling Conditions and Conditional Modifiers

An *Enabling Condition* is not a failure, error or a protection layer but makes it possible for an incident sequence to proceed to a consequence of concern. It consists of a condition or operating phase that does not directly cause the scenario, but that must be present or active in order for the scenario to proceed to a loss event; expressed as a dimensionless probability.

Time at Risk - One general category of enabling condition involves the concept of "time at risk," when an incident sequence may only be realized a certain fraction of the time when conditions are right for the event sequence to progress to a loss event. One common time-at-risk enabling condition is a sufficiently low ambient temperature to enable process or utility lines or instrumentation to freeze up following failure of designed freeze protection. Another type of time-at-risk enabling condition is when a process must be in a certain part of a non-continuous operation when a failure occurs for the incident sequence to be able to proceed to a loss event. (Note that a time at risk enabling condition may not be appropriate for *unrevealed failures*. For example, if an unloading hose may have been damaged at any time but only leaks when in use and while personnel may be present, a time at risk probability would not be considered.)

A *Conditional Modifier* is one of several possible probabilities included in scenario risk calculations, generally when risk criteria endpoints are expressed in impact terms (e.g., fatalities) instead of in primary loss event terms (e.g., release, vessel rupture). Conditional modifiers include, but are not limited to: probability of a hazardous atmosphere, probability of ignition, probability of explosion, probability of personnel presence, probability of injury or fatality, and probability of equipment damage or other financial impact.

Probability of Personnel Presence - is a conditional modifier that relates to the fraction of time people are likely to be within an effect area (also termed impact zone) when a loss event occurs. The probability of personnel presence should account for all personnel in the effect area, including routine operations, transient or short-term operations such as start-ups, maintenance work, anticipated abnormal situations and periods of time in which a larger group of people may be present. Personnel in adjacent units will also need to be considered if the event is large enough to affect more than the immediate area. The probability of personnel presence must be independent of the scenario being evaluated. This is often not the case when operator response to an alarm is involved or the presence of an operator would be required for the initiating event to occur, such as an error made during a loading or unloading operation.

Probability of Ignition - The LOPA conditional probability of a flammable vapor, explosible dust cloud or combustible mist igniting or an uncontrolled reaction (such as an explosive decomposition) initiating is treated in various ways by different companies. A probability of ignition or initiation may be associated with two basic scenario types:

- Igniting a flammable or explosible atmosphere inside process equipment, resulting in an internal combustion reaction (usually a deflagration; transition to a detonation may be possible under the right conditions) that may or may not breach the primary containment.
- Igniting flammable vapors or an ignitable dust cloud external to process equipment, resulting in a flash fire, pool fire, jet fire and/or vapor cloud explosion.

The probability of ignition of a flammable or explosible atmosphere *inside process equipment* will not always warrant a conditional modifier. Scenarios involving ignition inside process equipment must be carefully evaluated on a case-by-case basis. When there is normally a flammable or explosible atmosphere inside the process equipment, and an internal deflagration will be initiated as soon as a sufficiently energetic ignition source is present, then the presence of the ignition source is the initiating event (such as failure of the grounding and bonding system or where failure of mechanical components may result in hot surfaces).

Many of the same internal ignition considerations also apply to *ignition outside of process equipment*, such as following an atmospheric release or a loss of primary containment (LOPC) event. Other factors needing to be considered when assessing the probability of ignition include:

- Size of the flammable vapor cloud or ignitable dust cloud (larger releases may extend beyond electrical classification boundaries and involve more potential ignition sources)
- Duration of the release (since probability of ignition by e.g. vehicle traffic will increase as the duration of the release is extended)
- Overall number and strength of potential ignition sources
- Minimum ignition energy of the flammable vapors or ignitable dust.
- Particle size of ignitable dust.

For simplicity, the strength of all ignition sources may be assumed high such that the probability of ignition becomes primarily a function of the size of the flammable cloud, minimum ignition energy of the material and particle size of ignitable dust (Figure 14.5).

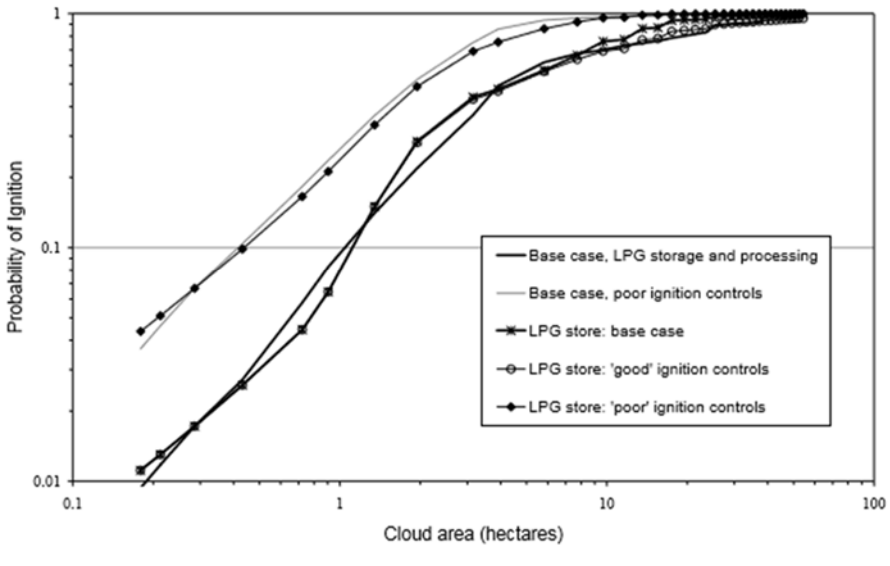


Figure 14.5 – Example Probability of Ignition versus Flammable Cloud Area for LPG release [65]

CCPS has developed a software tool for estimating the probability of ignition given certain conditions [66].

Probability of equipment or vessel rupture - The probability of internal vessel overpressurization exceeding the ultimate strength of the vessel may have a probabilistic aspect to it that can be treated using a conditional modifier. Perhaps most of the time the internal pressure would only be expected to exceed the vessel design pressure by an amount sufficient to be still within the safety margin of the vessel's ultimate strength (e.g., > 1.5x but < 2x the MAWP), but there may be a certain probability that the burst pressure would be exceeded (e.g., due to undetected corrosion, mechanical flaws, weakening by previous process deviations, etc.) and a vessel rupture would result. Most LOPAs treat this on more of a deterministic basis, by comparing the maximum expected internal pressure to the design pressure (MAWP) to determine the expected result, which may be a lesser consequence severity rather than a lower likelihood of the worst-case vessel rupture.

A *probability of injury or fatality* conditional modifier relates to the probability that, given a person is within an effect area (impact zone) as determined in the preceding section, a serious injury or fatality would actually result. This conditional modifier cannot be determined independently of the probability of personnel presence, since it will be affected by the endpoint chosen for calculating the effect area. Also, the analyst needs to ensure consistency with the consequence severity as this conditional modifier may already be inherent in the value for tolerable frequency. (For example, if consequence severity assumes a low probability of a single fatality equivalent to an injury or the number of people within an occupied building is estimated from vulnerability of the occupants based on damage, this modifier would not be used.)

An enabling condition or conditional modifier is expressed as a probability. The combination of the enabling condition or conditional modifier probability with the initiating event frequency must always be a frequency that represents the times per year an abnormal situation would be encountered that could lead to a loss event. Most companies provide guidance on estimating the frequency to achieve consistency in LOPA results. Note that many LOPA scenarios will not have enabling conditions or conditional modifiers. Detailed guidance on when use of enabling conditions or conditional modifiers described in more detail in the literature [67].

Protection Layers

A scenario may require one or many protection layers depending on the process complexity and potential consequence severity. For a given scenario, only one protection must work successfully for the consequence to be prevented. However, since no single protective layer is perfectly effective, sufficient layers must be provided to render the risk associated with the scenario tolerable. Figure 14.6 illustrates the concept of using "layers" of protection, as if they were layers of an onion (sometimes referred to as an "onion diagram"). In addition, there are many types of administrative and engineering barriers to help prevent or mitigate a scenario, some of which may be more effective than others in specific circumstances.

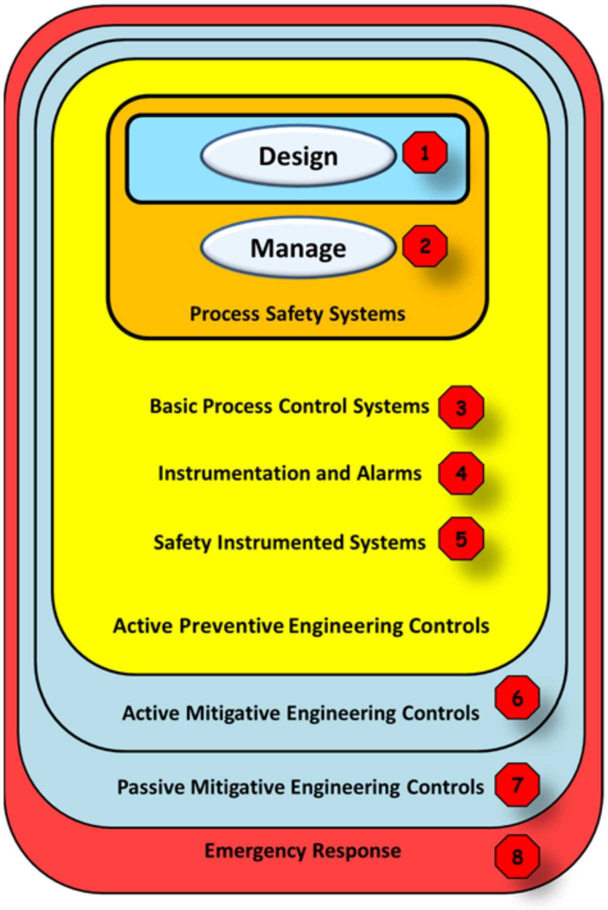


Figure 14.6 An Example of Protection Layer Hierarchy ([68], Adapted from [69]]

The hierarchy of these engineering and administrative controls, represented as "Stop" signs for each barrier in Figure 14.6, is as follows [68] [69]:

1. **Design**: These engineering controls are based on the basic process chemistry and design. The process safety information is used to design the protection layers that ensure safe process operation, including design of the instrumentation to control and monitor the process, helping minimize the likelihood of an initiating event that could lead to an incident. Inherently safer design principles are used in this protection layer to help reduce the need for additional protection layers [70].

Manage Risk with preventive and mitigative barriers:

2. **Process Safety Systems:** These administrative controls, the process safety and risk management systems, which have been designed to manage safe operation of facilities handling hazardous materials and energies. The process safety systems, one of the three foundations of an effective process safety program, include several elements, such as hazards identification and risk analyses, equipment and asset integrity, management of change, training, and auditing.
3. **Basic Process Control Systems:** These engineering controls are designed and used to ensure quality products and to operate the processes safely.

4. **Instrumentation and Alarms.** These engineering controls are designed to detect deviations from the normal, expected operating parameters. Once deviations are detected, automatic and/or human responses are required to keep the process operating in a safe state. These responses may involve emergency or safe process shutdowns.
5. **Safety Instrumented Systems (SIS):** These independent engineering controls are designed as the “last line of defense” before a hazardous release - a Loss of Primary Containment (LOPC). The SIS responses may involve emergency or safe process shutdowns, as well.
6. **Active Mitigative Engineering Controls:** These engineering controls are designed to reduce or mitigate the consequences of a hazardous release. They include pressure relief devices, flares, and scrubbers.
7. **Passive Mitigative Engineering Controls**: These engineering controls are designed to reduce or mitigate the consequences of a hazardous release. They include dikes and catch tanks.
8. **Emergency Response:** Emergency response systems are the engineering and administrative controls designed to contain, reduce and mitigate the consequences of the hazardous release. The engineering controls include foam systems; the administrative controls include emergency response plans with trained internal and/or emergency responders. There are two aspects to emergency response which are considered: 1) Internal – facility resources only; and 2) External – with both internal and external, community resources.

An Independent Protection Layer (IPL) is a device, system, or action that is capable of preventing a scenario from proceeding to the undesired consequence without being adversely affected by the initiating event or the action of any other protection layer associated with the scenario. The effectiveness of an IPL is quantified in terms of its probability of failure on demand (PFD). Safeguards that do not meet the requirements of an IPL are important as part of the overall risk reduction strategy and good engineering practice. All IPLs are safeguards but not safeguards are IPLs.

The general requirements for IPLs include:

- Is independent of other IPLs and the Initiating Event
- Functions in a way that prevents or mitigates the consequence of concern
- Has sufficient integrity to be capable of completely preventing the scenario consequence
- Can be relied upon to operate as intended, under stated conditions, for a specified period of time
- Can be audited to ensure that the management systems to support the IPL are in place and effective
- Is protected by access security, with controls in place to reduce the change of impairment
- Is covered by a management of change process to review, approve, and document changes.

Independence is a basic tenet of LOPA, although absolute independence is not truly achievable. Plants generally have common utilities, a single maintenance staff, common calibration instruments, and vendors who supply similar components to those in use. IPLs should be sufficiently independent such that the degree of interdependence is not statistically significant. A common cause failure is when a single event may result in failure of more than one device, procedure or system. An example is loss of power which could cause failure of multiple sensing instruments as well as electronic equipment such as pumps or agitators. Another example is the sharing of control loops between a protective layer and initiating event such as level control and high level shut off utilizing the same sensing instrument or same shut off valve.

For a device, system or action to be credited as an IPL, it must be *effective* in preventing the undesired consequence associated with the scenario. The IPL design basis must apply to the specific scenario for which it is credited and is valid for the mode of operation being analyzed (normal, start-up, or shut-down). For example, a relief device for a storage vessel may have been sized for fire exposure but be inadequate for a back-flow scenario. The IPL must also be able to accomplish its function in sufficient time to prevent the consequence of concern and perform reliably. When operator response is part of the IPL, there must be a well-written procedure and an effective training program to ensure that operators understand the hazard and how to respond to the initiating event, alarm, or emergency situation, as well as enough time to perform the response action to prevent the consequence of concern from occurring

Auditability reflects the ability of an organization to inspect procedures, records, previous validation assessments, and other documented information to ensure that design, testing, maintenance, and operation continue to conform to expectations. Maintenance systems are periodically audited to verify that the existing administrative processes ensure that maintenance is performed as required, design is performed by qualitied personnel following accepted engineering practices, and documentation is maintained. The Management of Change (MOC) process is audited to ensure changes to materials, operating parameters, equipment, procedures and organization are properly reviewed and documented, and that any action items generated have been completed.

Passive Protective Layers

A passive IPL is not required to take an action in order for it to achieve its function in reducing risk. Such IPLs achieve the intended function if their process or mechanical design is correct and if constructed, installed and maintained correctly. In general, crediting of a passive IPL applicable in the consequence severity can only result from the failure of the IPL to be effective. For example, if the scenario states that “flammable liquid spills into a diked area”, then the consequence severity has already assumed that the dike is in place and effective and would not be credited as an IPL. If the consequence of the scenario were defined as environmental contamination if the spill is not contained, then it may be appropriate to credit the dike as an IPL. Another example would be pool fire exposure to a vessel where fire-proof insulation has already been assumed in the estimation of fire heat input and so the insulation would not be credited as an IPL. Examples of Passive IPLs include:

- Flame, Deflagration or Detonation Arrester
- Overflow Lines to prevent overpressure
- Dikes, Berms and Bunds
- Remote Impoundment
- Fire-Resistant Insulation or Cladding
- Blast-Resistant Buildings
- Blast Walls or Explosion Barriers

Table 13.2 presents typical PFD values assigned to passive protection layers.

Active Protection Layers

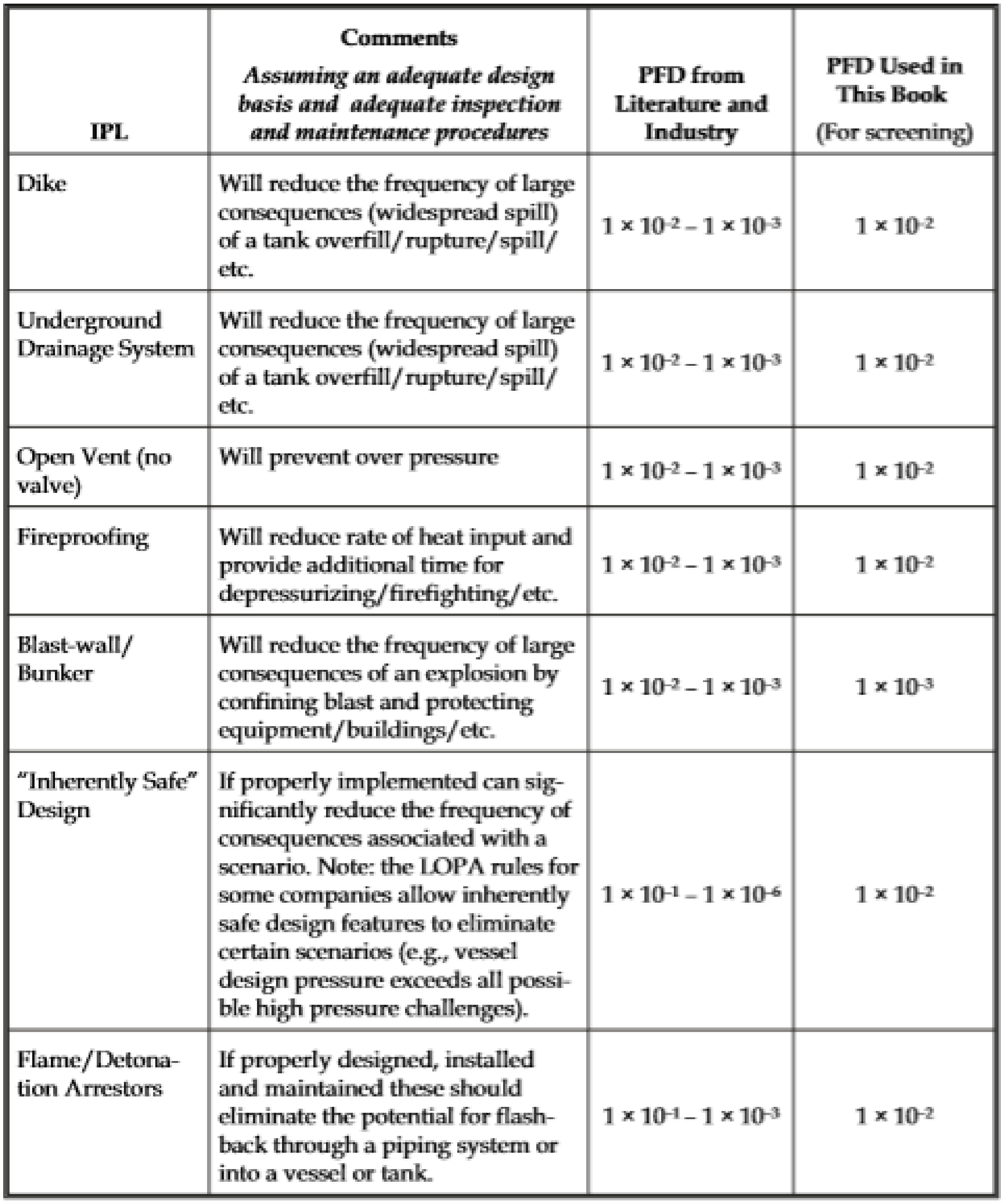
Active IPLs ensure the functional safety of the process by taking action to prevent the scenario from occurring. This action may be mechanical-only in nature or may use a combination of instruments, humans, and mechanical devices. Examples include:

- Basic Process Control System (BPCS)

- Safety Instrumented System (SIS)
- Pressure Relief Systems
- Vacuum Breaker
- Excess Flow Valve
- Pressure Regulator

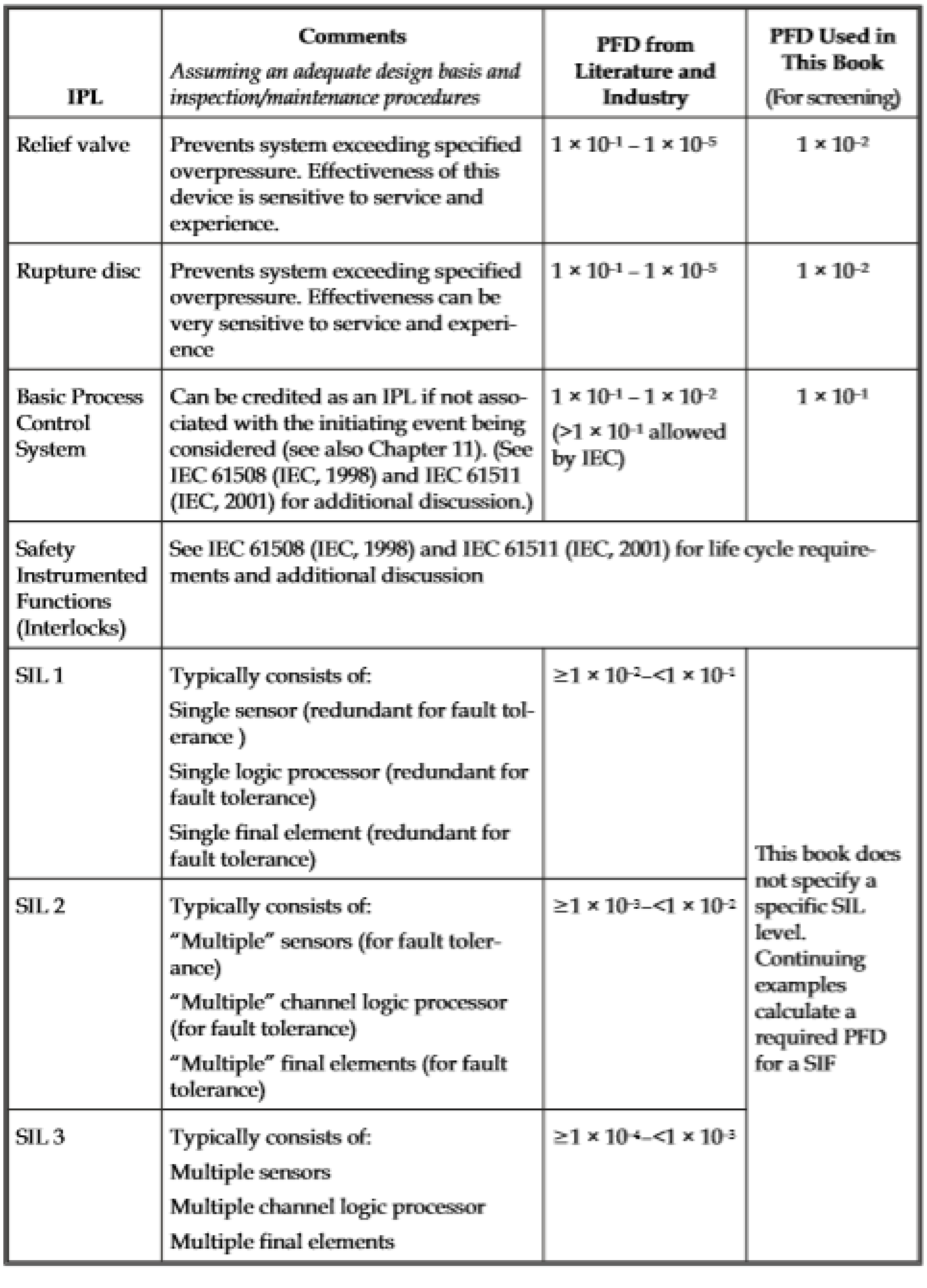
Table 13.3 presents typical PFD values assigned to active protection layers. In some cases, successful action of a protective layer may create another scenario. For example, a properly designed pressure relief device would prevent rupture of a vessel but cause a release to atmosphere of potentially hazardous materials (typically a less severe consequence) upon activation. Both scenarios need to be considered with credit of the relief device for preventing rupture but exclusion of the relief device credit for evaluation of the atmospheric release or effluent scenario.

TABLE 13-2 Typical PFD Values Assigned to Passive IPLs [64]



IPL	Comments *Assuming an adequate design basis and adequate inspection and maintenance procedures*	PFD from Literature and Industry	PFD Used in This Book (For screening)
Dike	Will reduce the frequency of large consequences (widespread spill) of a tank overfill/rupture/spill/etc.	$1 \times 10^{-2} - 1 \times 10^{-3}$	1×10^{-2}
Underground Drainage System	Will reduce the frequency of large consequences (widespread spill) of a tank overfill/rupture/spill/etc.	$1 \times 10^{-2} - 1 \times 10^{-3}$	1×10^{-2}
Open Vent (no valve)	Will prevent over pressure	$1 \times 10^{-2} - 1 \times 10^{-3}$	1×10^{-2}
Fireproofing	Will reduce rate of heat input and provide additional time for depressurizing/firefighting/etc.	$1 \times 10^{-2} - 1 \times 10^{-3}$	1×10^{-2}
Blast-wall/Bunker	Will reduce the frequency of large consequences of an explosion by confining blast and protecting equipment/buildings/etc.	$1 \times 10^{-2} - 1 \times 10^{-3}$	1×10^{-3}
"Inherently Safe" Design	If properly implemented can significantly reduce the frequency of consequences associated with a scenario. Note: the LOPA rules for some companies allow inherently safe design features to eliminate certain scenarios (e.g., vessel design pressure exceeds all possible high pressure challenges).	$1 \times 10^{-1} - 1 \times 10^{-6}$	1×10^{-2}
Flame/Detonation Arrestors	If properly designed, installed and maintained these should eliminate the potential for flashback through a piping system or into a vessel or tank.	$1 \times 10^{-1} - 1 \times 10^{-3}$	1×10^{-2}

TABLE 13-3 Typical PFD Values Assigned to Active IPLs [64]



IPL	Comments *Assuming an adequate design basis and inspection/maintenance procedures*	PFD from Literature and Industry	PFD Used in This Book (For screening)
Relief valve	Prevents system exceeding specified overpressure. Effectiveness of this device is sensitive to service and experience.	$1 \times 10^{-1} - 1 \times 10^{-5}$	1×10^{-2}
Rupture disc	Prevents system exceeding specified overpressure. Effectiveness can be very sensitive to service and experience	$1 \times 10^{-1} - 1 \times 10^{-5}$	1×10^{-2}
Basic Process Control System	Can be credited as an IPL if not associated with the initiating event being considered (see also Chapter 11). (See IEC 61508 (IEC, 1998) and IEC 61511 (IEC, 2001) for additional discussion.)	$1 \times 10^{-1} - 1 \times 10^{-2}$ ($>1 \times 10^{-1}$ allowed by IEC)	1×10^{-1}
Safety Instrumented Functions (Interlocks)	See IEC 61508 (IEC, 1998) and IEC 61511 (IEC, 2001) for life cycle requirements and additional discussion		
SIL 1	Typically consists of: Single sensor (redundant for fault tolerance) Single logic processor (redundant for fault tolerance) Single final element (redundant for fault tolerance)	$\geq 1 \times 10^{-2} - < 1 \times 10^{-1}$	This book does not specify a specific SIL level. Continuing examples calculate a required PFD for a SIF
SIL 2	Typically consists of: "Multiple" sensors (for fault tolerance) "Multiple" channel logic processor (for fault tolerance) "Multiple" final elements (for fault tolerance)	$\geq 1 \times 10^{-3} - < 1 \times 10^{-2}$	
SIL 3	Typically consists of: Multiple sensors Multiple channel logic processor Multiple final elements	$\geq 1 \times 10^{-4} - < 1 \times 10^{-3}$	

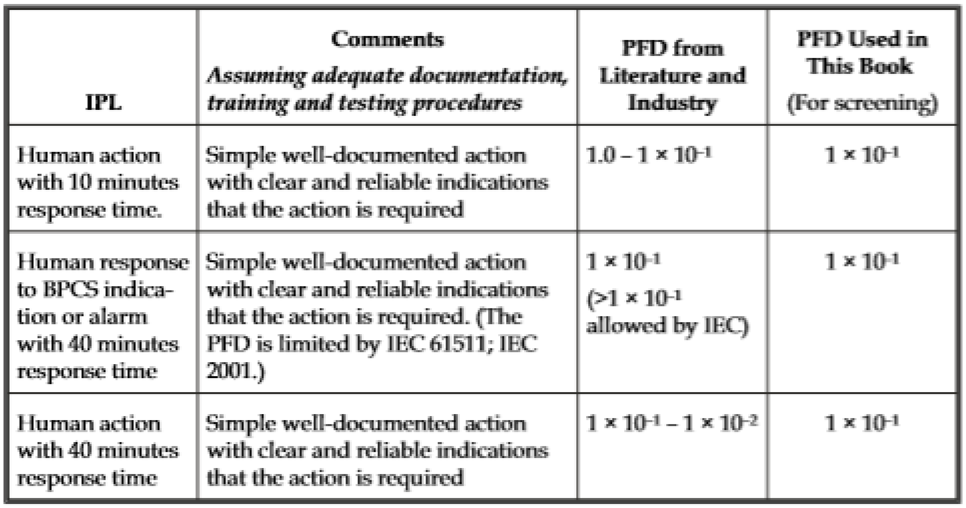
An IPL is considered Independent if it is not adversely affected by the initiating event or any other protection layer associated *within the scenario*. In some cases, however, *the same IPLs may be used to manage related scenarios* such that the PFD should be adjusted. If there are two scenarios with the same loss event and incident outcome but different initiating events, the PFD may need to be adjusted. For example: if there are two means for overfill of a tank, one a BPCS level control failure (at a frequency of 0.1 per year) and the other a human error, such as unloading into the wrong tank (at a frequency of 0.1 per year); then total demand on IPLs shared between these scenarios is 0.2 per year. At least one of the shared IPLs should be considered a PFD of 0.2 rather than 0.1 (or 0.02 rather than 0.01, etc.). This "correction" is typically ignored when using only order of magnitude assuming there is sufficient conservatism in the analysis. If, for example, the shared IPL is a SIS loop, then one could specify a PFD of 0.05 rather than 0.1 for a SIL-1 to accommodate.

Human Action IPLs

> "The fault, dear Brutus, is not in our stars,
>
> But in ourselves, that we are underlings."
>
> Shakespeare, W., *Julius Caesar, Act 1, Scene 2*.

Human IPLs rely on operators or staff to take action to prevent an undesired consequence, either in response to an alarm, following a routine check of the system, or while performing validation checks that are part of an established operating procedure. The general requirements for crediting human actions as IPLs are the same as other IPLs. The Probability of Failure on Demand (PFD) for Human IPLs includes the probability of failure of an incorrect or ineffective human response as well as the PFDs for and instrumentation or equipment used to detect the process deviation or take action to return the process to a safe state. Table 13.4 presents some typical PFD values for human response.

Table 13.4 Typical PFD Values Assigned to Human IPLs [64]



IPL	Comments *Assuming adequate documentation, training and testing procedures*	PFD from Literature and Industry	PFD Used in This Book (For screening)
Human action with 10 minutes response time.	Simple well-documented action with clear and reliable indications that the action is required	$1.0 - 1 \times 10^{-1}$	1×10^{-1}
Human response to BPCS indication or alarm with 40 minutes response time	Simple well-documented action with clear and reliable indications that the action is required. (The PFD is limited by IEC 61511; IEC 2001.)	1×10^{-1} ($>1 \times 10^{-1}$ allowed by IEC)	1×10^{-1}
Human action with 40 minutes response time	Simple well-documented action with clear and reliable indications that the action is required	$1 \times 10^{-1} - 1 \times 10^{-2}$	1×10^{-1}

Preventive versus Mitigating Protective Layers

When considering how an IPL will reduce the risk associated with a scenario it is important to maintain a clear understanding of what the IPL is intended to do. Some IPLs are intended to prevent the event sequence from reaching the loss event, thus preventing the scenario. Mitigating IPLs are intended to reduce the severity of the scenario consequence. Furthermore, Preventive IPLs may be categorized into two groups: those that act to prevent the occurrence of the Initiating Event (Pre-Initiating IPL) and those that act to interrupt the event sequence after the Initiating Event but before a loss event has occurred.

For example, a scenario involving overfill of vessel during batch transfer resulting in a release to the atmosphere may be several possible causes or Initiating Events such as: level control loop failure (sensor or final element) or by-pass valve inadvertently left open (Human Error). One might consider placing administrative controls (such as a lock or car seal) on the by-pass valve as an IPL. This prevents the specific Initiating Event (Human Error) from occurring and would be considered Pre-Initiating. It is not effective for preventing the Level Control failure. However, a High-Level interlock with a shut-off value (not used for level control) would prevent the event sequence following failure of the level control from reaching the loss event and considered a Post-Initiating IPL. If the shut-off valve is physically located between the by-pass valve and the vessel, this high-level interlock would also prevent the scenario where the Initiating Event is inadvertent opening of the by-pass valve. Only one IPL would be needed to manage both scenario cases.

A convenient way to represent a group of scenarios with the same Loss Event (but various possible Initiating Events and Incident Outcome) is a “Bow Tie Diagram” (Figure 14.7). This diagram helps the analysis team understand how the various IPLs are intended to work and how a minimum number of IPLs may be utilized to manage a group of release scenarios.

- The center of a “bow tie” diagram is the Top Event or Loss Event.
- To the left are possible causes (or threats) represented as a Fault Tree.
- To the right are potential Consequences represented as an Event Tree.
- Barriers that prevent the event sequence from occurring are shown to the left while mitigating barriers shown on the right.

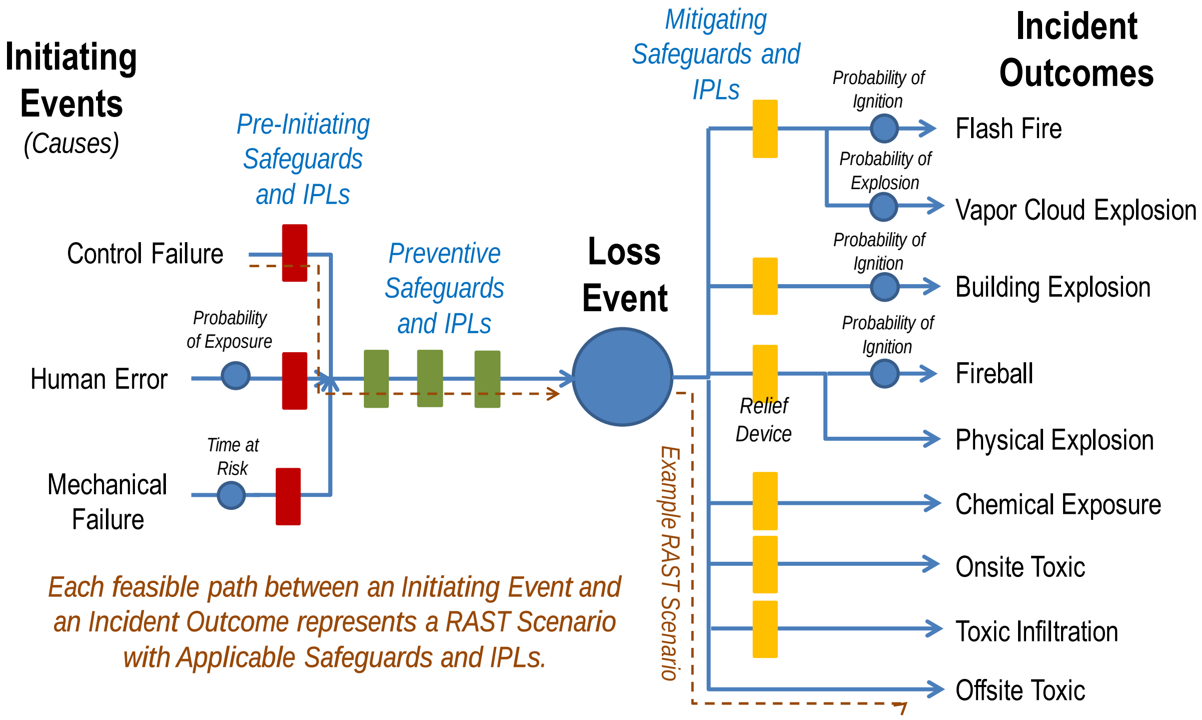


Figure 14.7 Generic Bow-Tie Diagram for LOPA Scenarios

Domino Effects

The term domino effect denotes a chain of events, or situations, in which a fire/explosion or other incident in one unit (or equipment item) in a facility causes secondary and higher order incidents in other units (or equipment). Most of the risk assessment study deals with incidents within one of the units of a manufacturing facility. But, often, an incident in one unit causes a secondary incident in a nearby unit, which in turn may trigger a tertiary incident, and so on. The probability of occurrence of such 'domino' or 'cascading' effects increase with increasing congestion in industrial complexes.

Incidents within one process unit that may affect another unit as the likelihood is very small are rarely evaluated. However, several situations with potentially catastrophic impacts have drawn more attention, including:

- Secondary Dust Explosions
- Impact of Pool Fire on Nearby Equipment
- Potential for Physical Damage to Nearby Equipment from Explosion Debris

Fault Tree and Event Tree Analysis can be used to estimate the frequencies associated with Domino Effects. In Fault Tree, the Top Event would be the secondary incident.

Estimating Scenario Frequency and Risk Decisions

The general procedure for estimating frequency for a scenario with a specific consequence endpoint is multiplication of the Initiating Frequency times the probability of any applicable Enabling Condition or Conditional Modifier times the product of all applicable IPLs. Typically, only order-of-magnitude values are used in Equation 14-1.

$$f_i^{\text{Consequence}} = f_i^{\text{Initiating Event}} \text{ X } p_i^{\text{Enabling Factors}} \text{ X } \prod_{j=1}^{j} \boldsymbol{PFD}_{ij}^{\text{IPL}} \qquad \text{Equation 14-1}$$

where:

f_i denotes frequency of scenario i in year^{-1} a

p_i denotes probability of a specific enabling factor for scenario i.

The Enabling Factor probabilities may include Probability of Ignition, Probability of Personnel within the Impact Zone, Probability of Injury, etc. but must be appropriate for the scenario. The Initiating Event frequency, Enabling Factor Probability and the Tolerable Frequency should represent a consistent set of values among analysis teams. If for example, an Initiating Event frequency accounts for infrequent execution of a procedure (Human Error), then a Time at Risk enabling condition is already included in the Initiating Event and a separate enabling probability should not be taken. If for example, an Injury consequence severity (based on a low fatality probability) is accounted for in the Tolerable Frequency, then a Probability of Injury should not be included in the scenario frequency.

As an example, consider the scenario described previously:

Tank-203 is involved in an Overfill event caused by Level Control failure with airborne release of 1500 kg acrylonitrile and potential for Toxic Infiltration to a nearby building resulting in up to 3 People seriously impacted (Table 13.5.)

Table 13.5. Risk Analysis of Tank Overflow Scenario

	Description	Probability	Frequency
Tolerable Frequency	Onsite Toxic Release with up to 3 fatalities		10^{-5}/year
Initiating Event	Level Control failure		10^{-1}/year
Enabling Condition/ Conditional Modifier	Presence Factor impacted by wind direction, time of day, etc.	1	
Independent Protection Layers	SIL-2 High Level Interlock shutting off Feed Pump	10^{-2}	
	SIL-1 Gas Detector in dike sump shutting off emergency Block Valve	10^{-1}	
	High Building Concentration Alarm with Shut-off of Building Ventilation System	10^{-1}	
Frequency of scenario mitigated consequences			10^{-5}/year

Estimation of Scenario Frequency

Sometimes the negative $\log_{10}$ of the Frequency or Probability are used as Likelihood Factors representing the order-of magnitude values. For example, a frequency of 10^{-3} per year would be a factor value of 3. Using this simple factor approach, the number of IPLs needed may be easily determined using Equation 14-2 or Equation 14-3:

$$\mathbf{N_{IPLs} = \mathit{f}_i^{Initiating\ Event} \times \mathit{p}_i^{Enabling\ Factors} / \mathit{f}_i^{Tolerable}} \qquad \text{Equation 14-2}$$

or

$$\mathbf{N_{IPLs} = Tolerable\ Frequency\ Factor - Initiating\ Event\ Factor - Enabling\ Factors} \qquad \text{Equation 14-3}$$

In this example where the tolerable frequency is 10^{-5} per year or a factor value of 5 and the Initiating Event Frequency X Enabling Probabilities is 10^{-1} per year or a factor value of 1. The number of IPLs needed is 5 – 1 = 4.

The consequence frequency for the scenario is compared to the company's tolerable risk frequency for the same consequence (commonly represented by a risk matrix). If the consequence frequency is at or below the tolerable frequency, the scenario is considered adequately managed. If the consequence frequency is higher than the tolerable frequency, then a risk decision is needed:

- Repeat the Risk Analysis using more detailed Chemical Process Quantitative Risk Analysis (CPQRA) methods (such as more sophisticated consequence analysis tools, fault tree analysis, or full QRA) to obtain more accurate results
- Implement additional IPLs to reduce the frequency to a tolerable level
- Accept the risk
- Discontinue the activity.

LOPA Documentation

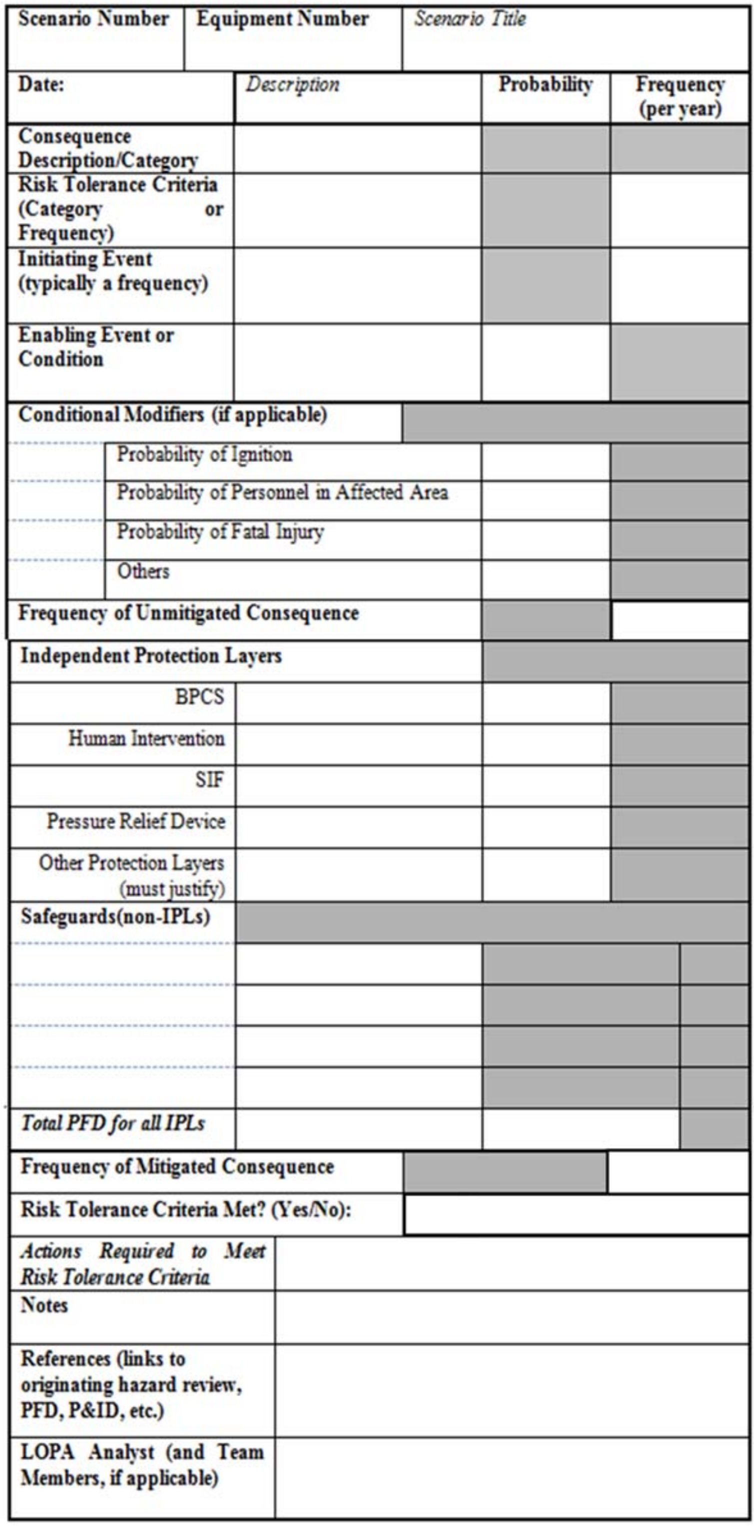
There are several formats for which LOPA scenarios may be documented. Documentation should be sufficiently clear such that future risk reviews will easily identify the basis for the analysis. Where possible identification numbers of other criteria for equipment, procedures, and instrumentation should be noted.

Figure 14.8 shows a suggested format [6]. It allows for clear documentation of a given cause-consequence pair and is easily used in a spreadsheet.

Limitations of LOPA

- Risk comparisons of scenarios are valid only if the same LOPA methods and same tolerance criteria are used. The numbers generated by a LOPA analysis are not precise values of the risk of a scenario (this is also a limitation of detailed quantitative risk analysis).
- LOPA is a simplified approach and should not be applied to all scenarios. The amount of effort required to implement LOPA may be excessive for some risk-based decisions or overly simplistic for others.
- LOPA requires more time to reach risk-based decisions that qualitative methods (such as HAZOP or What-If Analysis). This extra time is offset by improved risk decisions and consistency of results among evaluation teams.
- LOPA is not intended to be a hazard identification technique. However, the more rigorous procedure of LOPA frequently clarifies ill-defined scenarios from qualitative hazard reviews.

Differences in risk tolerance criteria and in LOPA implementation between organizations means the results cannot normally be compared directly from one organization to another.



Scenario Number	**Equipment Number**	*Scenario Title*	
Date:	*Description*	**Probability**	**Frequency (per year)**
Consequence Description/Category		▨	▨
Risk Tolerance Criteria (Category or Frequency)		▨	
Initiating Event (typically a frequency)		▨	
Enabling Event or Condition			▨
Conditional Modifiers (if applicable)		▨	▨
Probability of Ignition			▨
Probability of Personnel in Affected Area			▨
Probability of Fatal Injury			▨
Others			▨
Frequency of Unmitigated Consequence		▨	
Independent Protection Layers		▨	▨
BPCS			▨
Human Intervention			▨
SIF			▨
Pressure Relief Device			▨
Other Protection Layers (must justify)			▨
Safeguards(non-IPLs)	▨	▨	▨
		▨	▨
		▨	▨
		▨	▨
		▨	▨
Total PFD for all IPLs			▨
Frequency of Mitigated Consequence		▨	
Risk Tolerance Criteria Met? (Yes/No):			
Actions Required to Meet Risk Tolerance Criteria			
Notes			
References (links to originating hazard review, PFD, P&ID, etc.)			
LOPA Analyst (and Team Members, if applicable)			

Figure 14.8 Example LOPA Documentation Form [6]

GLOSSARY

These terms are current at the time of publication. Please refer to the CCPS Website for the latest definitions (www.aiche.org/ccps).

Acute Hazard: The potential for injury or damage to occur as a result of an instantaneous or short duration exposure to the effects of an incident.

Administrative Controls: Procedural mechanism for controlling, monitoring, or auditing human performance, such as lock out/tagout procedures, bypass approval processes, car seals, and permit systems.

Asset Integrity Management: A process safety management system for ensuring the integrity of assets throughout their life cycle.

Atmospheric Dispersion: The low momentum mixing of a gas or vapor with air. The mixing is the result of turbulent energy exchange, which is a function of wind (mechanical eddy formation) and atmospheric temperature profile (thermal eddy formation).

Audit: A systematic, independent review to verify conformance with prescribed standards of care using a well-defined review process to ensure consistency and to allow the auditor to reach defensible conclusions.

Barrier: Anything used to control, prevent, or impede energy flows. Includes engineering (physical, equipment design) and administrative (procedures and work processes). See also Layer of Protection.

Basic Process Control System: A system that responds to input signals from the process and its associated equipment, other programmable systems, and/or from an operator, and generates output signals causing the process and its associated equipment to operate in the desired manner and within normal production limits.

Blast Wave: The overpressure wave traveling outward from an explosion point.

Boiling Liquid Expanding Vapor Explosion (BLEVE): A type of rapid phase transition in which a liquid contained above its atmospheric boiling point is rapidly depressurized, causing a nearly instantaneous transition from liquid to vapor with a corresponding energy release. A BLEVE of flammable material is often accompanied by a large aerosol fireball, since an external fire impinging on the vapor space of a pressure vessel is a common cause. However, it is not necessary for the liquid to be flammable to have a BLEVE occur.

Bow-Tie Diagram: A diagram for visualizing the types of preventive and mitigative barriers which can be used to manage risk. These barriers are drawn with the threats on the left, the unwanted event at the center, and the consequences on the right, representing the flow of the hazardous materials or energies through its barriers to its destination. The hazards or threats can be proactively addressed on the left with specific barriers (safeguards, layers of protection) to help prevent a hazardous event from occurring; barriers reacting to the event to help reduce the event’s consequences are shown on the right.

Catastrophic Release: An uncontrolled loss of containment of toxic, reactive, or flammable materials from a process that has the potential for causing onsite or offsite acute health effects, significant environmental effects (e.g., compromise of a public drinking water supply), or significant on-site or off-site property damage.

Center for Chemical Process Safety (CCPS): is a not-for-profit, corporate membership organization within the American Institute for Chemical Engineers (AIChE) that identifies and addresses process safety needs for a variety of facilities involved with handling, storing, using or processing, and transporting hazardous materials

Checklist Analysis: A hazard evaluation procedure using one or more pre-prepared lists of process safety considerations to prompt team discussions of whether the existing safeguards are adequate.

Chemical Process Quantitative Risk Assessment (CPQRA or QRA): The quantitative evaluation of expected risk from potential incident scenarios. It examines both consequences and frequencies, and how they combine into an overall measure of risk. The CPQRA process is always preceded by a qualitative systematic identification of process hazards. The CPQRA results may be used to make decisions, particularly when mitigation of risk is considered.

Combustible Dust: A finely divided combustible particulate solid that presents a flash fire hazard or explosion hazard when suspended in air or the process specific oxidizing medium over a range of concentrations.

Common Cause Failure: The failure of more than one component, item, or system due to the same cause.

Condensed Phase Explosion: An explosion that occurs when the material is present in the form of a liquid or solid.

Conditional Modifier: One of several possible probabilities included in scenario risk calculations, generally when risk criteria endpoints are expressed in impact terms (e.g., fatalities) instead of in primary loss event terms (e.g., release, vessel rupture). Conditional modifiers include, but are not limited to: probability of a hazardous atmosphere, probability of ignition, probability of explosion, probability of personnel presence, probability of injury or fatality, and probability of equipment damage or other financial impact.

Confined Explosion (or Building Explosion): An explosion of fuel-oxidant mixture inside a closed system (e.g. vessel or building).

Confinement: Obstacles such as walls and ceilings of a building, vessel, pipe, etc. that serve to limit the expansion of a dispersing or exploding vapor cloud.

Congestion: Obstacles in the path of the flame that generate turbulence.

Consequence: The undesirable result of a loss event, usually measured in health and safety effects, environmental impacts, loss of property, and business interruption costs.

Consequence Analysis: The analysis of the expected effects of incident outcome cases, independent of frequency or probability.

Consequence Screening: The evaluation of consequence severity to determine the extent and detail to which risk analysis is warranted.

De Minimis Risk: A level of risk that would be perceived by most to be broadly acceptable, and not requiring further reduction.

Deflagration: A combustion that propagates by heat and mass transfer through the un-reacted medium at a velocity less than the speed of sound.

Demand: A plant condition or event which requires a protective system or device to take appropriate action in order to prevent a hazard. (1) A signal or action that should change the state of a device, or (2) an opportunity to act, and thus, to fail.

Detection System: A mechanical, electrical, or chemical device that automatically identifies the presence of a material or a change in environmental conditions such as pressure, temperature, or composition.

Detonation: A release of energy caused by the propagation of a chemical reaction in which the reaction front advances into the unreacted substance at greater than sonic velocity in the unreacted material.

Deviation: A process condition outside of established design limits, safe operating limits, or standard operating procedures.

Dike: An embankment or wall built to act as a barrier blocking passage of liquids to surrounding areas.

Domino Effect: The triggering of secondary events, such as toxic releases, by a primary event, such as an explosion, such that the result is an increase in consequences or area of an effect zone. Generally considered only when a significant escalation of the original incident results.

Dose: Time-integrated concentration

Effect Zone: For an incident that produces an incident outcome of toxic release, the area over which the airborne concentration equals or exceeds some level of concern. For a flammable release, the area over which a particular incident outcome case produces an effect based on a specified criterion.

Equipment: A piece of hardware which can be defined in terms of mechanical, electrical or instrumentation components contained within its boundaries.

Enabling Condition: A condition that is not a failure, error or a protection layer but makes it possible for an incident sequence to proceed to a consequence of concern. It consists of a condition or operating phase that does not directly cause the scenario, but that must be present or active in order for the scenario to proceed to a loss event; expressed as a dimensionless probability.

Event: An occurrence involving a process that is caused by equipment performance or human action or by an occurrence external to the process.

Event Sequence: A specific unplanned sequence of events composed of initiating events and intermediate events that may lead to an incident

Explosion: A release of energy that causes a pressure discontinuity or blast wave.

F-N Curve: A plot of cumulative frequency versus consequences (often expressed as number of fatalities).

Facility: The physical location where a management system activity is performed. In early life-cycle stages, a facility may be the company's central research laboratory, pilot plant, or the engineering offices of a technology vendor. In later stages, the facility may be a typical chemical plant, storage terminal, distribution center, or corporate office. In the context of this document, a facility is a portion of or a complete plant, unit, site, complex or offshore platform or any combination thereof.

Failure: an unacceptable difference between expected and observed performance.

Fault Tree Analysis: A method used to analyze graphically the failure logic of a given event, to identify various failure scenarios (called cut-sets), and to support the probabilistic estimation of the frequency of the event.

Final Element: Process control or safety device that implements the physical action necessary to achieve or maintain a safe state; e.g., valves, switch gear, and motors, including their auxiliary elements (such as the solenoid valve used to operate a valve).

Fireball: The atmospheric burning of a fuel-air cloud in which the energy is mostly emitted in the form of radiant heat. The inner core of the fuel release consists of almost pure fuel whereas the outer layer in which ignition first occurs is a flammable fuel-air mixture. As buoyancy forces of the hot gases begin to dominate, the burning cloud rises and becomes more spherical in shape.

Flammable: A gas that can burn with a flame if mixed with a gaseous oxidizer such as air or chlorine and then ignited. The term flammable gas includes vapors from flammable or combustible liquids above their flash points.

Flash Fire: A fire that spreads by means of a flame front rapidly through a diffuse fuel, such as a dust, gas, or the vapors of an ignitable liquid, without the production of damaging pressure.

Frequency: Number of occurrences of an event per unit time (e.g., 1 event in 1000 yr. = 1 x 10-3 events/yr.).

Globally Harmonized System (**GHS):** system for Classification and Labeling of Chemicals adopted by the United Nations

Hazard: An inherent chemical or physical characteristic that has the potential for causing damage to people, property, or the environment.

Hazard and Operability Study (HAZOP): A systematic qualitative technique to identify process hazards and potential operating problems using a series of guide words to study process deviations. A HAZOP is used to question every part of a process to discover what deviations from the intention of the design can occur and what their causes and consequences may be. This is done systematically by applying suitable guidewords. This is a systematic detailed review technique, for both batch and continuous plants, which can be applied to new or existing processes to identify hazards.

Hazard Evaluation: Identification of individual hazards of a system, determination of the mechanisms by which they could give rise to undesired events, and evaluation of the consequences of these events on health (including public health), environment and property. Uses qualitative techniques to pinpoint weaknesses in the design and operation of facilities that could lead to incidents.

Hazard Identification: The inventorying of material, system, process and plant characteristics that can produce undesirable consequences through the occurrence of an incident.

Hazard Identification and Risk Analysis Study (HIRA): A collective term that encompasses all activities involved in identifying hazards and evaluating risk at facilities, throughout their life cycle, to make certain that risks to employees, the public, or the environment are consistently controlled within the organization's risk tolerance.

Hazard Screening: The evaluation of hazard severity to determine the extent to which hazard assessment and subsequent risk analysis is warranted.

Hazardous Chemical: A material that is toxic, reactive, or flammable and is capable of causing a process safety incident if released. Also Hazardous material.

Human Error: Intended or unintended human action or inaction that produces an inappropriate result. Includes actions by designers, operators, engineers, or managers that may contribute to or result in accidents.

Human Reliability Analysis: A method used to evaluate whether system-required human-actions, tasks, or jobs will be completed successfully within a required time period. Also used to determine the probability that no extraneous human actions detrimental to the system will be performed.

Hybrid Mixture: A mixture of a flammable gas with either a combustible dust or combustible mist.

Impact: A measure of the ultimate loss and harm of a loss event. Impact may be expressed in terms of numbers of injuries and/or fatalities, extent of environmental damage and/or magnitude of losses such as property damage, material loss, lost production, market share loss, and recovery costs.

Incident: An event, or series of events, resulting in one or more undesirable consequences, such as harm to people, damage to the environment, or asset/business losses. Such events include fires, explosions, releases of toxic or otherwise harmful substances, and so forth.

Incident Investigation: A systematic approach for determining the causes of an incident and developing recommendations that address the causes to help prevent or mitigate future incidents. See also Root cause analysis and Apparent cause analysis.

Incident Outcome: The physical manifestation of the incident: for toxic materials, the incident outcome is a toxic release, while for flammable materials; the incident outcome could be a boiling liquid expanding vapor explosion (BLEVE), flash fire, vapor cloud explosion (VCE), etc.

Independent Protection Layer (IPL): A device, system, or action that is capable of preventing a scenario from proceeding to the undesired consequence without being adversely affected by the initiating event or the action of any other protection layer associated with the scenario.

Individual Risk: The risk to a person in the vicinity of a hazard. This includes the nature of the injury to the individual, the likelihood of the injury occurring, and the time period over which the injury might occur.

Inherently Safer Design: A way of thinking about the design of chemical processes and plants that focuses on the elimination or reduction of hazards, rather than on their management and control.

Initiating Cause (or Initiating Event): The operational error, mechanical failure, or external event or agency that is the first event in an incident sequence and marks the transition from a normal situation to an abnormal situation.

Interlock: A protective response which is initiated by an out-of-limit process condition. Instrument which will not allow one part of a process to function unless another part is functioning. A device such as a switch that prevents a piece of equipment from operating when a hazard exists. To join two parts together in such a way that they remain rigidly attached to each other solely by physical interference. A device to prove the physical state of a required condition and to furnish that proof to the primary safety control circuit.

Jet Fire: A fire type resulting from the discharge of liquid, vapor, or gas into free space from an orifice, the momentum of which induces the surrounding atmosphere to mix with the discharged material.

Layer of Protection Analysis: An approach that analyzes one incident scenario (cause-consequence pair) at a time, using predefined values for the initiating event frequency, independent protection layer failure probabilities, and consequence severity, in order to compare a scenario risk estimate to risk criteria for determining where additional risk reduction or more detailed analysis is needed. Scenarios are identified elsewhere, typically using a scenario-based hazard evaluation procedure such as a HAZOP Study.

Likelihood: A measure of the expected probability or frequency of occurrence of an event. This may be expressed as an event frequency (e.g., events per year), a probability of occurrence during a time interval (e.g., annual probability) or a conditional probability (e.g., probability of occurrence, given that a precursor event has occurred).

Loss Event: Point in time in an abnormal situation when an irreversible physical event occurs that has the potential for loss and harm impacts. Examples include release of a hazardous material, ignition of flammable vapors or ignitable dust cloud, and over-pressurization rupture of a tank or vessel. An incident might involve more than one loss event, such as a flammable liquid spill (first loss event) followed by ignition of a flash fire and pool fire (second loss event) that heats up an adjacent vessel and its contents to the point of rupture (third loss event). Generally synonymous with hazardous event.

Loss of Primary Containment (LOPC): An unplanned or uncontrolled release of material from primary containment, including non-toxic and non-flammable materials (e.g., steam, hot condensate, nitrogen, compressed CO2 or compressed air).

Management of Change: A management system to identify, review, and approve all modifications to equipment, procedures, raw materials, and processing conditions, other than replacement in kind, prior to implementation to help ensure that changes to processes are properly analyzed (for example, for potential adverse impacts), documented, and communicated to employees affected.

Mechanical Integrity (or Equipment Integrity): A management system focused on ensuring that equipment is designed, installed, and maintained to perform the desired function.

Mean Time Between Failure (MTBF): For a stated period in the life of a functional unit, the mean value of the length of time between consecutive failures under stated conditions.

Mitigate: Reduce the impact of a loss event.

Mitigative Safeguard: A safeguard that is designed to reduce loss event impact.

National Fire Protection Agency (**NFPA**): a United States trade association that creates and maintains standards and codes for usage and adoption by local governments.

Near-Miss: An unplanned sequence of events that could have caused harm or loss if conditions were different or were allowed to progress, but actually did not.

Normal Operations: Any process operations intended to be performed between startup and shutdown to support continued operation within safe upper and lower operating limits.

Occupant Vulnerability: Proportion of building occupants that could potentially suffer an injury or fatality if a postulated event were to occur. The level of injury is defined according to the technical basis of the occupant vulnerability model being used.

Off-Site Population: Persons located outside of the site property line that may be impacted by an on-site incident.

On-Site Personnel: Employees, contractors, visitors, service providers, and others present at the facility.

Operating Procedures: Written, step by step instructions and information necessary to operate equipment, compiled in one document including operating instructions, process descriptions, operating limits, chemical hazards, and safety equipment requirements.

Operator: An individual responsible for monitoring, controlling, and performing tasks as necessary to accomplish the productive activities of a system. Operator is also used in a generic sense to include people who perform a wide range of tasks (e.g., readings, calibration, incidental maintenance, manage loading/unloading, and storage of hazardous materials).

OSHA Process Safety Management (OSHA PSM): A U.S. regulatory standard that requires use of a 14-element management system to help prevent or mitigate the effects of catastrophic releases of chemicals or energy from processes covered by the regulations (49 CFR 1910.119).

Parameter: A quantity describing the relation of variables within a given system. Note: A parameter may be constant or depend on the time or the magnitude of some system variables.

Passive System: A system in which failures are only revealed by testing or when a demand has occurred.

Personal Protective Equipment (PPE): Equipment designed to protect employees from serious workplace injuries or illnesses resulting from contact with chemical, radiological, physical, electrical, mechanical, or other workplace hazards. Besides face shields, safety glasses, hard hats, and safety shoes, PPE includes a variety of devices and garments, such as goggles, coveralls, gloves, vests, earplugs, and respirators.

Physical Explosion: The catastrophic rupture of a pressurized gas/vapor-filled vessel by means other than reaction, or the sudden phase-change from liquid to vapor of a superheated liquid.

Piping and Instrument Diagram (P&ID): A diagram that shows the details about the piping, vessels, and instrumentation.

Pool Fire: The combustion of material evaporating from a layer of liquid at the base of the fire.

Potential Explosion Site (PES): A volume within a plant with sufficient congestion and/or confinement that a flammable vapor cloud ignited there could likely develop into an explosion.

Pre-Initiating Safeguard: A safeguard that acts to prevent an initiating event or cause from occurring.

Preventive Safeguard: A safeguard that forestalls the occurrence of a particular loss event, given that an initiating cause has occurred; i.e., a safeguard that intervenes between an initiating cause and a loss event in an incident sequence.

Prevention: The process of eliminating or preventing the hazards or risks associated with a particular activity. Prevention is sometimes used to describe actions taken in advance to reduce the likelihood of an undesired event.

Probability: The expression for the likelihood of occurrence of an event or an event sequence during an interval of time, or the likelihood of success or failure of an event on test or on demand. Probability is expressed as a dimensionless number ranging from 0 to 1.

Probit: A random variable with a mean of 5 and a variance of 1, which is used in various effect models. Probit-based models derived from experimental dose-response data, are often used to estimate the health effect that might result based upon the intensity and duration of an exposure to a harmful substance or condition (e.g., exposure to a toxic atmosphere, or a thermal radiation exposure).

Process Hazard Analysis: An organized effort to identify and evaluate hazards associated with processes and operations to enable their control. This review normally involves the use of qualitative techniques to identify and assess the significance of hazards. Conclusions and appropriate recommendations are developed. Occasionally, quantitative methods are used to help prioritized risk reduction.

Process Safety Management Systems: Comprehensive sets of policies, procedures, and practices designed to ensure that barriers to episodic incidents are in place, in use, and effective.

Process Safety: A disciplined framework for managing the integrity of operating systems and processes handling hazardous substances by applying good design principles, engineering, and operating practices. It deals with the prevention and control of incidents that have the potential to release hazardous materials or energy. Such incidents can cause toxic effects, fire, or explosion and could ultimately result in serious injuries, property damage, lost production, and environmental impact.

Process Safety Review: An inspection of a plant/process unit, drawings, procedures, emergency plans and/or management systems, etc., usually by an on-site team and usually problem-solving in nature. (See "Audit" for contrast).

Qualitative: Based primarily on description and comparison using historical experience and engineering judgment, with little quantification of the hazards, consequences, likelihood, or level of risk.

Quantitative Risk Analysis: The systematic development of numerical estimates of the expected frequency and severity of potential incidents associated with a facility or operation based on engineering evaluation and mathematical techniques.

Recognized and Generally Accepted Good Engineering Practice (RAGAGEP): a term originally used by OSHA, stems from the selection and application of appropriate engineering, operating, and maintenance knowledge when designing, operating and maintaining chemical facilities with the purpose of ensuring safety and preventing process safety incidents. It involves the application of engineering, operating or maintenance activities derived from engineering knowledge and industry experience based upon the evaluation and analyses of appropriate internal and external standards, applicable codes, technical reports, guidance, or recommended practices or documents of a similar nature. RAGAGEP can be derived from singular or multiple sources and will vary based upon individual facility processes, materials, service, and other engineering considerations.

Reliability: Core attribute of a protection layer related to the probability that the equipment operates according to its specification for a stated period of time under all relevant conditions.

Risk: A measure of human injury, environmental damage, or economic loss in terms of both the incident likelihood and the magnitude of the loss or injury.

Risk Analysis: The estimation of scenario, process, facility and/or organizational risk by identifying potential incident scenarios, then evaluating and combining the expected frequency and impact of each scenario having a consequence of concern, then summing the scenario risks, if necessary, to obtain the total risk estimate for the level at which the risk analysis is being performed.

Risk-Based Process Safety (RBPS): The Center for Chemical Process Safety's process safety management system approach that uses risk-based strategies and implementation tactics that are commensurate with the risk-based need for process safety activities, availability of resources, and existing process safety culture to design, correct, and improve process safety management activities.

Risk Matrix: A tabular approach for presenting risk tolerance criteria, typically involving graduated scales of incident likelihood on the Y-axis and incident consequences on the X-Axis.

Risk Management: The systematic application of management policies, procedures, and practices to the tasks of analyzing, assessing, and controlling risk in order to protect employees, the general public, the environment, and company assets, while avoiding business interruptions. Includes decisions to use suitable engineering and administrative controls for reducing risk.

Risk Tolerance Criteria: A predetermined measure of risk used to aid decisions about whether further efforts to reduce the risk are warranted.

Safeguard: Any device, system, or action that either interrupts the chain of events following an initiating event or that mitigates the consequences. A safeguard can be an engineered system or an administrative control. Not all safeguards meet the requirements of an IPL.

Safety Instrumented System (SIS): A separate and independent combination of sensors, logic solvers, final elements, and support systems that are designed and managed to achieve a specified safety integrity level. A SIS may implement one or more Safety Instrumented Functions (SIFs).

Scenario: A detailed description of an unplanned event or incident sequence that results in a loss event and its associated impacts, including the success or failure of safeguards involved in the incident sequence.

Screening Criteria: A predetermined measure, standard, or rule (typically based upon company or regulatory requirements), on which a judgment or decision can be based.

Severity: The maximum credible consequences or effects, assuming no safeguards are in place.

Screening Tool: A simplified model with limited capabilities, suitable for screening-level studies.

Spray Distance: The maximum distance a fluid travels before the velocity slows and/or the fluid falls to the ground.

Societal Risk: A measure of risk to a group of people. It is most often expressed in terms of the frequency distribution of multiple casualty events.

Source Term: The release parameters (e.g. magnitude, rate, duration, orientation, temperature) that are the initial conditions for determining the consequences of the loss event for a hazardous material and/or energy release to the surroundings. For vapor dispersion modeling, it is the estimation, based on the release specification, of the actual cloud conditions of temperature, aerosol content, density, size, velocity and mass to be input into the dispersion model.

Tolerable Frequency: The maximum frequency for a specific consequence that is regarded as tolerable/

Tolerable Frequency Factor (TFF): - $\log_{10}$ of the tolerable frequency

Tolerable Risk Level: The maximum level of risk of a particular technical process or condition that is regarded as tolerable in the context of the circumstances in questions.

Vapor Cloud Explosion (VCE): The explosion resulting from the ignition of a cloud of flammable vapor, gas, or mist in which flame speeds accelerate to sufficiently high velocities to produce significant overpressure.

Virtual Source: The offset in distance to the specified source of a gas or vapor release that results in a maximum concentration of 100% at the source using a Gaussian dispersion model.

What-If Analysis: A scenario-based hazard evaluation procedure using a brainstorming approach in which typically a team that includes one or more persons familiar with the subject process asks questions or voices concerns about what could go wrong, what consequences could ensue, and whether the existing safeguards are adequate.

Worst Case: A conservative (high) estimate of the consequences of the most severe incident identified.

APPENDIX A – REACTIVE CHEMICALS CHECKLIST

The checklist is adapted from a CCPS Safety Alert [71].

1.1 Chemical reaction hazard identification

1. Know the heat of reaction for the intended and other potential chemical reactions.

There are a number of techniques for measuring or estimating heat of reaction, including various calorimeters, plant heat and energy balances for processes already in operation, analogy with similar chemistry (confirmed by a chemist who is familiar with the chemistry), literature resources, supplier contacts, and thermodynamic estimation techniques. All potential reactions should be identified that could occur in the reaction mixture and understand the heat of reaction of these reactions.

2. Calculate the maximum adiabatic temperature for the reaction mixture.

Use the measured or estimated heat of reaction, assume no heat removal, and that 100% of the reactants actually react. Compare this temperature to the boiling point of the reaction mixture. If the maximum adiabatic reaction temperature exceeds the reaction mixture boiling point, the reaction is capable of generating pressure in a closed vessel and the safeguards will have to be evaluated that help prevent uncontrolled reaction and consider the need for emergency pressure relief systems.

3. Determine the stability of all individual components of the reaction mixture at the maximum adiabatic reaction temperature.

This might be done through literature searching, supplier contacts, or experimentation. Note that this does not ensure the stability of the reaction mixture because it does not account for any reaction among components, or decomposition promoted by combinations of components. This evaluation shows if any of the individual components of the reaction mixture can decompose at temperatures which are theoretically attainable. If any components can decompose at the maximum adiabatic reaction temperature, the decomposition nature must be understood and the safeguards (including emergency pressure relief systems) will need to be evaluated.

4. Understand the stability of the reaction mixture at the maximum adiabatic reaction temperature. A

re there any chemical reactions, other than the intended reaction, which CCPS Safety Alert, March 1, 2004 3 can occur at the maximum adiabatic reaction temperature? Consider possible decomposition reactions, particularly those which generate gaseous products. These are a particular concern because a small mass of reacting condensed liquid can generate a very large volume of gas from the reaction products, resulting in rapid pressure generation in a closed vessel. Again, if this is possible, how these reactions will impact the need for safeguards, including emergency pressure relief systems, must be understood. Understanding the stability of a mixture of components may require laboratory testing.

5. Determine the heat addition and heat removal capabilities of the pilot plant or production reactor.

Don’t forget to consider the reactor agitator as a source of energy – about 2550 Btu/hour/horsepower. Understand the impact of variation in conditions on heat transfer capability. Consider factors such as reactor fill level, agitation, fouling of internal and external heat transfer surfaces, variation in the temperature of heating and cooling media, variation in flow rate of heating and cooling fluids.

6. Identify potential reaction contaminants. In particular, consider possible contaminants which are ubiquitous in a plant environment, such as air, water, rust, oil and grease.

Think about possible catalytic effects of trace metal ions such as sodium, calcium, and others commonly present in process water. These may also be left behind from cleaning operations such as cleaning equipment with aqueous sodium hydroxide. Determine if these materials will catalyze any decomposition or other reactions, either at normal conditions or at the maximum adiabatic reaction temperature.

7. Consider the impact of possible deviations from intended reactant charges and operating conditions.

For example, is a double charge of one of the reactants a possible deviation, and, if so, what is the impact? This kind of deviation might affect the chemistry which occurs in the reactor – for example, the excess material charged may react with the product of the intended reaction or with a reaction solvent. The resulting unanticipated chemical reactions could be energetic, generate gases, or produce unstable products. Consider the impact of loss of cooling, agitation, and temperature control, insufficient solvent or fluidizing media, and reverse flow into feed piping or storage tanks.

8. Identify all heat sources connected to the reaction vessel and determine their maximum temperature.

Assume all control systems on the reactor heating systems fail to the maximum temperature. If this temperature is higher than the maximum adiabatic reaction temperature, review the stability and reactivity information with respect to the maximum temperature to which the reactor contents could be heated by the vessel heat sources.

9. Determine the minimum temperature to which the reactor cooling sources could cool the reaction mixture.

Consider potential hazards resulting from too much cooling, such as freezing of reaction mixture components, fouling of heat transfer surfaces, increase in reaction mixture viscosity reducing mixing and heat transfer, precipitation of dissolved solids from the reaction mixture, and a reduced rate of reaction resulting in a hazardous accumulation of unreacted material.

10. Consider the impact of higher temperature gradients in plant scale equipment compared to a laboratory or pilot plant reactor.

Agitation is almost certain to be less effective in a plant reactor, and the temperature of the reaction mixture near heat transfer surfaces may be higher (for systems being heated) or lower (for systems being cooled) than the bulk mixture temperature. For exothermic reactions, the temperature may also be higher near the point of introduction of reactants because of poor mixing and localized reaction at the point of reactant contact. The location of the reactor temperature sensor relative to the agitator, and to heating and cooling surfaces may impact its ability to provide good information about the actual average reactor temperature. These problems will be more severe for very viscous systems, or if the reaction mixture includes solids which can foul temperature measurement devices or heat transfer surfaces. Either a local high temperature or a local low temperature could cause a problem. A high temperature, for example, near a heating surface, could result in a different chemical reaction or decomposition at the higher temperature. A low temperature near a cooling coil could result in slower reaction and a buildup of unreacted material, increasing the potential chemical energy of reaction available in the reactor. If this material is subsequently reacted because of an increase in temperature or other change in reactor conditions, there is a possibility of an uncontrolled reaction due to the unexpectedly high quantity of unreacted material available.

11. Understand the rate of all chemical reactions.

It is not necessary to develop complete kinetic models with rate constants and other details, how fast reactants are consumed and generally how the rate of reaction increases with temperature must be understood. Thermal hazard calorimetry testing can provide useful kinetic data.

12. Consider possible vapor phase reactions.

These might include combustion reactions, other vapor phase reactions such as the reaction of organic vapors with a chlorine atmosphere, and vapor phase decomposition of materials such as ethylene oxide or organic peroxide.

13. Understand the hazards of the products of both intended and unintended reactions.

For example, does the intended reaction, or a possible unintended reaction, form viscous materials, solids, gases, corrosive products, highly toxic products, or materials which will swell or degrade gaskets, pipe linings, or other polymer components of a system? If there is an unexpected material in reaction equipment, its potential impact on the system hazards must be determined. For example, in an oxidation reactor, solids were known to be present, however the solid characteristics were not identified. It turned out that the solids were pyrophoric, and they caused a fire in the reactor.

14. Consider doing a Chemical Interaction Matrix and/or a Chemistry Hazard Analysis.

These techniques can be applied at any stage in the process life cycle, from early research through an operating plant. They are intended to provide a systematic method to identify chemical interaction hazards and hazards resulting from deviations from intended operating conditions.

2.2 Reaction process design considerations

1. Rapid reactions are desirable.

In general, chemical reactions often occur immediately when the reactants come into contact. The reactants are immediately consumed and the reaction energy quickly released, this allows for better reaction control due to better control of the contact time between reactants. However, the reactor must be capable of removing all of the heat and any gaseous products generated by the rapid reaction.

2. Avoid batch processes in which all of the potential chemical energy is present in the system at the start of the reaction step.

These types of processes require both knowledge of the heat of reaction and understanding that the maximum adiabatic temperature and pressure are within the design capabilities of the reactor.

3. Use gradual addition or “semi-batch” processes for exothermic reactions.

The inherently safer way to operate exothermic reaction process is to determine a temperature at which the reaction occurs very rapidly. Operate the reaction at this temperature, and feed at least one of the reactants gradually to limit the potential energy contained in the reactor. This type of gradual addition process is often called “semi-batch.” A physical limit to the possible rate of addition of the limiting reactant is desirable – a metering pump, flow limited by using a small feed line, or a restriction orifice, for example. Ideally, the limiting reactant should react immediately, or very quickly, when it is charged. The reactant feed can be stopped if necessary if there is any kind of a failure (for example, loss of cooling, power failure, loss of agitation) and the reactor will contain little or no potential chemical energy from unreacted material. Some way to confirm actual reaction of the limiting reagent is also desirable. A direct measurement is best, but indirect methods such as monitoring of the demand for cooling from an exothermic batch reactor can also be effective.

4. Avoid using control of reaction mixture temperature as the only means for limiting the reaction rate.

If the reaction produces a large amount of heat, this control philosophy is unstable – an increase in temperature will result in faster reaction and even more heat being released, causing a further increase in temperature and more rapid heat release. If there is a large amount of potential chemical energy from reactive materials, a runaway reaction results. This type of process is vulnerable to mechanical failure or operating error. A false indication of reactor temperature can lead to a higher than expected reaction temperature and possible runaway because all of the potential chemical energy of reaction is available in the reactor. Many other single failures could lead to a similar consequence – a leaking valve on the heating system, operator error in controlling reactor temperature, failure of software or hardware in a computer control system.

5. Account for the impact of vessel size on heat generation and heat removal capabilities of a reactor.

Remember that the heat generated by a reactive system will increase more rapidly than the capability of the system to remove heat when the process is operated in a larger vessel. Heat generation increases with the volume of the system – by the cube of the linear dimension. Heat removal capability increases with the surface area of the system, because heat is generally only removed through an external surface of the reactor. Heat removal capability increases with the square of the linear dimension. A large reactor is effectively adiabatic (zero heat removal) over the short time scale (a few minutes) in which a runaway reaction can occur. Heat removal in a small laboratory reactor is very efficient, even heat leakage to the surroundings can be significant. If the reaction temperature is easily controlled in the laboratory, this does not mean that the temperature can be controlled in a plant scale reactor. Heat of reaction data discussed previously is required when confirming that the plant reactor is capable of maintaining the desired temperature.

6. Use multiple temperature sensors, in different locations in the reactor for rapid exothermic reactions.

This is particularly important if the reaction mixture contains solids, is very viscous, or if the reactor has coils or other internal elements which might inhibit good mixing.

7. Avoid feeding a material to a reactor at a higher temperature than the boiling point of the reactor contents.

This can cause rapid boiling of the reactor contents and vapor generation.

3.3 Resources and Publications

There are many valuable books and other resources to help in understanding and managing reactive chemistry hazards. Some particularly useful resources include:

- American Institute of Chemical Engineers, Center for Chemical Process Safety, Safety Alert: Reactive Material Hazards, New York, 2001.
- Bretherick's Handbook of Reactive Chemical Hazards, Butterworth-Heineman, 1999.
- Chemical Reactivity Worksheet, U. S. National Oceanic and Atmospheric Administration, http://response.restoration.noaa.gov/chemaids/react.html
- American Institute of Chemical Engineers, Center for Chemical Process Safety, Guidelines for Safe Storage and Handling of Reactive Materials, 1995.
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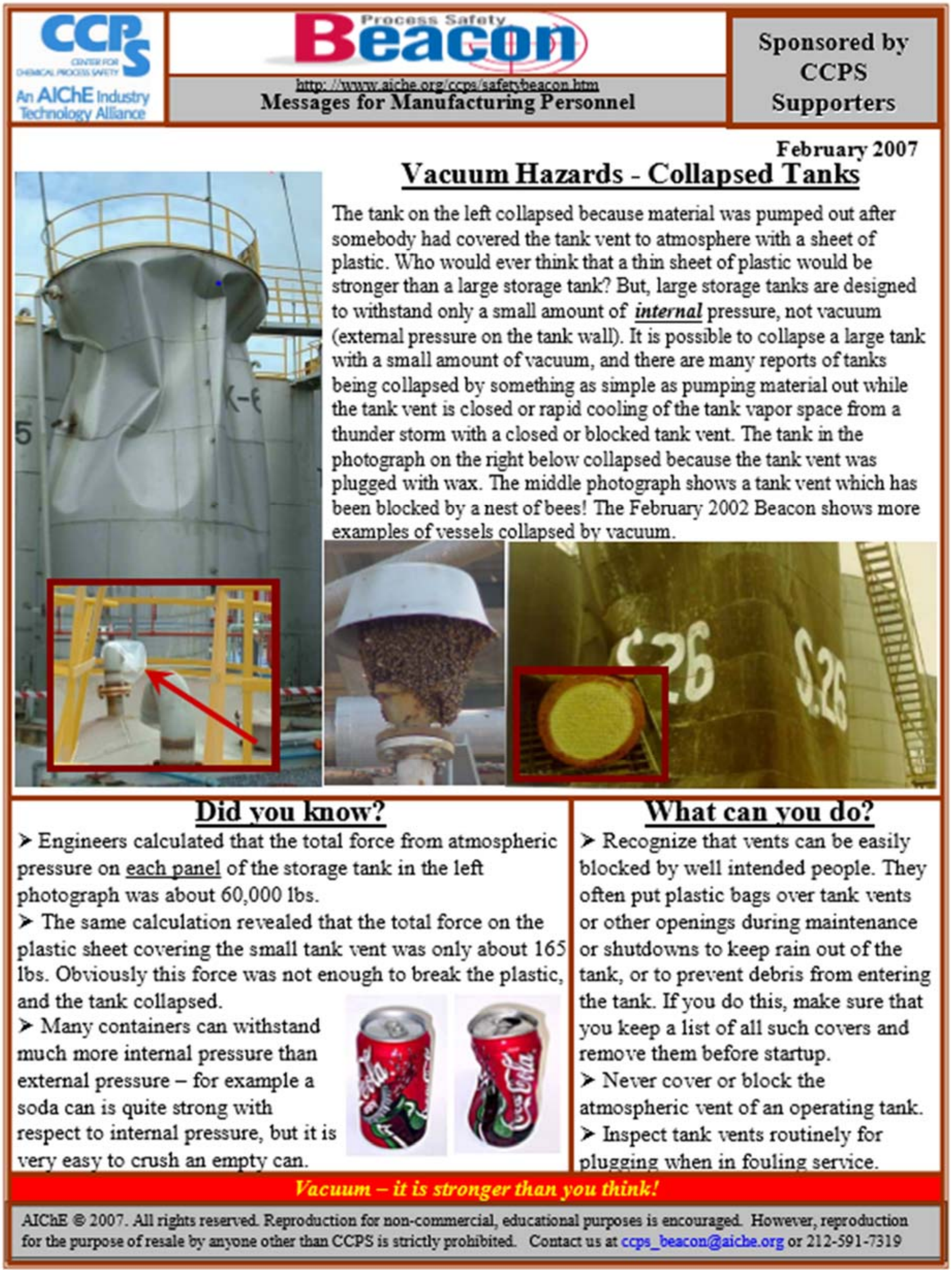
APPENDIX B – EXAMPLES OF OTHER HAZARDS

B.1 Example of vacuum damage



http://www.aiche.org/ccps/safetybeacon.htm

Messages for Manufacturing Personnel

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February 2007

Vacuum Hazards - Collapsed Tanks

The tank on the left collapsed because material was pumped out after somebody had covered the tank vent to atmosphere with a sheet of plastic. Who would ever think that a thin sheet of plastic would be stronger than a large storage tank? But, large storage tanks are designed to withstand only a small amount of ***internal*** pressure, not vacuum (external pressure on the tank wall). It is possible to collapse a large tank with a small amount of vacuum, and there are many reports of tanks being collapsed by something as simple as pumping material out while the tank vent is closed or rapid cooling of the tank vapor space from a thunder storm with a closed or blocked tank vent. The tank in the photograph on the right below collapsed because the tank vent was plugged with wax. The middle photograph shows a tank vent which has been blocked by a nest of bees! The February 2002 Beacon shows more examples of vessels collapsed by vacuum.

Did you know?

- ➢ Engineers calculated that the total force from atmospheric pressure on each panel of the storage tank in the left photograph was about 60,000 lbs.
- ➢ The same calculation revealed that the total force on the plastic sheet covering the small tank vent was only about 165 lbs. Obviously this force was not enough to break the plastic, and the tank collapsed.
- ➢ Many containers can withstand much more internal pressure than external pressure – for example a soda can is quite strong with respect to internal pressure, but it is very easy to crush an empty can.

What can you do?

- ➢ Recognize that vents can be easily blocked by well intended people. They often put plastic bags over tank vents or other openings during maintenance or shutdowns to keep rain out of the tank, or to prevent debris from entering the tank. If you do this, make sure that you keep a list of all such covers and remove them before startup.
- ➢ Never cover or block the atmospheric vent of an operating tank.
- ➢ Inspect tank vents routinely for plugging when in fouling service.

Vacuum – it is stronger than you think!

B.2 Example of a blocked-in water pump

www.aiche.org/ccps

Process Safety Beacon

http://www.aiche.org/CCPS/Publications/Beacon/index.aspx

Messages for Manufacturing Personnel

This issue sponsored by ioMosaic

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Can a water pump explode?

August 2013

The answer must be "yes" or we wouldn't have a subject for this *Beacon*! The centrifugal pumps in the pictures are all water pumps which exploded. The explosions did not occur because of any contamination or chemical reaction with something that was not supposed to be in the pump. In fact, explosions like this have happened with very pure water – boiler feed water pumps, condensate pumps, and deionized water pumps.

How did these explosions happen? The pumps were operated for some period of time with both the pump suction and discharge valves closed. Because water could not flow through the pump, all of the energy which normally goes into pumping is instead converted to heat. When water is heated, it expands generating hydrostatic pressure inside the pump. This may be enough pressure to cause the pump to fail – perhaps the seal would fail, or the pump casing might rupture. These explosions may cause significant damage or injuries because of the built-up energy. However, if the water exceeds its boiling point before the pump fails, a more energetic explosion may occur because the released superheated water will rapidly boil and expand (a boiling liquid expanding vapor explosion - BLEVE). The severity and damage will be similar to a steam boiler explosion.

This type of explosion can happen with any fluid if a pump is operated with suction and discharge valves closed. If a non-hazardous fluid like water can result in the damage shown in the pictures, think how much more severe the damage might be if the fluid is flammable - the released material could catch fire. If the fluid is toxic or corrosive, people near the pump could be severely injured by the released material.

What can you do?

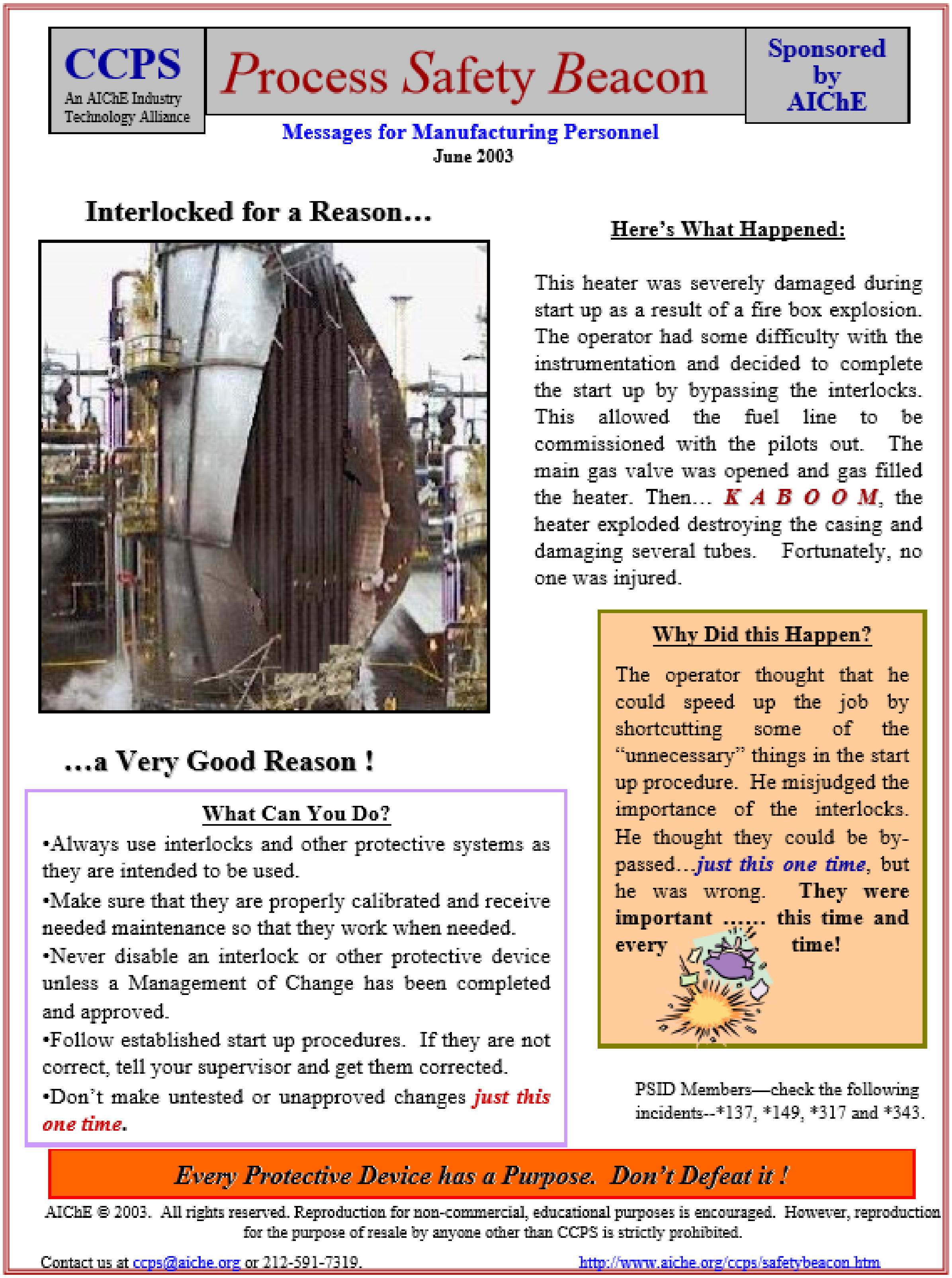
- ➔ Before starting any pump, check that all valves are in the correct position. Be sure that the valves in the intended flow path are open, and other valves, such as drains and vents, are closed.
- ➔ If you are starting a pump from a remote location such as a control room, be sure that the pump is ready for operation. If you are not sure, go to the pump and check it, or have somebody else check it.
- ➔ Make sure that key steps important for safe operation of pumps, including all valve positions, are included in your plant operating procedures and checklists.
- ➔ Some pumps are started automatically – for example by a process control computer or a level instrument to automatically empty a tank when it is filled. Make sure that all of the valves are in the correct positions when putting these pumps into automatic operation, for example, after maintenance.
- ➔ Some pumps have instrumentation installed to prevent running while blocked in – for example, low flow, high temperature, or high pressure interlocks. Be sure that these safety systems are properly maintained and tested.

See the October 2002 *Process Safety Beacon* for a similar incident.

Don't let your pumps run while blocked in!

The Beacon is usually available in Arabic Afrikaans Chinese Czech Danish Dutch English French German Greek Gujarati Hebrew Hindi Hungarian Italian Japanese

B.3 Example of a fire box explosion



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Process Safety Beacon

Sponsored by AIChE

Messages for Manufacturing Personnel
June 2003

Interlocked for a Reason…

…a Very Good Reason !

Here's What Happened:

This heater was severely damaged during start up as a result of a fire box explosion. The operator had some difficulty with the instrumentation and decided to complete the start up by bypassing the interlocks. This allowed the fuel line to be commissioned with the pilots out. The main gas valve was opened and gas filled the heater. Then… ***K A B O O M***, the heater exploded destroying the casing and damaging several tubes. Fortunately, no one was injured.

What Can You Do?

- •Always use interlocks and other protective systems as they are intended to be used.
- •Make sure that they are properly calibrated and receive needed maintenance so that they work when needed.
- •Never disable an interlock or other protective device unless a Management of Change has been completed and approved.
- •Follow established start up procedures. If they are not correct, tell your supervisor and get them corrected.
- •Don't make untested or unapproved changes *just this one time*.

Why Did this Happen?

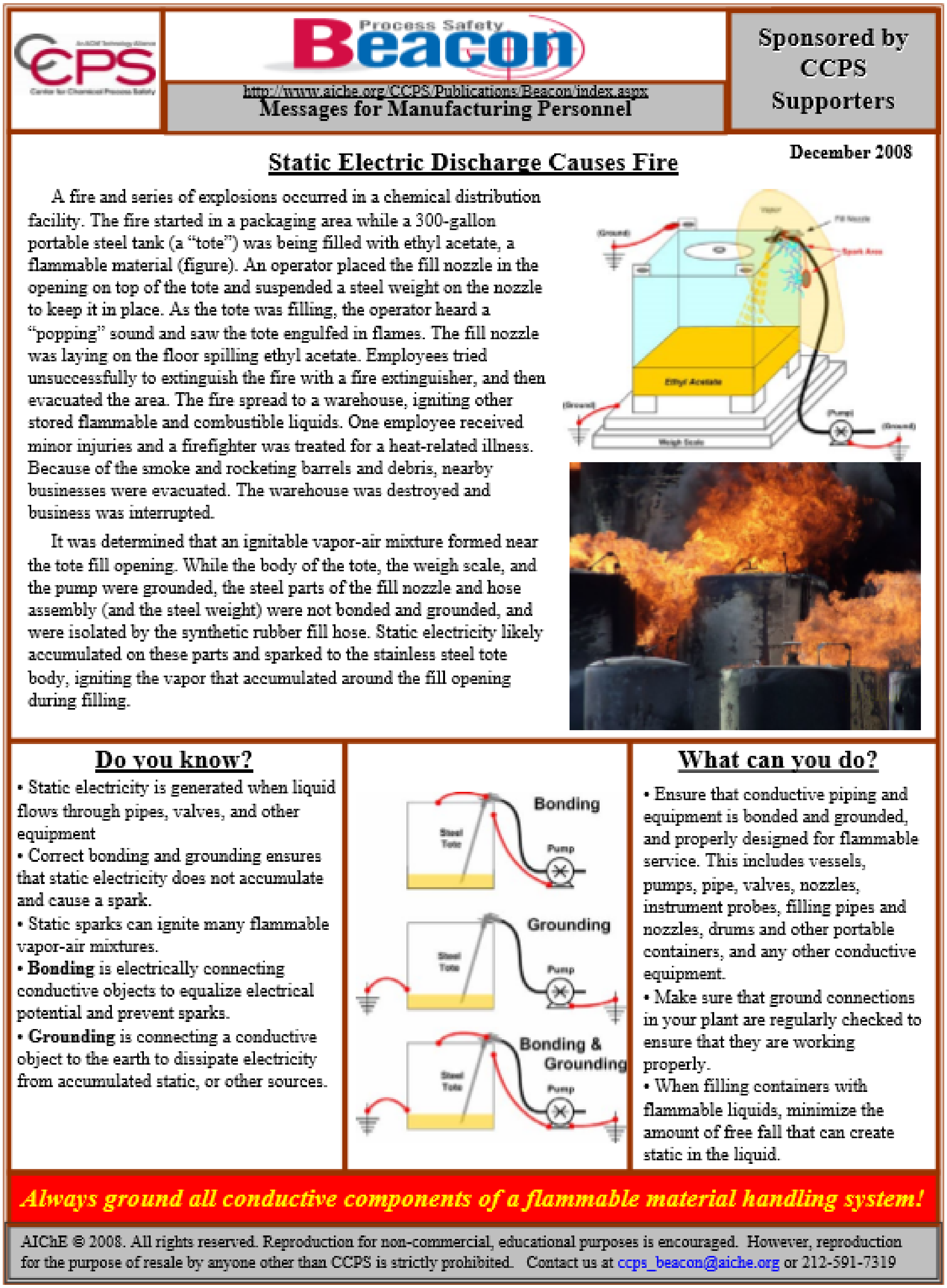
The operator thought that he could speed up the job by shortcutting some of the "unnecessary" things in the start up procedure. He misjudged the importance of the interlocks. He thought they could be by-passed…***just this one time***, but he was wrong. **They were important …… this time and every time!**

PSID Members—check the following incidents--*137, *149, *317 and *343.

Every Protective Device has a Purpose. Don't Defeat it !

Contact us at ccps@aiche.org or 212-591-7319. http://www.aiche.org/ccps/safetybeacon.htm

B.4 Example of static electric discharge incident



Process Safety Beacon

http://www.aiche.org/CCPS/Publications/Beacon/index.aspx

Messages for Manufacturing Personnel

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December 2008

Static Electric Discharge Causes Fire

A fire and series of explosions occurred in a chemical distribution facility. The fire started in a packaging area while a 300-gallon portable steel tank (a "tote") was being filled with ethyl acetate, a flammable material (figure). An operator placed the fill nozzle in the opening on top of the tote and suspended a steel weight on the nozzle to keep it in place. As the tote was filling, the operator heard a "popping" sound and saw the tote engulfed in flames. The fill nozzle was laying on the floor spilling ethyl acetate. Employees tried unsuccessfully to extinguish the fire with a fire extinguisher, and then evacuated the area. The fire spread to a warehouse, igniting other stored flammable and combustible liquids. One employee received minor injuries and a firefighter was treated for a heat-related illness. Because of the smoke and rocketing barrels and debris, nearby businesses were evacuated. The warehouse was destroyed and business was interrupted.

It was determined that an ignitable vapor-air mixture formed near the tote fill opening. While the body of the tote, the weigh scale, and the pump were grounded, the steel parts of the fill nozzle and hose assembly (and the steel weight) were not bonded and grounded, and were isolated by the synthetic rubber fill hose. Static electricity likely accumulated on these parts and sparked to the stainless steel tote body, igniting the vapor that accumulated around the fill opening during filling.

Do you know?

- Static electricity is generated when liquid flows through pipes, valves, and other equipment
- Correct bonding and grounding ensures that static electricity does not accumulate and cause a spark.
- Static sparks can ignite many flammable vapor-air mixtures.
- **Bonding** is electrically connecting conductive objects to equalize electrical potential and prevent sparks.
- **Grounding** is connecting a conductive object to the earth to dissipate electricity from accumulated static, or other sources.

What can you do?

- Ensure that conductive piping and equipment is bonded and grounded, and properly designed for flammable service. This includes vessels, pumps, pipe, valves, nozzles, instrument probes, filling pipes and nozzles, drums and other portable containers, and any other conductive equipment.
- Make sure that ground connections in your plant are regularly checked to ensure that they are working properly.
- When filling containers with flammable liquids, minimize the amount of free fall that can create static in the liquid.

Always ground all conductive components of a flammable material handling system!

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REVISION HISTORY

Revision	Date	Description
1.0	02-Apr-2018	Initial issue. Originally donated documentation with minor modifications.
1.1	12-Sep-2018	Corrected coefficient for aerosol evaporation from 0.1 to 0.043, added correlation for aerosol temperature, and added heat loss to ground term for pool temperature. Updated Vapor Cloud Explosion to reference Lower Flammable Limit (LFL) rather than ½ LFL and updated cloud volume. Added section for Offsite Toxic evaluation
1.2	11-Feb-2019	Added section 13: LOPA. Updated BLEVE energy estimation to method of Prugh. Changes in terminology to match CCPS glossary. Added Glossary of Terms. Updated several diagrams including HIRA work flow diagram. Renumber equations.
2.0	25-Mar-2019	Major revisions in this CHEF Manual (also reflected in the CHEF Calculation Aid, the RAST User's Manual, and the RAST Software). Includes some technical clarification, updates and improved descriptions reflecting feedback on earlier editions.
3.0	12-Mar-2020	Updated the Calculation aid with enhancements to several equations and concepts. Updated Calculation Aid-related screen shots in Manual for consistency. Updated various modeling discussion sections in Manual to reflect changes to Aid. Issued in conjunction with updates made to the Risk Analysis and Screening Tool (RAST) software and RAST User's Manual. Updated literature references. Removed inadvertently duplicated Glossary from Version 2.0.