

CHEF Manual

Chemical Hazards Engineering Fundamentals



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Chemical Hazards Engineering Fundamentals (CHEF) Manual

Purpose

This document provides an overview of methods and techniques used within the Risk Analysis Screening Tool (RAST). It is intended to fill the gap between qualitative and detailed quantitative methods.

Feedback Request:

Please provide feedback or comments on the content of this document to the RAST Committee, via the CCPS webpage (www.aiche.org/ccps)

Revision History:

A complete document history is located at the end of this document.

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TABLE OF CONTENTS

Contents

| | |
|---|-----------|
| Purpose | 3 |
| Disclaimer | 3 |
| TABLE OF CONTENTS | 4 |
| 1. INTRODUCTION | 12 |
| Intended Audience | 12 |
| Sections | 12 |
| Process Risk Management..... | 12 |
| Hazard Evaluation and Risk Analysis | 13 |
| Risk Assessment..... | 13 |
| 2. HAZARD SCREENING | 16 |
| Hazard Definition..... | 16 |
| Process Hazards..... | 16 |
| Safety Data Sheets (SDS)..... | 16 |
| Hazard Classification criteria under NFPA 704 | 17 |
| Hazard Classification criteria under <i>European Dangerous Substances Directive</i> | 17 |
| Other Sources for Chemical Hazards Information | 18 |
| Guidance for Determining Equipment or Unit Operations to Include in Hazard Evaluation | 18 |
| Hazard Screening Summary..... | 19 |
| 3.FLAMMABILITY | 20 |
| Module Objectives..... | 20 |
| Fire Triangle | 20 |
| Flammability Parameters..... | 20 |
| Where to Obtain Flammability Data..... | 21 |
| Estimation of Flammable Limits for Vapor Mixtures..... | 22 |
| Example Estimation of LFL for Vapor Mixtures | 22 |

| | |
|--|-----------|
| Estimation of Flash Point for Liquid Mixtures | 23 |
| Combustible Dusts | 23 |
| Liquid Aerosol or Mist | 23 |
| Limiting Oxygen Concentration | 23 |
| Fire and Explosion..... | 24 |
| Fundamental Burning Velocity | 25 |
| Dust Explosion Pentagon | 25 |
| Secondary Dust Explosion | 26 |
| Deflagration Index | 26 |
| Maximum Explosion Pressure | 27 |
| Minimum Ignition Energy..... | 27 |
| Managing Ignition Sources | 28 |
| Adiabatic Compression | 28 |
| Static Electricity..... | 29 |
| Managing Electrostatic Discharge from Liquids and Solids | 29 |
| 4. TOXICITY | 30 |
| Module Objectives | 30 |
| How Toxicants Enter Biological Organisms | 30 |
| Toxicological Studies | 30 |
| Response to Toxic Dose | 31 |
| Lethal Concentration and Lethal Dose | 31 |
| Toxic Criteria for Risk Screening | 32 |
| Emergency Response Planning Guidelines (ERPG) | 32 |
| Inhalation Toxic Dose | 33 |
| Inhalation Toxic Mixtures | 33 |
| Example Estimation of Equivalent ERPG-3 for Vapor Mixtures | 34 |
| Relationship of Lethality to a Multiple of ERPG-3..... | 34 |
| People in Occupied Buildings | 35 |
| Asphyxiation | 35 |
| Dermal Toxicity | 36 |

| | |
|---|-----------|
| Thermal/ Chemical Burns..... | 37 |
| Environmental Toxicity..... | 37 |
| 5. REACTIVITY | 39 |
| Module Objectives..... | 39 |
| Reactivity Hazards Evaluation | 39 |
| The Search for Reactivity Hazards..... | 39 |
| Key Steps in Reactivity Hazard Evaluation..... | 40 |
| Reactive Chemicals Screening | 41 |
| Key Reactivity Hazard Screening Information..... | 41 |
| Categorization of Reactivity Hazard from Heat of Reaction per Mass | 42 |
| Estimation of the Maximum Reaction Temperature and Pressure | 42 |
| Example Estimation of Maximum Reaction Temperature and Pressure | 43 |
| Example Estimation of Maximum Reaction Pressure from Gas Generation | 43 |
| Inter-reactivity <i>Charts</i> | 43 |
| Differential Scanning Calorimetry (DSC)..... | 44 |
| Yoshida's Correlation of Highly Energetic Reactions..... | 44 |
| Detected Reaction Onset Temperature..... | 45 |
| When to Consider Additional Reactive Chemicals Testing..... | 45 |
| Accelerating Rate Calorimetry (ARC) | 46 |
| Vent Sizing Package (VSP)..... | 46 |
| Simple Kinetic Modeling to Obtain Reaction Rate Information..... | 46 |
| Temperature of No Return..... | 47 |
| Reactivity Screening..... | 48 |
| Autocatalytic Behavior | 48 |
| Evaluation of Common Process Upsets involving Reactions..... | 48 |
| 6. HAZARD IDENTIFICATION | 50 |
| Module Objectives..... | 50 |
| Non-Scenario and Scenario Based Hazard Evaluation Techniques..... | 50 |
| When to Perform Hazard Evaluation | 51 |
| Preparing for Hazard Evaluation | 51 |

| | |
|---|-----------|
| Process Equipment to Include in a Hazard Evaluation Study | 52 |
| Key Process Information Needed for Hazard Evaluation | 53 |
| Process Hazard Assessments | 53 |
| Checklist Analysis | 54 |
| Relative Ranking | 55 |
| Scenario-Based Hazard Evaluation Definitions..... | 55 |
| Scenario Development..... | 55 |
| Initiating and Loss Events | 56 |
| Initiating Events..... | 57 |
| Incidents or Loss Events | 57 |
| Incident Outcome | 58 |
| What-If Analysis | 59 |
| What-If Checklist..... | 59 |
| Hazard and Operability Study (HAZOP)..... | 60 |
| HAZOP Study Terms | 60 |
| Simple HAZOP Example Node, Parameter and Deviation | 61 |
| Additional HAZOP Study Terms..... | 62 |
| HAZOP Documents | 62 |
| Other Hazard Identification Methods | 63 |
| Scenario Libraries | 64 |
| Example Scenario Library | 65 |
| Scenario Feasibility | 66 |
| 7. INTRODUCTION TO RISK ANALYSIS..... | 67 |
| Overall Work Process Steps for Risk Analysis..... | 67 |
| Chemical Process Risk | 68 |
| Measurement of Risk..... | 68 |
| “Sharpening the Pencil” | 69 |
| 8. ESTIMATION OF AIRBORNE QUANTITY | 70 |
| Module Objectives..... | 70 |
| Flowchart for Determination of Airborne Quantity..... | 70 |

| | |
|---|-----------|
| Selection of a Discharge Model | 71 |
| Hole Size Release Rate for Vapor or Subcooled Liquid | 72 |
| Hole Size Release Rate Example-Vapor..... | 72 |
| Hole Size Release Rate Example-Liquid..... | 72 |
| Hole or Short Pipe Size Release Rate for Flashing Liquid | 72 |
| Example Hole or Short Pipe Size Release Rate for Flashing Liquid..... | 73 |
| Liquid Trajectory from a Hole..... | 73 |
| Overflow or Specified Discharge Rate | 74 |
| Discharge Rate from Excessive Heat Input..... | 74 |
| Example Discharge Rate from Excessive Heat Input | 74 |
| Test for Two-Phase Flow | 75 |
| Example Test for Two-Phase Flow..... | 76 |
| Equipment Rupture | 76 |
| Estimation of Mixture Properties | 76 |
| Estimation of Flash Fraction | 77 |
| Flash Fraction for Chemical Mixtures | 77 |
| Aerosol Evaporation | 77 |
| Example Aerosol Evaporation..... | 79 |
| Evaporation from a Liquid Pool..... | 79 |
| Example Evaporation from a Liquid Pool | 80 |
| Example Airborne Quantity for a Flashing Liquid Release | 80 |
| 9. VAPOR DISPERSIONS | 82 |
| Module Objectives..... | 82 |
| Vapor Dispersion Mechanisms | 82 |
| Jet Mixing..... | 83 |
| Jet Mixing Example | 84 |
| Continuous versus Instantaneous Release | 84 |
| Atmospheric Dispersion Modeling..... | 85 |
| Dense Gas Dispersion Models..... | 86 |
| Neutrally Buoyant Gaussian Models..... | 86 |
| Simple Vapor Dispersion Correlation..... | 87 |

| | |
|--|-----------|
| Correction for Initial Dilution in Simple Vapor Dispersion Model | 87 |
| Vapor Dispersion Example – Estimate Distance to a Concentration | 88 |
| Vapor Dispersion Model Example – Estimate Concentration at a Distance..... | 88 |
| Evaluation of Short Duration Release | 88 |
| Estimation of Toxic Exposure Duration | 89 |
| Correction for Elevation in Simple Vapor Dispersion Model | 89 |
| Estimation of Maximum Ground Level Concentration | 90 |
| Example Correction for Elevation | 90 |
| Relief Device Effluent Screening | 91 |
| Simplified Relief Effluent Screening Process | 91 |
| Relief Effluent Screening Criteria | 92 |
| Relief Effluent Screening Tool and Additional Information..... | 93 |
| Releases Impacting Personnel Located Indoors | 94 |
| Releases within an Enclosed Process Area | 94 |
| Toxic Infiltration from an Outdoor Release | 94 |
| Typical Ventilation Rates..... | 95 |
| 10. EXPLOSIONS | 95 |
| Module Objectives..... | 96 |
| Explosion Definitions | 96 |
| Damage and Blast Overpressure | 96 |
| Physical Explosion Using Simple TNT Model | 97 |
| TNT Model Example | 98 |
| Baker-Strehlow-Tang Explosion Model | 98 |
| Potential Explosion Site (PES)..... | 101 |
| Building Explosion and Equipment Deflagration..... | 102 |
| Building Explosion Example | 102 |
| Vapor Cloud Explosion Using Simplified Baker-Strehlow-Tang Model | 102 |
| Vapor Cloud Explosion Example..... | 103 |
| Class Exercise | 104 |
| Limitations of Simple Explosion Models | 104 |

| | |
|---|------------|
| 11. IMPACT ASSESSMENT | 105 |
| Module Objectives..... | 105 |
| Incident Outcome | 105 |
| Generalized Outcome Event Tree | 106 |
| Incident Outcome Selection Criteria | 106 |
| On-Site Consequence Severity..... | 107 |
| Example Screening Criteria for Levels of Concern | 109 |
| Chemical Exposure Example Criteria | 109 |
| Thermal Radiation Example Criteria | 110 |
| Estimating Number of People Impacted for On-site Incident | 110 |
| Estimating the On-site Probability of Exposure | 111 |
| Example Impact Assessment for Outdoor Release | 111 |
| Estimating Number of People Impacted within Occupied Buildings..... | 112 |
| Example Impact Assessment for an Occupied Building Example | 113 |
| Offsite Toxic Impacts | 113 |
| Summary of Key Consequence Analysis Steps | 115 |
| | |
| 12. LIKELIHOOD EVALUATION | 115 |
| Module Objectives..... | 116 |
| Definition of Terms | 116 |
| Failure Frequency | 116 |
| Reliability and Failure Probability | 117 |
| Interactions Between Hardware or System Components | 117 |
| Probability of Failure on Demand | 118 |
| Failure Frequency from Historical Data..... | 119 |
| Human Reliability | 120 |
| Enabling Conditions..... | 120 |
| Unmitigated Risk..... | 121 |
| Likelihood Modeling..... | 121 |
| Fault Tree Likelihood Modeling | 122 |
| Example Fault Tree Analysis | 122 |
| Event Tree Likelihood Modeling..... | 123 |

Example Event Tree Analysis for Series of Protective Layers 124

Domino Effects 124

Simplified Pool Fire Frequency Analysis 124

Analysis of Protective Layers..... 125

Barrier Analysis..... 126

Layers of Protection Analysis 126

Tolerable Frequency..... 127

13. SUMMARY 129

 Hazard Evaluation and Risk Analysis 129

 Overall Work Process Steps for Hazard Evaluation and Risk Analysis..... 129

REFERENCES 130

REVISION HISTORY..... 132

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 is:

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

Sections

There are 13 sections or modules included in this Chemical Hazard Engineering Fundamental manual including:

1. Introduction (this section)
2. Hazard Screening
3. Flammability
4. Toxicity
5. Reactivity
6. Hazard Identification
7. Introduction to Risk Analysis
8. Estimation of Airborne Quantity
9. Vapor Dispersions
10. Explosions
11. Impact Assessment
12. Likelihood Evaluation
13. Summary

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.

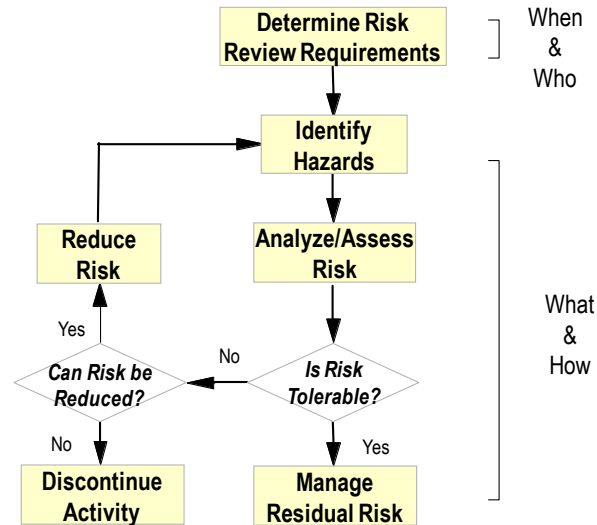


Figure 1.1 Simplified Risk Management Process

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.

Hazard Evaluation and Risk Analysis

Hazard Evaluation and Risk Analysis are processes whereby hazards are evaluated by answering basic questions:

- What are the Hazards?
- What can go wrong?
- What are the potential consequences?
- How likely is it to happen?
- Is the Risk Tolerable?

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.

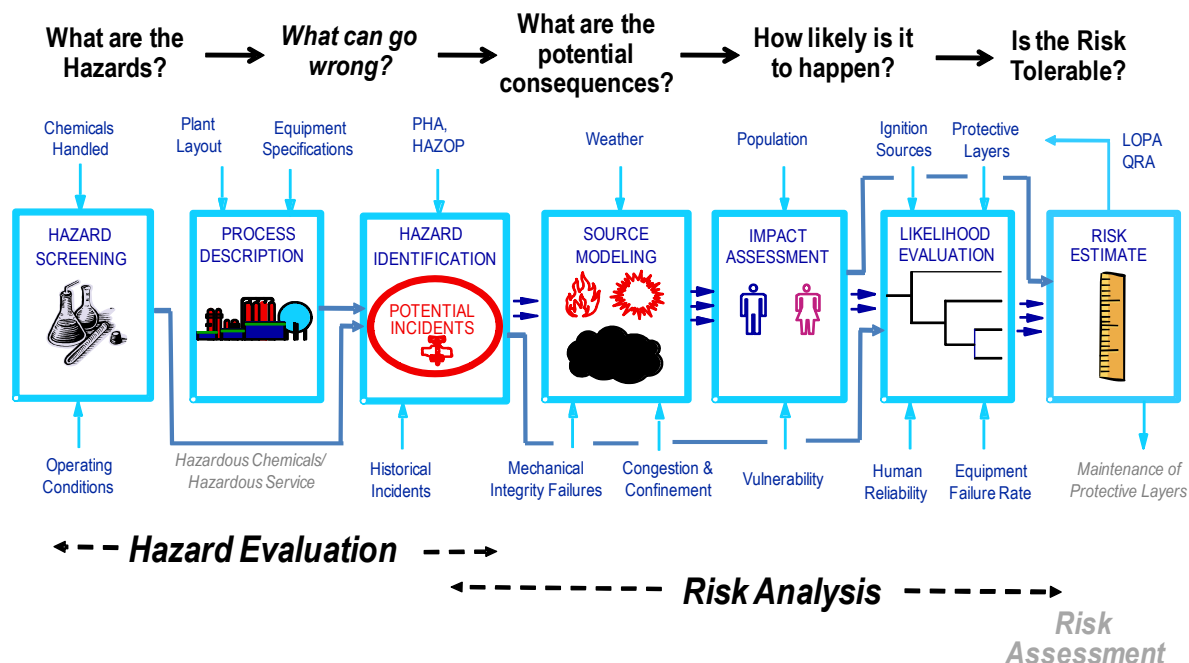


Figure 1.2 Overall Work Process Steps for Hazard Evaluation and Risk Analysis

The overall Work Process for Hazard Evaluation and Risk Analysis includes:

- *Hazard Screening* is an assessment of inherent chemical properties and process conditions to support design of basic processes and determine if the potential for causing harm is sufficient to warrant further evaluation for a specific process unit.
- *Process Description* involves chemical, equipment, process conditions, and facility layout information appropriate for the Risk Analysis being performed. Much of this information is documented on Material and Energy Balance summaries, Process Flowsheets, and Piping and Instrument Diagrams.
- *Hazard Identification* is often qualitative and common techniques include simple Brainstorming, What-If Checklists, and Hazard & Operability Analysis (HAZOP). It represents the pinpointing of weaknesses in the design and operation of facilities that could lead to an incident through a sequence of events.
- *Consequence Analysis* yields incident outcome cases independent of frequency or probability. For simplified Risk Analysis, simplifying assumptions (such as 3 m/sec wind speed and Class D atmospheric stability with direction directly toward personnel) are used. Consequence Analysis primarily involves *estimation of airborne quantity, vapor dispersion modeling, and explosion modeling*.
- *Impact Assessment* provides an estimate of the magnitude of the consequence, most commonly based on a maximum number of people severely impacted. Lethality (probit) models are used for higher levels of Risk Assessment.
- *Likelihood Evaluation* provides a measure for the expected probability or frequency of occurrence for an event or event sequence. It is "order of magnitude" for simplified risk analysis but factors may not always be "independent".
- *Risk Estimate* is a measure of human injury, environmental damage, or economic loss in terms of both the incident magnitude and frequency.

The Risk Assessment process for decisions regarding specific requirements or management systems to appropriately manage or control risk are beyond the scope of Chemical Hazard Engineering Fundamentals training.

2. HAZARD SCREENING

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 Evaluation or Risk Analysis, Process Hazards must be identified and screened to determine which equipment or unit operations should be analyzed.

Hazard Definition

A Hazard is defined as an inherent physical or chemical characteristic that has the potential for causing harm to people, property, or the environment.

Process Hazards

Process Safety addresses acute hazards; one to which a single or short duration exposure may cause harm or damage. In addition to chemical and explosion hazards, asphyxiation and dermal exposure to corrosive, hot or cold materials as a result of a release is also included. 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 Evaluation study. In addition to these, any chemical or chemical that the study teams feel represents a hazard should be included.

Typical Chemical Hazards include:

- Flammability
- Toxicity (*Inhalation, Dermal, or Environmental*)
- Reactivity or Instability
- Chemicals considered Hazardous by a Regulatory Agency

Hazardous Process Conditions include:

- High/Low Temperature
- Corrosive
- High/Low Pressure

Safety Data Sheets (SDS)

Material Safety Data Sheets (SDS) are a tremendous source of information for hazards associated with the chemicals we handle. 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 MSDS. The European Dangerous Substances Directive on Classification, Labeling and Packaging of Substances and Mixtures, utilizes *Physical Hazard Statements* and *Health Hazard Statements* based on quantitative measures which may be referenced on an SDS.

Hazard Classification criteria under NFPA 704

Classification criteria under the US National Fire Protection Agency (NFPA 704):

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 Material Safety Data Sheets for the associated chemical supplier.

Hazard Classification criteria under *European Dangerous Substances Directive*

Classification criteria under European Dangerous Substances Directive on Classification, Labeling and Packaging of Substances and Mixtures:

Flammability

Extremely Flammable – 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

Highly Flammable – 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.

Flammable – 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

Fatal, Very Toxic – Oral LD₅₀, rat, < 25 mg/kg (Very Toxic if swallowed); Dermal LD₅₀, rat or rabbit, < 50 mg/kg (Very Toxic in Contact with Skin); Inhalation LC₅₀, 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 LD₅₀, rat, between 25 and 200 mg/kg (Toxic if swallowed); Dermal LD₅₀, rat or rabbit, between 50 and 400 mg/kg (Toxic in Contact with Skin); Inhalation LC₅₀, 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 LD₅₀, rat, between 200 and 2000 mg/kg (Harmful if swallowed); Dermal LD₅₀, rat or rabbit, between 400 and 2000 mg/kg (Harmful in Contact with Skin); Inhalation LC₅₀, 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, and reactivity information such as heat of reaction may be used. This information may be found in open literature.

Guidance for Determining Equipment or Unit Operations to Include in Hazard Evaluation

The following guidance is an example that may be used in determining what equipment items should be included in a Hazard Evaluation study. In addition to these criteria, any chemical or chemical that the study teams feel represents a hazard should be included.

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, vessels, or piping handling chemicals are not considered as **Hazardous Conditions** sufficient for evaluation 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*

If equipment or piping is not located within an enclosed area that a release could pose an asphyxiation hazard

Hazard Screening Summary

Hazards to be evaluated include potential for thermal burns, chemical burns, equipment rupture, relief device activation, and asphyxiation in addition to flammability, toxicity, and reactivity. When in doubt if a hazard sufficient to include equipment, vessels or piping in the evaluation; *include it*. There are steps later in the Risk Analysis process when scenarios, incidents or outcome will be screening out from further evaluation.

3.FLAMMABILITY

Potential consequences from fires within chemical and hydrocarbon facilities are very significant. In the US, property damage exceeds \$300 MM annually from fire related incidents. Business interruption and loss of life are also substantial.

Module Objectives

In this module you will learn:

- 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 and how it is measured.
- 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. Combustion occurs in the vapor phase: liquids are volatilized and solids are decomposed into vapor prior to combustion.

Flammability Parameters

- 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.

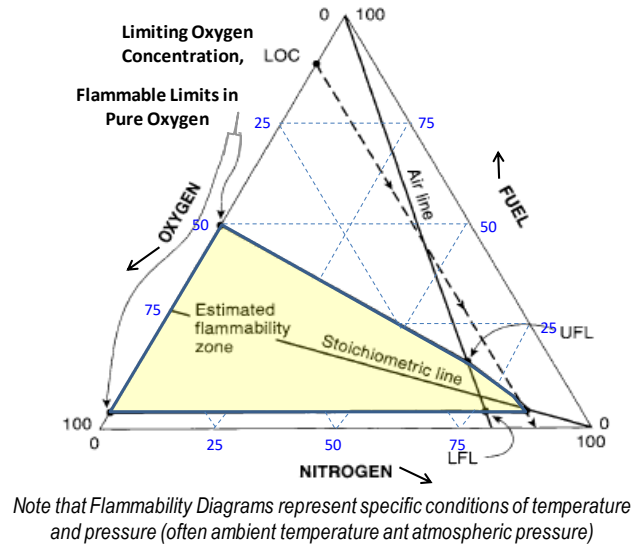


Figure 3.1 Flammability Diagram

Several flammability properties can be explained by the use of a triangular flammability diagram. 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.:

Where to Obtain Flammability Data

Flammability data for common chemicals can often be found in the open literature.

| 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 |

Table 3.1 Example Flammability Data

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/m³ for many hydrocarbons. As mixtures are very common in chemical processing, the mixture LFL is routinely needed and may be estimated from Le Chatelier's equation^{7,11}:

$$LFL_{\text{mix}} = 1 / \sum (y_i / LFL_i) \quad (1)$$

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 Le Chatelier's equation. 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:

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

Estimation of Flash Point for Liquid Mixtures

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 than one flammable component.

Combustible Dusts

A Combustible Dust is any finely divided solid material, 420 microns¹⁵ (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. In addition, the Explosible Range of dust concentration is very broad⁹, typically from 20 to 6000 g/m³.

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 Velocity¹⁷. 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 size⁸. Aerosol droplets greater than 0.6 mm typically do not support flame propagation⁷.

Limiting Oxygen Concentration

Most organics have a Limiting Oxygen Concentration (LOC) of roughly 9 to 10 volume % if N₂ is the inert. 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.

| Gas/Vapor | Adjusted LOC (Volume % O ₂ Above Which Deflagration Can Take Place) per 7.2.3 | |
|-------------------------|--|------------------------------|
| | N ₂ -Air Mixture | CO ₂ -Air Mixture |
| Methane | 10.0 | 12.5 |
| Ethane | 9.0 | 11.5 |
| Propane | 9.5 | 12.5 |
| <i>n</i> -Butane | 10.0 | 12.5 |
| <i>n</i> -Butyl acetate | 9.0 | — |
| Isobutane | 10.0 | 13.0 |
| <i>n</i> -Pentane | 10.0 | 12.5 |
| Isopentane | 10.0 | 12.5 |
| <i>n</i> -Hexane | 10.0 | 12.5 |
| <i>n</i> -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

Table 3.2 Limiting Oxygen Concentration

Notable exceptions to 9-10% Limiting Oxygen are:

- Acetylene
- Carbon disulfide
- Carbon monoxide
- Ethylene Oxide
- Hydrogen
- Propylene Oxide

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

Fire and Explosion

The major distinction between Fire and 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.

- **Explosion:** Sudden expansion of gases resulting in a rapidly moving pressure or shock 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”.

| Fundamental Burning Velocities for Selected Flammable Gases in Air (NFPA 68 Annex C) | |
|---|------------------------|
| | <u>(cm/sec)</u> |
| 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 |

Table 3.3 Fundamental Burning Velocities

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.

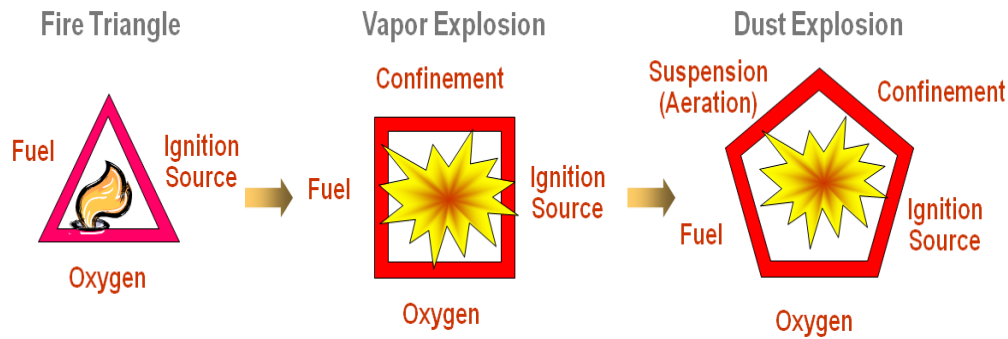


Figure 3.2 the Dust Pentagon

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

Secondary Dust Explosion

An initial explosion or process upset creates a pressure wave that dislodges accumulated dust from the structure. Ignition of this suspended dust may lead to a devastating secondary explosion that may result in 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.

Deflagration Index

Deflagration Index 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. These effects cannot be determined theoretically so it is better to have test data on specific materials at the operating conditions of concern. Deflagration Index for dusts is categorized into three classes with Class “ST-3” (or Class 3) being the most energetic.

| Deflagration Characteristics of Selected Combustible Dusts (NFPA 68 Annex E) | | | | |
|---|---------------------------------|------------------------|-----------------------------|-------------------|
| Material | Particle Size (μm) | P _{max} (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 | K _{st} (bar m/sec) | P _{max} (bar) |
|-------------------|-----------------------------|------------------------|
| ST-1 | <200 | 10 |
| ST-2 | 201-300 | 10 |
| ST-3 | >300 | 12 |

Table 3.4 Dust Deflagration Characteristics and Deflagration Index

Maximum Explosion Pressure

The maximum explosion pressure for organic materials (gas, vapor, or dust) 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.

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). 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. Beware of locations where fine dust can accumulate (such as a dust collector or overhead beams / rafters).

NFPA 68 Figure 4.3.4.2.1 Effect of Average Particle Diameter of a Typical Agricultural Dust on the Minimum Ignition Energy

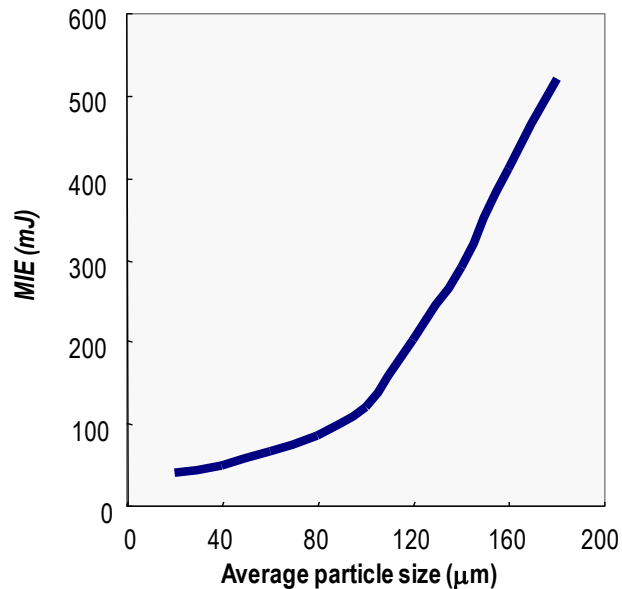


Figure 3.3 Impact of Particle Size on Minimum Ignition Energy

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. Common ignition sources include:

- Hot surfaces (such as heaters, dryers, and hot bearings)
- Open flames (such as a fired heater or boiler)
- Nearby Combustion Engine (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.

$$T_f = T_0 (P_f / P_0)^{(\gamma-1)/\gamma} \quad (2)$$

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 discharge⁷. 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. Since a high ignition risk is also associated with charged surfaces, nonconductive materials of construction or nonconductive linings, (examples: fiberglass, glass) should not be used with flammable liquids.

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, API 2003 recommends that velocity times pipe diameter less than 0.5 m²/sec be used for filling of tank trucks to minimize static build-up of nonconductive liquids.

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.

4. TOXICITY

A toxic vapor release into a public area represents one of the most feared events for regulatory authorities. Although fire and explosion have caused a far greater number of serious injuries including fatalities than exposure to toxic chemicals, the potential for an extremely catastrophic incident may be greater for a large toxic vapor (such as occurred at Bhopal in 1984). Since most of us are less familiar with toxicity than flammability hazards, we will spend time covering background information.

Module Objectives

In this module you will learn:

- Response to Toxic Dose
- The definition of LC₅₀ and LD₅₀.
- 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/m³) 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, resulting in a bimodal distribution of the dose versus response curve. Some chemicals attack the respiratory system (such as acid gases), induce narcosis, attack the central nervous system or other 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.

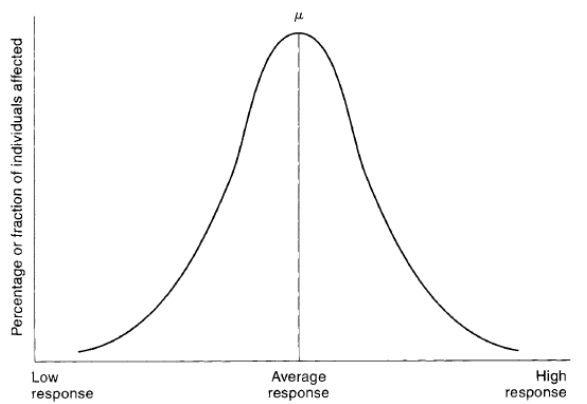


Figure 4.1 Typical Toxic Dose-Response Curve

Lethal Concentration and Lethal Dose

LC 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 LC₅₀ value. The LC₁₀ value is the concentration which kills 10% of the test animals in a given exposure time.

LD is “Lethal Dose”. LD₅₀ 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 LD₅₀ is one way to measure the short-term poisoning potential (acute toxicity) of a material.

LC₅₀ is used in the comparison of toxicities. For inhalation, LC₅₀ 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 LC₅₀ 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 promulgated by government agencies and private associations including:

- 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
- Toxic Endpoints promulgated by the US EPA as part of the Risk Management Process (RMP)

Emergency Response Planning Guidelines (ERPG)

Emergency Response Planning Guideline (ERPG) concentration values are published by the American Industrial Hygiene Association and undergo comprehensive peer review. The list of values has expanded 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.

| Chemical | Concentration (ppm) | | |
|-----------------------|---------------------|--------|--------|
| | ERPG-1 | ERPG-2 | ERPG-3 |
| Ammonia | 25 | 150 | 750 |
| 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 |

Table 4.1 Example ERPG Values

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^{2,10}:

$$\text{Toxic Dose} = C^n t \quad (3)$$

For time varying concentration, dose is commonly evaluated by summation of time increments:

$$\text{Toxic Dose} = \sum C_i^n \Delta t_i \quad (4)$$

where C is concentration, n an exponent specific to the chemical evaluated, and 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 is often used if there is not sufficient data at different test durations for estimation of “time scaled” ER values to exposure duration less than 1 hour. If extrapolation of the “time scaled” ER to greater than 1 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 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)^{7,19}.

$$\text{ERPG}_{\text{Mixture}} = 1 / \sum (y_i / \text{ERPG}_i) \quad (5)$$

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:

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

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. 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.

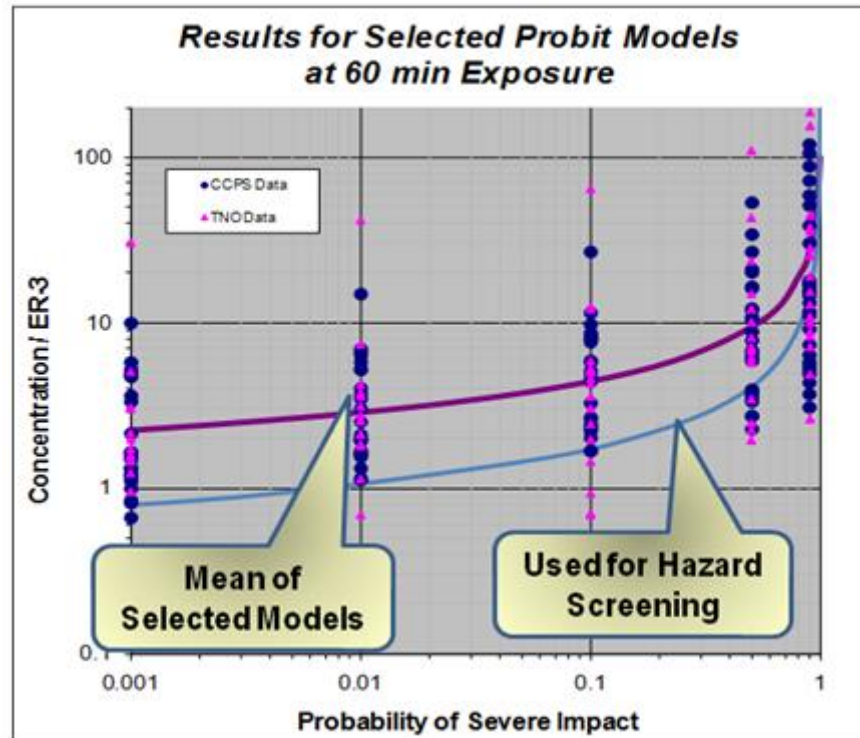


Figure 4.2 Multiple of ERPG-3 Concentration Vs Lethality for 60-minute Exposure

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. Relatively non-toxic chemicals may pose an asphyxiation hazard, particularly for release within an enclosed process area. The oxygen content may be estimated as: associated

$$\text{Average Percent Oxygen} = 21 \left(1 - \frac{C_{\text{Indoor}}}{1000000} \right) \quad (6)$$

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

| Atmospheric Oxygen Concentration (%) | Possible Results |
|---|---|
| 20.9 | Normal |
| 19.0 | Some unnoticeable adverse physiological effects |
| 16.0 | Increased pulse and breathing rate, impaired thinking and attention, reduced coordination |
| 14.0 | Abnormal fatigue upon exertion, emotional upset, faulty coordination, poor judgment |
| 12.5 | Very poor judgment and coordination, impaired respiration that may cause permanent heart damage, nausea, and vomiting |
| < 10 | Inability to move, loss of consciousness, convulsions, death |

SOURCE: Compressed Gas Association, 2001.

Table 4.2 Effects of Oxygen Deficiency

- 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.

Dermal Toxicity

Dermal Toxicity is a key parameter for evaluation of exposure to *liquids*. 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. Phenol, for example, requires only a small area of skin to be exposed for a sufficient quantity to be absorbed resulting in 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 LD₅₀, < 200 mg/kg (Fatal in Contact with Skin, Very Toxic in Contact with Skin) with Category 1 as Dermal LD₅₀ < 50 mg/kg.
- *Toxic* – Dermal LD₅₀, between 200 and 1000 mg/kg (Toxic in Contact with Skin)
- *Harmful* – Dermal LD₅₀ 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.

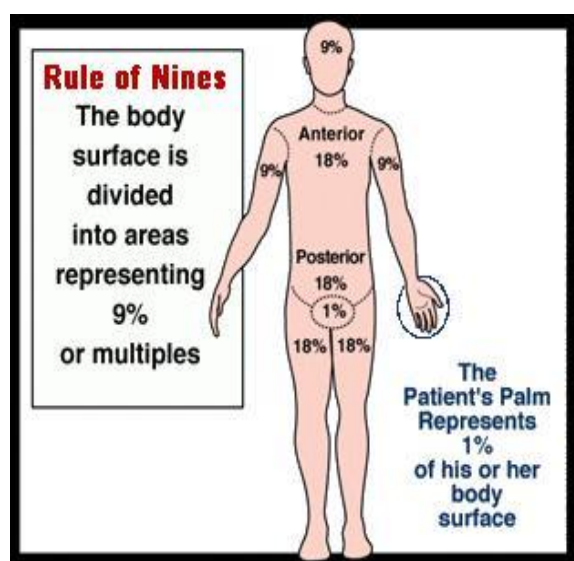
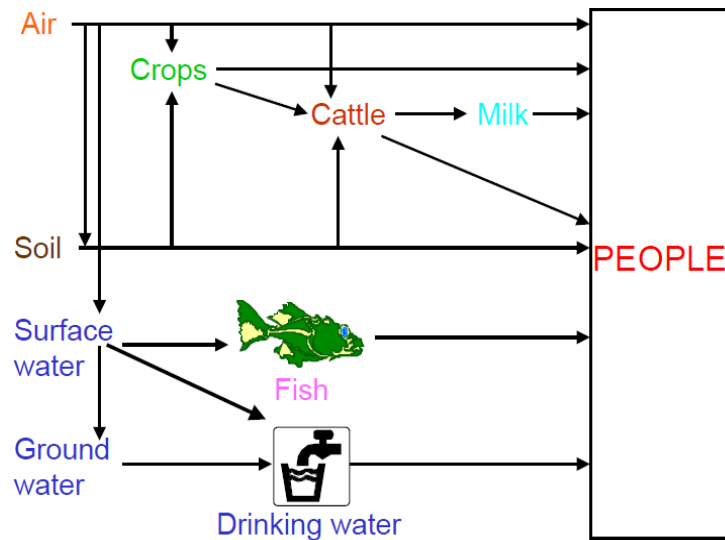


Figure 4.3 Estimation of Percent Body Surface

Environmental Toxicity

Risk Analysis for the possible effects of a substance entering the environment which may harm people should consider exposures through all routes 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.



Acute Pathway →

Figure 4.4 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.

Ingestion Toxicity

- Fatal, Very Toxic – Oral LD₅₀ < 50 mg/kg (Fatal if swallowed, Very Toxic if swallowed) with Category 1 as Oral LD₅₀ < 5 mg/kg
- Toxic – Oral LD₅₀ between 50 and 300 mg/kg (Toxic if swallowed)
- Harmful – Oral LD₅₀ between 300 and 2000 mg/kg (Harmful if swallowed)

Aquatic Toxicity

- Very Toxic – 96 hr. LC₅₀ fish < 1 mg/liter, or 48 hr. LC₅₀ Daphnia < 1 mg/liter, or 72 hr. LC₅₀ algae < 1 mg/liter (Very Toxic to Aquatic Organisms)
- Toxic – 96 hr. LC₅₀ fish between 1 and 10 mg/liter, or 48 hr. LC₅₀ Daphnia between 1 and 10 mg/liter, or 72 hr. LC₅₀ algae between 1 and 10 mg/liter (Toxic to Aquatic Organisms)
- Harmful – 96 hr. LC₅₀ fish between 10 and 100 mg/liter, or 48 hr. LC₅₀ Daphnia between 10 and 100 mg/liter, or 72 hr. LC₅₀ algae between 10 and 100 mg/liter (Harmful to Aquatic Organisms)

5. 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.

Module Objectives

In this module you will learn:

- 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 shall be required 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.:

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. *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.

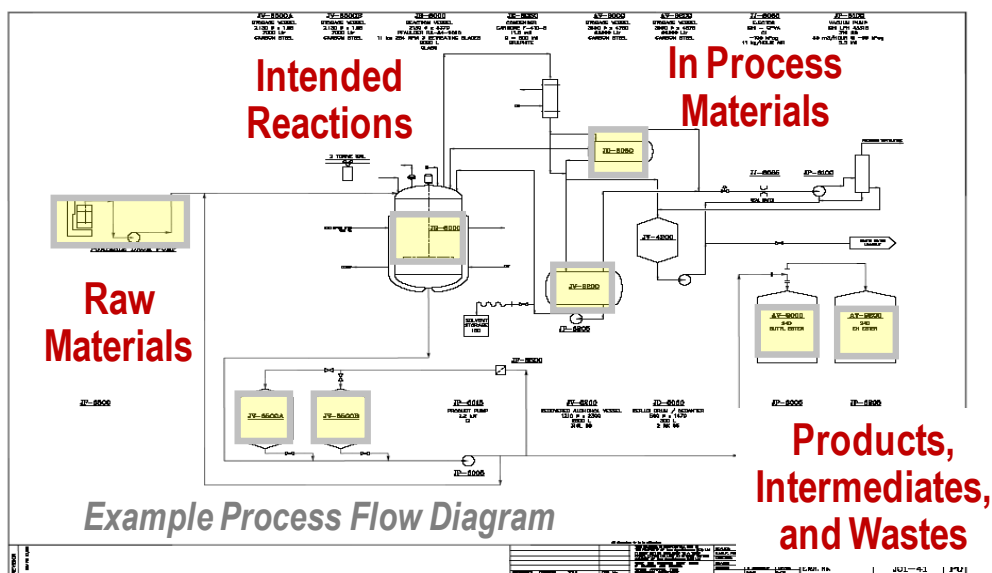


Figure 5.1 Search for Reactivity Hazards

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 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 in 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 as:

$$T_{\max} = T_0 - \Delta H_R / C \quad (7)$$

Note that heat evolved is a negative value by convention. The corresponding maximum pressure for a liquid phase reaction may be estimated as:

$$P_{\max} = P_{\text{pad}} (T_{\max}/T_0) + P_{\text{VP}@T_{\max}} + \beta R T_{\max} (V_L/V_V) \quad (8)$$

where:

T_0 is the initial temperature

ΔH_R is heat of reaction per mass

C is liquid heat capacity

$P_{\text{VP}@T_{\max}}$ is vapor pressure at maximum temperature

P_{pad} is initial pad gas pressure

β is mole gas created per liquid volume

R is gas law constant

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

Note that the gas generation term in the above equation is based on an ideal gas with no liquid solubility. For example, if $\beta = 0.1$ 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 $\beta R T_{\max} (V_L/V_V) = 0.1 (0.082 \text{ mole/liter-atm-K}) 300 \text{ K} (0.8 \text{ fraction liquid} / 0.2 \text{ fraction vapor}) = 9.84 \text{ atm}$.

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:

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

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.

$$\begin{aligned} P_{max} &= P_{VP@T_{max}} + \beta R T_{max} (V_L/V_V) \\ &= 2 \text{ atm} + 0.1 \text{ mole/liter} (0.082) (373 \text{ K}) (0.8 \text{ volume liquid} / 0.2 \text{ volume vapor}) \\ &= 14.2 \text{ atmospheres} \end{aligned}$$

Inter-reactivity Charts

Inter-reactivity (or 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.

| Gesundheit / Health Erzundbarkeit / Flammability Reaktivitat / Reactivity | | | Chemical Compatibility Chart UNIT 300 This compatibility chart was compiled for the Technology Package. Compatibility is scenario dependent Reviewed by tech expert: J.Adi Date: | | | | | | | | | | | | | | | | | | |
|--|---|---|---|------------------------------|----------------------|--------------------|------------------------|------------------|-----------------|---|----------------------------|---------------------------|------------|--|--|--|--|--|--|--|--|
| | | | Atmer 163 (Alkylaminethoxylate) | Polypropylen / Polypropylene | Propylen / Propylene | Ethylen / Ethylene | Wasserstoff / Hydrogen | Butylen / Butene | Killgas (CO/N2) | Katalysator (aktiviert) / Catalyst (active) | Kuhlwasser / Cooling water | Mineral oel / Mineral oil | Luft / Air | | | | | | | | |
| | | | Atmer 163 (Alkylaminethoxylate) | | | | | | | | | | | | | | | | | | |
| | | | Polypropylen / Polypropylene | | | | | | | | | | | | | | | | | | |
| 1 | 4 | 1 | Propylen / Propylene | | | | | | | | | | | | | | | | | | |
| 1 | 4 | 2 | Ethylen / Ethylene | | | | | | | | | | | | | | | | | | |
| 0 | 4 | 0 | Wasserstoff / Hydrogen | | | | | | | | | | | | | | | | | | |
| 1 | 4 | 0 | Butylen / Butene | | | | | | | | | | | | | | | | | | |
| 3 | | 0 | Killgas (CO/N2) | | | | | | | | | | | | | | | | | | |
| | | | Katalysator (aktiviert) / Catalyst (active) | | | | | | | | | | | | | | | | | | |
| | | | Kuhlwasser / Cooling water | X | X | | | | | | X | X | | | | | | | | | |
| | | | Mineral oel / Mineral oil | X | X | | | | | | X | X | | | | | | | | | |
| | | | Luft / Air | | | | | | | | | | | | | | | | | | |

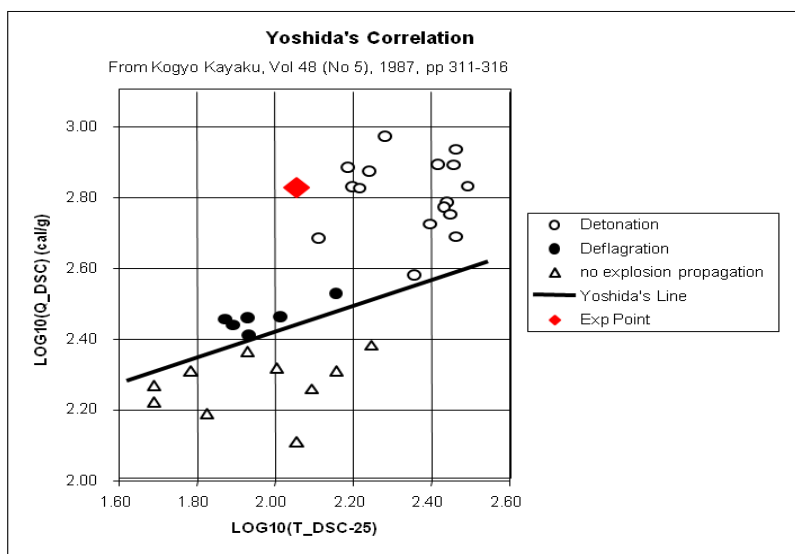
Figure 5.2 Example Inter-Reactivity Chart

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 Correlation²⁴ 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*.



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 calorimeter²².

The “rule of thumb” that a “safe operating temperature limit” of 50 C below a detected onset temperature by Differential Scanning Calorimetry 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 reaction rate 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. 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 to:

$$\text{Reaction Rate} = r_0 (1-X) \exp \left[\frac{\Delta E}{R} \left(\frac{1}{T_0} - \frac{1}{T} \right) \right] \quad (9)$$

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 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.

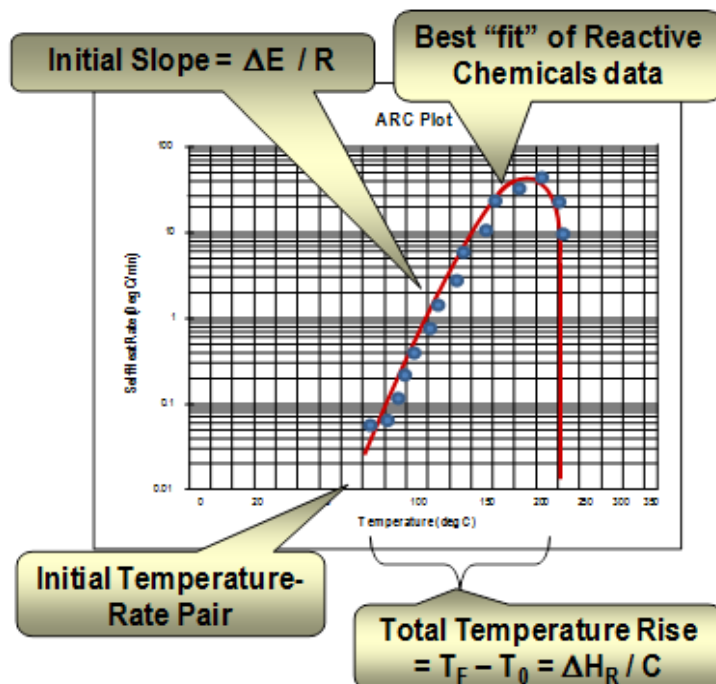


Figure 5.4 Example ARC Temperature Rate vs Temperature Plot

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.

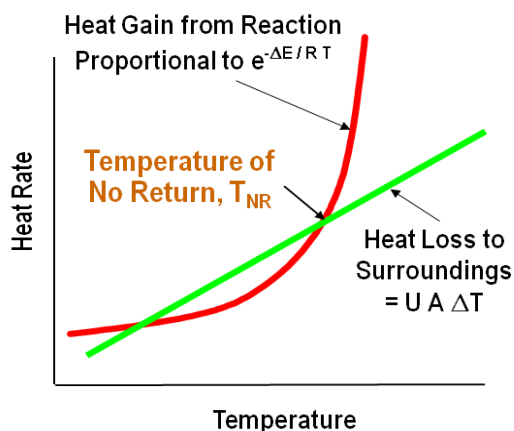


Figure 5.5 Temperature of No Return

The Temperature of No Return, T_{NR} , is commonly used to determine Safe Operating Conditions²³. 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 temperature 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 as²³:

$$t_{MR} = R T_0^2 / (q_0 \Delta E) \quad (10)$$

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 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.

6. HAZARD IDENTIFICATION

Hazard Identification is an organized effort to identify and analyze “what can go wrong” in a chemical process. Fortunately, the number of catastrophic incidents is very small relative to the total number of incidents or near misses each year. Most of us will not personally experience a catastrophic incident during our career. This may present a challenge in appreciating the importance in developing a thorough Hazard Evaluation.

Module Objectives

In this module you will learn:

- 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 scenario cases.

Non-Scenario and Scenario Based Hazard Evaluation Techniques

Hazard Evaluation involves both experience-based and predictive techniques¹. 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.

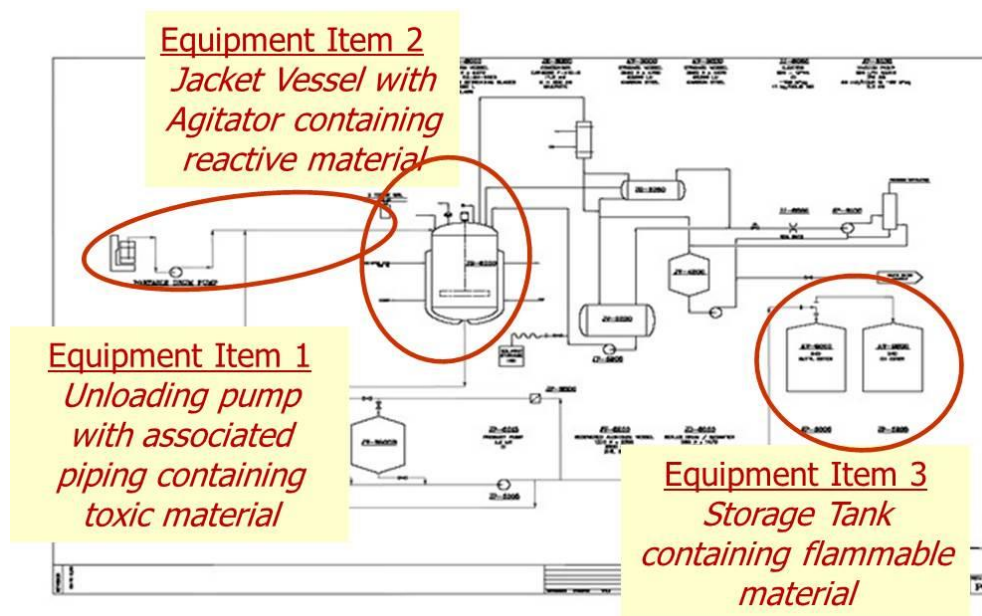


Figure 6.1 Example Equipment Depiction on Process Flowsheet

Hazard Identification typically begins with a review Index Flowsheets, Process Flowsheets, 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.

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 also 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 most of us 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)¹:

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 related to equipment performance, human action, or an occurrence external to the system that causes system upset.
- **Event Sequence** – A specific, unplanned series of events composed of an initiating event and intermediate events that may lead to an incident.
- **Incident (or Loss Event)** – the unintended loss of containment of material or energy (such as explosion, leak or spill, etc.).
- **Initiating Event** – the first event in an event sequence and marks the transition from a normal to an abnormal situation.
- **Outcome** – the physical manifestation or generic result of an incident. Examples include: toxic release, flash fire, vapor cloud explosion, etc.
- **Scenario** – an unplanned sequence of events leading to an incident and its associated outcome, including the success or failure of safeguards, barriers or protective layers.

Scenario Development

Scenario development is the step in which the team or analyst constructs a series of events, including initiating events that lead to an incident with undesired consequence.

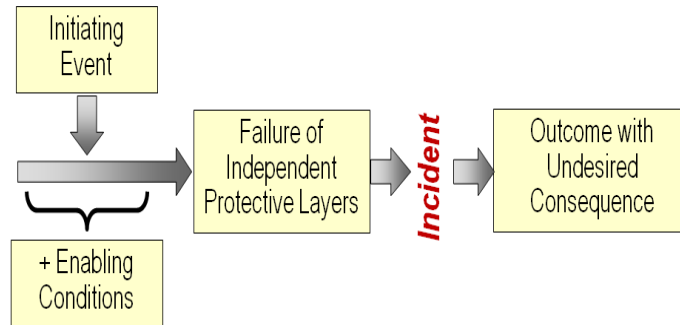


Figure 6.2 Hazard Scenario

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 Incident or 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

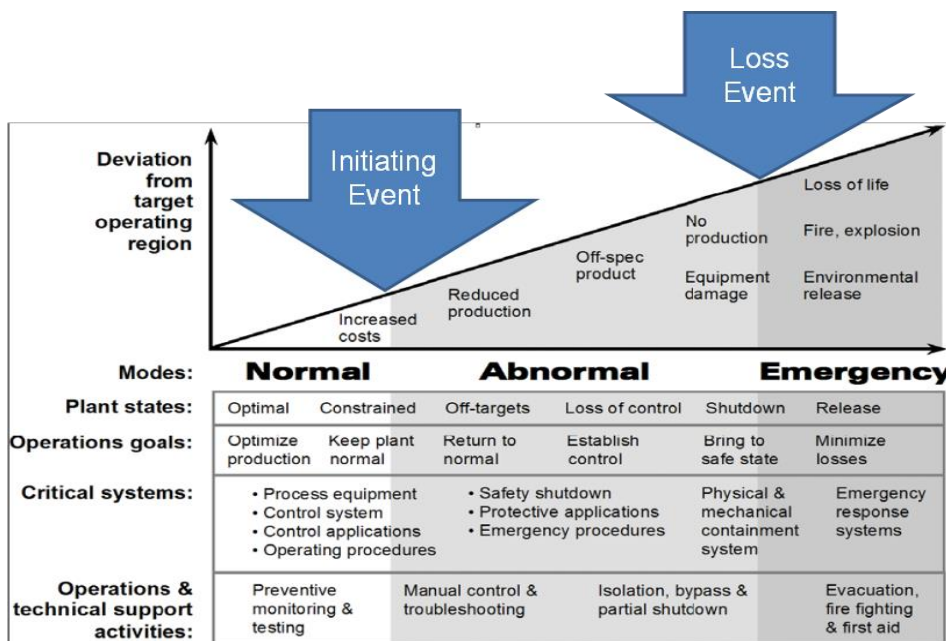


Figure 6.3 Common Operating Modes

Initiating Events

Initiating Events typically fall into broad categories⁵:

- **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, we sometimes consider **Domino Effects** from fires or explosions in adjacent equipment as a cause or Initiating Event.

Management systems are not normally listed as potential initiating events, although ineffective management systems are quite often a root cause of human error.

Incidents or Loss Events

An Incident or Loss Event is 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 (or Incident) 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), Incidents 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 impact 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.

| Thought Provoking Issue | Scenarios Worth Further Evaluation | Controls | Hazard Category and Recommendations |
|--|--|-------------------------------|--|
| Sub System: | | | |
| A. Releases via Mechanical Failure Causing Emissions, Fires, Explosions: | | | |
| 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. | <i>Note: If using this checklist to do analysis, list scenario, hazard/consequence</i> | <i>List existing controls</i> | <i>List any recommendations, and follow-up needs</i> |
| 1. Vessel Failure | | | |
| a. Installation | | | |
| (1) vibration | | | |
| (2) fatigue | | | |
| (3) embrittlement, (e.g., cast iron/steel, H ₂) | | | |
| b. Impingement | | | |
| (1) crane drop | | | |
| (2) heavy equipment impact | | | |
| (3) vehicle impact | | | |
| (4) tank car/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 | | | |

Figure 6.4 Example What-If Checklist

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 industry¹. 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 a point of reference 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 is important for an efficient HAZOP. Too small & you will repeat the same discussion with the same deviations. Too large & 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 tank, vessel, reactor
 - At tank, vessel, reactor
 - Through pump, compressor, filter
 - To reactor, vessel, column

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

| 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 |

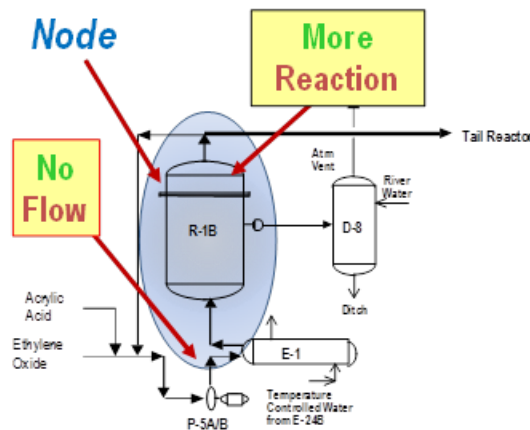
Figure 6.5 HAZOP Guidewords

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. The analysis team may be able to build upon a pre-determined list of reasonable scenario cases to more quickly identify other cases to consider.



Simplified HAZOP Example

Figure 6.6 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. 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.

Project: Source Job Number: 91001 Date: 2/14/91
 Node: 1 Section: Raw Material Storage
 Intention: Transfer 100 gpm of RM1 at 70 °F and 50 psig from V-100 to R-100 Study Leader: C. A. Schiappa

| DEVIATION | POSSIBLE CAUSES | CONSEQUENCES | SAFEGUARDS | RECOMMENDATIONS |
|-----------|---|--|---|--|
| No Flow | <ol style="list-style-type: none"> 1. Block VLV closed 2. Broken pipeline 3. Plugged pipeline 4. Pump failure 5. V-100 empty | <ol style="list-style-type: none"> 1. Potential for off spec product 2. Potential spill with resulting fire 3. NNC*, see Item 1 4. Potential backflow from reactor may cause relief to vent on V-100 5. NNC, See Items 1, 4 | <ol style="list-style-type: none"> 1. FT with low flow alarm 2. FT with high flow alarm, LELs in area 3. FT with low flow alarm 4. Check valve in line 5. LT on V-100 with low level alarm | <ol style="list-style-type: none"> 1. Consider position switch on block valve and flow ration control of reactants 2. NNR** 3. NNR 4. Consider use of spring loaded check valve with TFE seat and PT at pump discharge. Consider programming to closed auto block valve when pump PT < reactor PT 5. NNR |
| More Flow | | | | |

*No New Consequences (NNC)

** No New Recommendations (NNR)

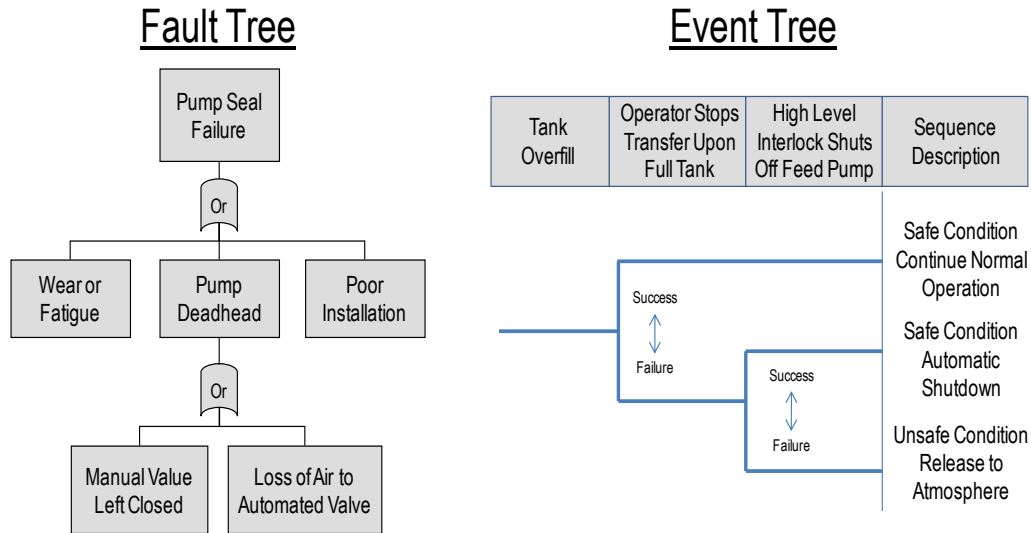
Figure 6.7 Example HAZOP Document

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.

Other Hazard Identification Methods

Fault Tree and **Event Tree** methods can be applied qualitatively or quantitatively¹. 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 Incident or Loss Event. Event Tree may be used to identify feasible Outcomes for a specific Incident.



For Illustration Only – these diagrams do not reflect complete results

Figure 6.8 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 Module.

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 incidents (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 cases based on their personal experience and plant or industry history.

Example Scenario Library

Parameters, Deviations, Initiating Events, Incidents (Loss Events) and potential Outcome may be related to an overall Scenario Category. This technique provides a framework for a Scenario Library such that scenario cases may be easily added and updated.

| Scenario Category | Parameter/ Deviation | Equipment Types | Initiating Events | Incidents | Conditions |
|--------------------------------------|---|-------------------------------|---|--|--|
| Deadhead | Flow-None Temp-High | Pump Compressor | Control Failure Human Error Utility Failure | Rupture | Max. Pressure > Burst Pressure |
| | | | | Seal Failure – Small Hole | No Flow but not Blocked-in |
| Overflow, Overfill, or Backflow | Level-High Flow-Backflow | Vessel Column | Control Failure Human Error | Overflow (Vent) | Inventory > Equip Volume Feed Pressure > Op Pressure |
| | | | | Overflow (Relief) | Inventory > Equip Volume Max Pressure > Relief Pressure |
| Entrainment | Flow-High Press Drop-High | Column Condenser | Control Failure | Overflow (Vent) | Release through Vent System |
| Excessive Pressure | Pressure-High | Vessel Column | Control Failure Human Error | Overflow (Relief) | Max Pressure > Relief Set Pressure |
| | | | | Rupture | Max Pressure > Burst Pressure |
| Excessive Heating | Temp-High Heat Input-High | Vessel Column Exchanger | Control Failure Human Error | Vapor Release (Relief) | Max Pressure > Relief Set Pressure |
| | | | | Rupture | Max Pressure > Burst Pressure |
| Drain or Vent Open | Flow-Loss of Containment | All | Human Error | Small Hole | Typically associated with infrequent maintenance, equipment cleaning, or rail car/ tank truck loading or unloading |
| Seal Leak | Flow-Loss of Containment | Pump Agitator | Mechanical Wear Human Error | Small Hole | Failure Frequency may depend on type of seal. |
| Thermal Expansion | Temp-High Flow-None | Piping Exchanger | Control Failure Human Error | Small Hole (Gasket) Large Hole (Pipe Failure) | Equipment Blocked-in with Heat Input |
| Hydraulic Surge | Flow-None | Piping | Control Failure | Small Hole (Gasket) Large Hole (Pipe Failure) | Rapid valve closure or sudden pump start-up for long pipelines |
| Air Ingress | Composition-Wrong | Vessel Column | Control Failure Utility Failure | Deflagration Equipment Damage | Temperature > Pressure > Burst Pressure |
| Vacuum Damage | Pressure-Low | Vessel Column | Control Failure Human Error | Equipment Damage | Equipment Not Designed for Full Vacuum |
| Physical Damage | Flow/Loss of Containment | Vessel Piping | Human Error | Large Hole (Pipe Failure) | Equipment or Piping Location Vulnerable to Impact Damage |
| Vibration or Low Temp. Embrittlement | Temp-Low Speed-High | All | Control Failure | Large Hole (Pipe Failure) | Min. Temp < Brittle Temp or Vibration, Stress, or Shock |
| Loss of Containment | Flow-Loss of Containment | All | Mechanical Integrity | Small Hole Medium Hole Large Hole | Frequency depends upon internal or external corrosion and screwed versus welded construction. |
| Uncontrolled Reaction | Temp-High Composition-Wrong Flow-Backflow | Vessel Exchanger Pump | Control Failure Human Error Utility Failure | Vapor Release (Relief) | Max Pressure > Relief Pressure |
| | | | | Rupture | Max Pressure > Burst Pressure |

Figure 6.9 Example Scenario Listing

Scenario Feasibility

primarily based on qualitative assessment. In order to narrow the list to those of greatest significance, feasibility criteria based on chemical properties, process capability and equipment design may be helpful.

Flammability

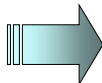
Flash Point
Lower Flammability Limit
Minimum Ignition Energy

Fire and Explosion

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

Toxicity

Inhalation Toxicity
Dermal Toxicity
Aquatic Toxicity



Toxicity

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

Reactivity

Heat of Reaction
Detected Onset Temperature
Gas Generation

Reactivity

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

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. 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 *overflow* incident may result as a release through the outlet or vent. If the downstream equipment pressure exceeds the normal operating pressure, then a *back-flow* incident 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 incident through the relief device may also occur.

7. INTRODUCTION TO RISK ANALYSIS

Risk Analysis is the development of 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 estimation of airborne quantity, vapor dispersion concentration, and explosion overpressure are presented in the subsequent modules. 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.

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 an actual incident. 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).

Overall Work Process Steps for Risk Analysis

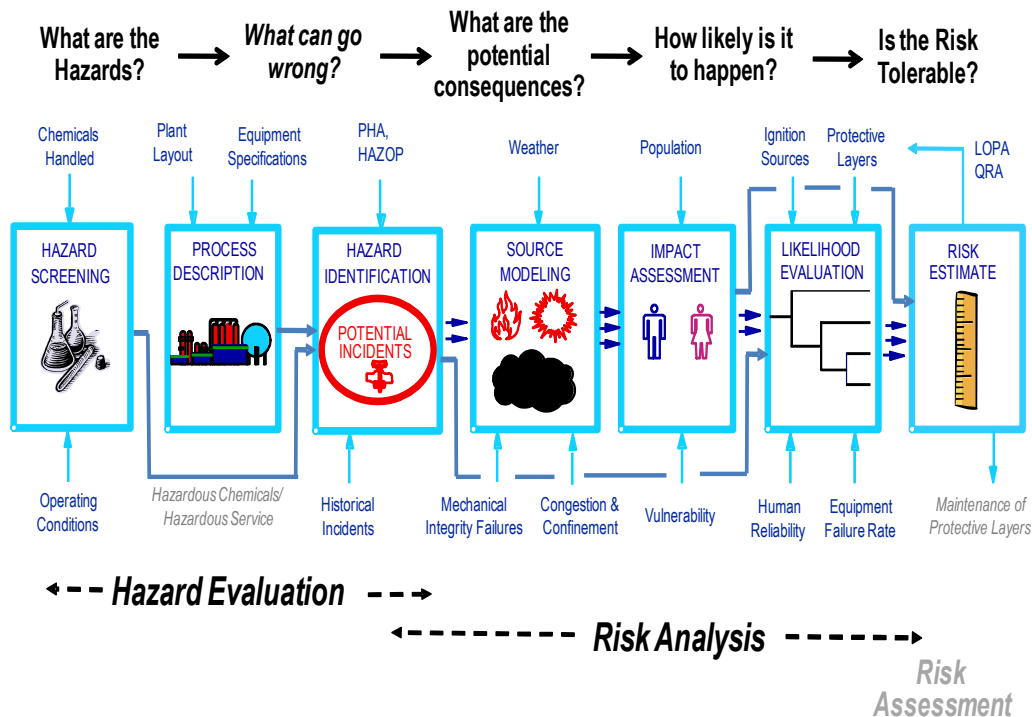


Figure 7.1 Hazard Identification and Hazard Analysis Work Process

Consequence Analysis and Frequency Evaluation play an important part in Process Risk Analysis.

- 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.

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:

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 2.0×10^{-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:

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

In this example, we have identified 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.

“Sharpening the Pencil”

Typically, an estimate is 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. Required inputs and the associated outputs are shaded “yellow” for various release cases.

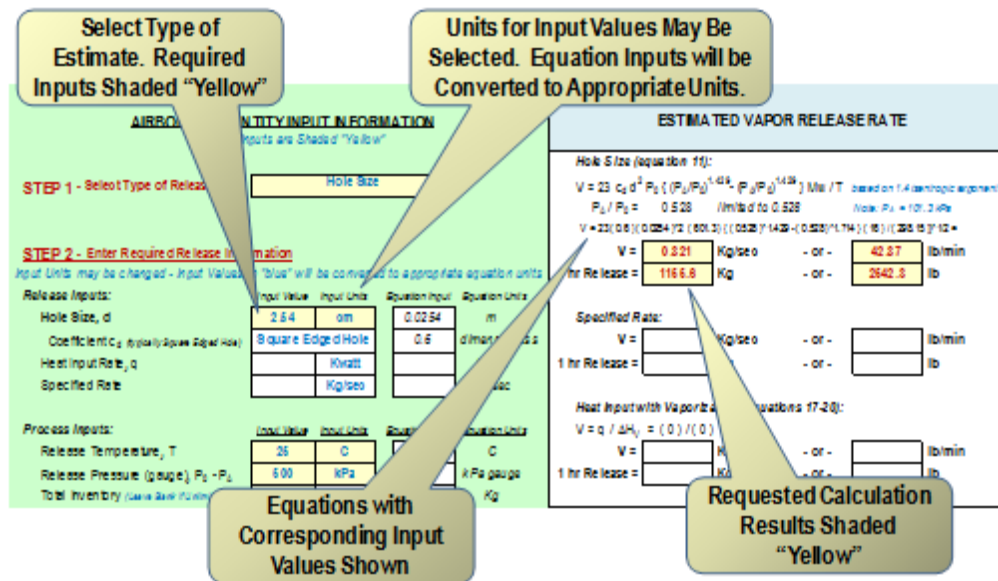


Figure 7.2 Example CHEF Calculation Aid worksheet

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

8. ESTIMATION OF AIRBORNE QUANTITY

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.

Module Objectives

In this module you will learn:

- 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

Flowchart for Determination of Airborne Quantity

The steps for estimation of Airborne Quantity include selection of the appropriate release model (based on a specified rate, hole size, heat balance, or catastrophic failure).

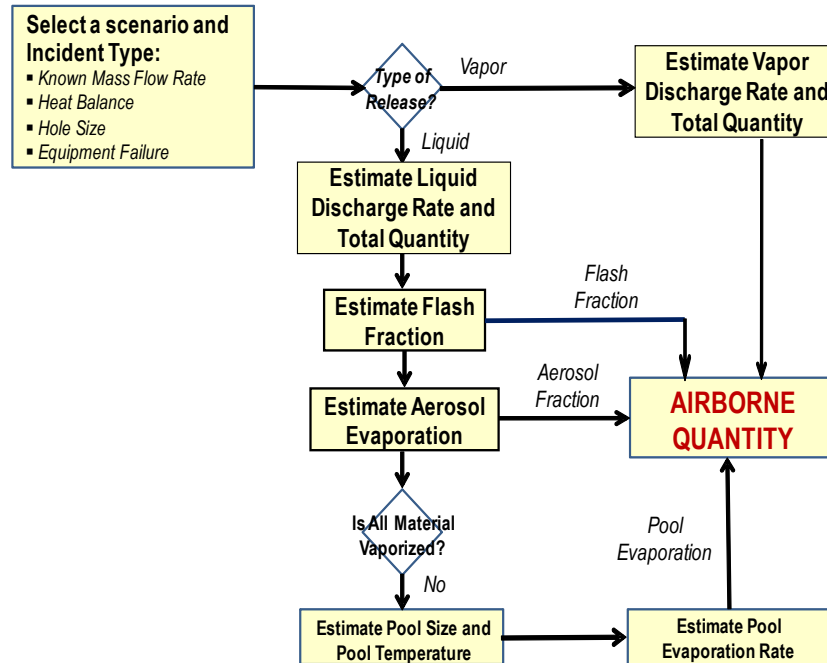


Figure 8.1 Flowchart for Estimation of Airborne Quantity

Selection of a Discharge Model

The release rate for a hazard scenario is typically determined as the *maximum feasible quantity*. There are four primary Incident 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 incidents 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 by²:

$$V = 23 c_d d^2 P_0 \{ [(P_A/P_0)^{1.429} - (P_A/P_0)^{1.714}] Mw / T \}^{1/2} \quad (11)$$

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 as⁷:

$$L = 1.2 c_d d^2 \{ \rho_L [1000 (P_0 - P_A) + 9.8 \rho_L h'] \}^{1/2} \quad (12)$$

where:

d = hole diameter (m)

L = liquid release rate (kg/sec)

Mw = vapor molecular weight

V = vapor release rate (kg/sec)

c_d = discharge coefficient

h' = liquid height (m)

P_0 = upstream pressure (kPa)

T = release temperature (K)

P_A = atmospheric pressure (101.3 kPa)

ρ_L, ρ_V = liquid or vapor density (kg/m³)

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/m³.

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

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 as²:

$$L_F = 20 d^2 [\Delta H_V / \{ 1/\rho_V - 1/\rho_L \}] / [C_s T]^{1/2} \quad (13)$$

where:

$$C_s = \text{liquid heat capacity (J/g C)} \quad d = \text{hole diameter (m)}$$

$$T = \text{temperature (K)} \quad L_F = \text{flashing liquid release rate (kg/sec)}$$

$$\Delta H_V = \text{heat of vaporization (J/g)} \quad \rho_V, \rho_L = \text{vapor, liquid density (kg/m}^3\text{)}$$

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. 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 ($M_w=92.1$) 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/m³, liquid heat capacity of 2.2 Joule/g C, and heat of vaporization of 310 Joule/g.

The vapor density (assuming an ideal gas) is approximately $\rho_V = 0.12 P M_w / T = 0.12 (601.3 \text{ kPa}) 92.1 / 458 \text{ K} = 14.5 \text{ kg/m}^3$

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

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

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.

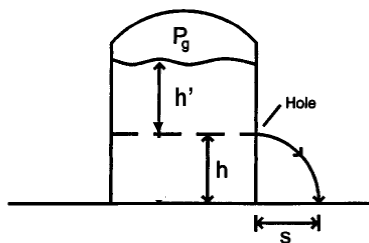


Figure 8.2 Liquid Trajectory from a Hole

The distance away from the tank the liquid stream will impact the ground, s , is given by²:

$$s = v_d t \quad (14)$$

$$\text{and discharge velocity, } v_d = 4 L / (\pi d^2 c_d \rho_L) = 1.27 L / (d^2 c_d \rho_L) \quad (15)$$

where:

L is mass release rate (kg/sec)
 d is hole diameter (m)

ρ_L is the density of the discharging fluid (kg/m³)

The time, t , for the liquid to fall the distance h , is given by simple acceleration due to gravity,

$$t = 0.45 h^{1/2} \quad (16)$$

Liquid trajectory distance and time may be used to estimate duration of aerosol droplets associated with a high velocity liquid leak or 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 overflow 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 incidents involve excessive heat rate where the vapor release rate (and corresponding airborne quantity) is determined as heat rate divided by heat of vaporization.

- **Fire Venting** = $q_{\text{Fire}} / \Delta H_V$ where q_{Fire} is evaluated per NFPA-30 or other (17)

- **Heat Transfer Venting** = $U A_{\text{HT}} (T_{\text{HM}} - T_R) / \Delta H_V$ for $T_{\text{HM}} > T_R$ (18)

- **Mechanical Energy Venting** = $\{ q_{\text{ME}} - U A_s (T_R - T_A) \} / \Delta H_V$ for $T_{\text{ME}} > T_R$ (19)

- **Reaction Venting** = $M q_{\text{RX}} / \Delta H_V$ (20)

Where:

ΔH_V is heat of vaporization

T_{HM} is heating media temperature

U is heat transfer coefficient

T_R is temperature at relief set pressure

A is heat transfer or surface area T_A is ambient temperature

q_{ME} is mechanical energy input

T_{ME} is maximum mechanical energy temperature

q_{RX} is reaction energy per mass

M is reactant mass

Example Discharge Rate from Excessive Heat Input

Estimate the average (or sizing) vapor release rate of toluene ($M_w = 92$) 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 m³, “wetted” surface area of 170 m², heat of vaporization of 350 Joule/g and $q_{Fire} = 630 A_s^{0.338}$ kJoule for A_s in m².

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

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. Superficial velocity, v^* , (m/sec) is determined as:

$$v^* = 8.3 \sqrt{V T / \{ M_w P A_{cs} \}} \quad (21)$$

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).

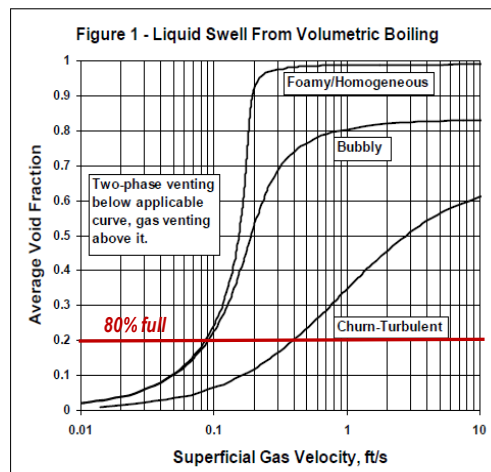


Figure 8.3 Liquid Swell from Volumetric Boiling

A “best estimate” two-phase density (Churn-Turbulent), ρ_{TP} , is related by:

$$\rho_{TP} / \rho_V = [1 + (\rho_L / \rho_V)^{1/2}] / [1 + (\rho_V / \rho_L)^{1/2}] \quad (22)$$

The liquid portion of the two-phase release, L^* , may be estimated from a “best estimate” vapor quality and vapor release rate, V , as:

$$L^* = V \{ \rho_{TP} / \rho_V - 1 \} = V \{ [(\rho_L / \rho_V)^{1/2} - (\rho_V / \rho_L)^{1/2}] / [1 + (\rho_V / \rho_L)^{1/2}] \} \quad (23)$$

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:

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

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

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 as:

$$y_i = x_i P_i / \Pi \quad (24)$$

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 $\sum x_i P_i$.

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 properties¹¹.

Mixture Liquid Density estimated by additive volumes:

$$1/\rho_L \text{ mixture} = \text{sum of mass fraction times } (1/\rho_L \text{ component}). \quad (25)$$

Vapor Density estimated as an ideal gas by:

$$\rho_V = 0.12 P M_{w,avg} / T \quad \text{where } P \text{ is pressure in kPa and } T \text{ in K} \quad (26)$$

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, liquid heat capacity and heat of vaporization by:

$$F_V = (T - T_B) C_s / \Delta H_V \quad (27)$$

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 component¹¹:

$$z_i = (1-F_V) x_i + F_V y_i \quad (28)$$

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 application such as ASPEN.

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 references¹⁷ note multiplying the flash fraction by factors of 1 to 4 to provide a rough approximation for the impact of aerosols. 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”^{2,17}. 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^{10,17} of 10, typical surface tension of 0.02 N/m, assumed proportional to $1 - F_V$, and ambient air density of 1.18 kg/m³) is:

$$\text{Critical Weber Number} \sim 10 = \rho_a v_d^2 d_d / \sigma \quad \text{and droplet diameter proportional to } (1 - F_V)$$

$$d_d \sim 0.17 (1 - F_V) / v_d^2 \quad (29)$$

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 two-phase flow 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 as:

$$\text{Diffusion Limited Surface Evaporation, } m = 0.0027 Mw^{2/3} P_{sat} / T \text{ per reference 2 in kg/sec m}^2$$

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

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

$$F_D = 0.043 v_d^2 Mw^{2/3} P_{sat} h^{1/2} / [\rho_L T_{Aerosol} (1 - F_V)] \quad (30a)$$

where:

v_d = release velocity (m/sec)

h = release height (m)

Mw = molecular weight

ρ_L = liquid density (kg/m³)

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 as:

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

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

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

$$T_{Aerosol} = \{ 7.9 U_D h^{1/2} v_d^2 T_A / [\rho_L (1 - F_V)] + C_S T' - F_D \Delta H_V / 2 \} / \{ 7.9 U_D h^{1/2} v_d^2 / [\rho_L (1 - F_V)] + C_S \} \quad (30b)$$

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 m²)

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/m² 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 ($M_w = 92$) at 100 C (373 K) and height of 2 meter. The density of toluene at 100 C is 785 kg/m³, 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:

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

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

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. The pool area is limited to the area of a dike or bund if it exists.

$$A_P = L' / [\rho_L / (100 t_L) + m_P / 2] \quad \text{in } m^2 \text{ limited to the dike area} \quad (31a)$$

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 m²)

t_L = liquid release duration (sec) ρ_L = liquid density (kg/m³)

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 merely:

$$A_P = \text{Total Liquid Released} (100 / \rho_L) \quad \text{in } m^2 \text{ limited to the dike area} \quad (31b)$$

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 as:

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

$$T_P = \{T' L' C_S + A_P (S - m_P \Delta H_V + U_{Gnd} T_A)\} / \{L' C_S + U_{Gnd} A_P\} \quad (32)$$

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/m² for outdoor spills

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_P = pool evaporation rate (kg/sec m²)

C_S = liquid heat capacity (Joule/g K)

U_{Gnd} = heat transfer coefficient to ground, typically 0.02 kW/m² K to 0.2 kW/m² K

Evaporation rate from a liquid pool, m_P (kg/sec m²), is evaluated as diffusion at the estimated pool temperature¹², T_P , as:

$$m_P = 0.0021 M_w^{2/3} u^{0.78} P^{sat} / T_P \quad (33)$$

where:

M_w = molecular weight

P^{sat} = saturation vapor pressure (kPa)

u = wind speed (m/sec)

T_P = pool temperature (K)

The pool evaporation correlation selected is from the US EPA's Risk Management Program Guidance for Offsite Consequence Analysis, Appendix D (1999). 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 $m_P A_P$ 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 ($M_w = 92$) 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/m³ 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:

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

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

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

$$= 7.1 \text{ kg/sec}$$

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 m² 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/m³

Vapor Density (at 10 C and 50 kPa gauge) of 3.7 kg/m³

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

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

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

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,

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

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

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.

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

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

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 m² as:

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

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

The Airborne Quantity = $L [F_V + (1 - F_V) F_D] + m_P A$

= $0.68 [0.07 + (1 - 0.07) 0.34] + 0.028 (10) = 0.54 \text{ kg/sec}$ which is close to the liquid release rate of 0.68 kg/sec.

9. 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.

Module Objectives

In this module you will learn:

- 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.

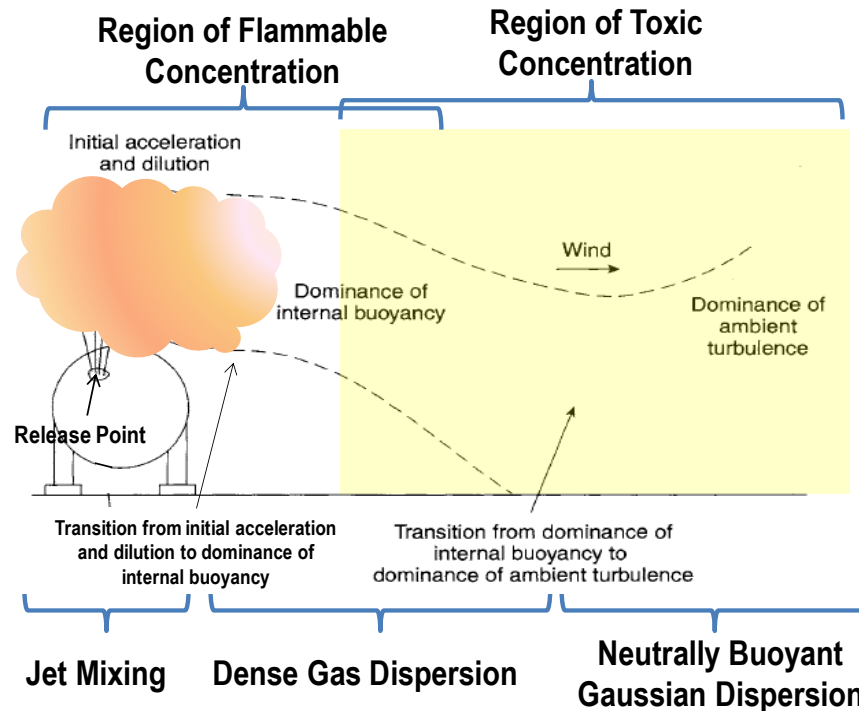


Figure 9.1 Vapor Release Mechanisms

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 is¹⁰:

$$C_0 / C = 0.32 (\rho_0 / \rho)^{1/2} X / d_0 \quad (34a)$$

$$C_0 / C_t = (\rho_0 / \rho_t) (v_0 / u) \text{ at } X = X_t \quad (34b)$$

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)

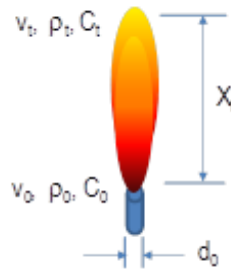


Figure 9.2 Jet Mixing

The transition distance or point where the jet velocity has diminished such that Dense Gas (or Neutrally Buoyant) Dispersion may apply is:

$$X_t = (d_0 / 0.32) (v_0 / u) (\rho_0 / \rho_t)^{1/2} \quad (35)$$

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 the above correlations 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/m^3

ρ_0 of propane at 25 C and atmospheric pressure of 1.8 kg/m^3

$v_0 = 1.27 (1 \text{ kg/sec}) / [1.8 \text{ kg/m}^3 (0.05 \text{ m})^2] = 282 \text{ m/sec}$

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

$C_t = 100 / 143 = 0.7 \text{ volume \%}$ (using C_0 as 100% at the release point)

The transition distance is $X_t = (d_0 / 0.32) (v_0 / u) (\rho_0 / \rho_t)^{1/2}$
 $= (0.05 / 0.32) (282 / 3) (1.8 / 1.2)^{1/2} = 18 \text{ meter}$

Continuous versus Instantaneous Release

When the release duration is very short, a "puff" or instantaneous model is more appropriate to use. An example short duration release would be catastrophic failure of a vessel.

Characteristic plume formed by a continuous release of material

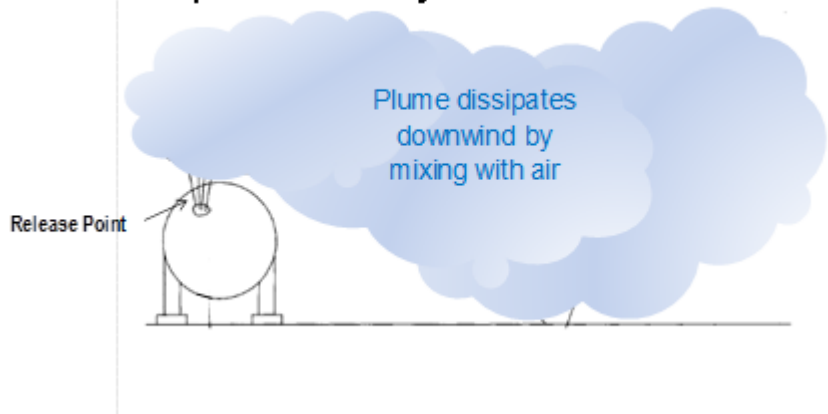


Figure 9.3 Continuous Release

Puff formed by near instantaneous release of material

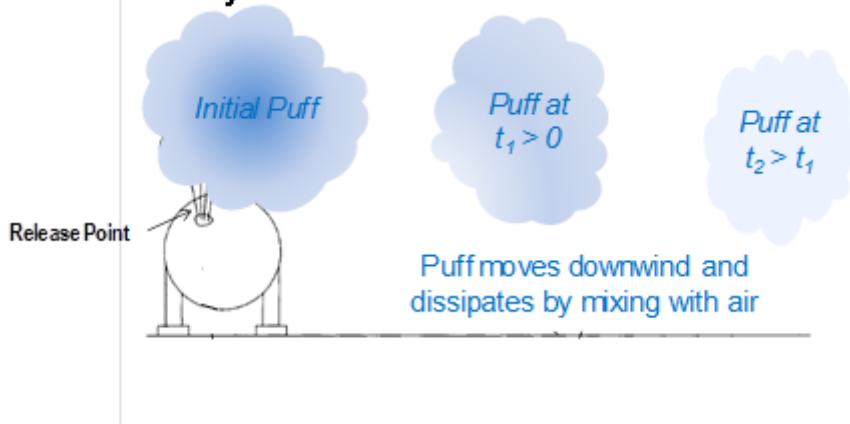


Figure 9.4 Instantaneous Release

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 increases in width^{2,7}. 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.

Neutrally Buoyant Gaussian Models

Neutrally Buoyant models are based on a random mixing process driven by turbulence in the atmosphere^{2,7}. 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.

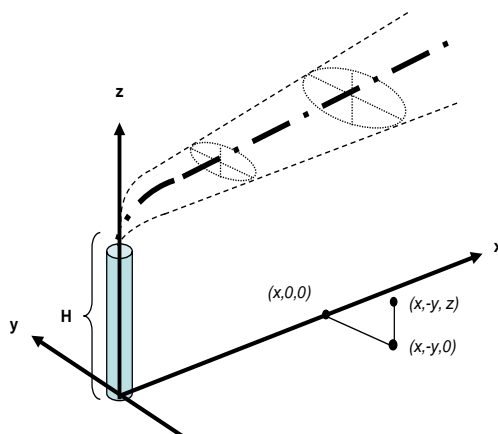


Figure 9.5 Neutrally Buoyant Model

Simple Vapor Dispersion Correlation

Combining the Britter-McQuaid Dense Gas model⁷ and Pasquill-Gifford Neutrally Buoyant model², vapor dispersion may be estimated as a simple “power” correlation of modeling results over a broad range of concentration.

Simple Correlation – Continuous Release:

$$X = 20000 [Q / (Mw C_c)]^{0.5} - \Delta X_t \quad \text{for } C_c < \text{initial dilution, } C_0 \quad (36a)$$

$$C_c = 4.0 \times 10^8 Q / [Mw (X + \Delta X_t)^2] \quad \text{for } X > X_t \quad (36b)$$

Simple Correlation – Instantaneous Release:

$$X' = 4000 [Q^* / Mw]^{1/3} / C_c^{0.5} - \Delta X_t \quad \text{for } C_c < \text{initial dilution, } C_0 \quad (37a)$$

$$C_c' = 1.6 \times 10^7 [Q^* / Mw]^{2/3} / (X + \Delta X_t)^2 \quad \text{for } X > X_t \quad (37b)$$

where:

Q = airborne rate (kg/sec)

Mw = molecular weight

Q* = total airborne release (kg)

X = downwind distance (m)

C_c = centerline conc. (ppm by volume)

ΔX_t = distance correction for initial dilution (m)

These simple correlations are the result of a “best fit” power correlation to results of a dense gas model combined with the neutrally buoyant Gaussian model. The parameters for vapor dispersion modeling have been selected to be slightly conservative in screening studies at 3 m/sec wind, Class D weather, and “industrial” surface roughness.

When considering offsite consequences, the simple vapor dispersion correlations based on 1.5 m/sec wind speed, class F atmospheric stability, and industrial roughness are sometimes used:

Simple Correlation - Continuous Release (1.5 F):

$$X = 88000 [Q / (Mw C_c)]^{0.55} - \Delta X_t \quad \text{for } C_c < \text{initial dilution, } C_0$$

$$C_c = 1.0 \times 10^9 Q / [Mw (X + \Delta X_t)^{1.82}] \quad \text{for } X > X_t$$

Simple Correlation - Instantaneous Release (1.5 F):

$$X = 16000 [Q^* / Mw]^{1/3} / C_c^{0.6} - \Delta X_t \quad \text{for } C_c < \text{initial dilution, } C_0$$

$$C_c = 1.0 \times 10^7 [Q^* / Mw]^{0.56} / (X + \Delta X_t)^{1.67} \quad \text{for } X > X_t$$

where:

Q = airborne release rate (kg/sec)

Mw = molecular weight

Q* = total airborne release (kg)

X = downwind distance (m)

C_c = centerline conc (ppm by volume)

ΔX_t = distance correction for initial dilution (m)

Correction for Initial Dilution in Simple Vapor Dispersion Model

This simple dispersion model may require a “virtual” distance correction for the transition from initial dilution by jet mixing to improve accuracy **for downwind distance much less than 100 m**. For many situations, this correction can be ignored. The correction for a continuous vapor release is estimated as:

$$\Delta X_t \sim 37 [AQ v_0 / T]^{0.5} \text{ for a vertical release} \quad (38a)$$

$$\Delta X_t \sim 37 [AQ v_0 / T]^{0.5} - 3.3 d_0 v_0 (Mw / T)^{0.5} \text{ for a horizontal release} \quad (38b)$$

At low vapor velocity, liquid or two-phase release, the distance correction is evaluated such that the concentration at zero downwind distance, $X=0$, is limited to 100% or 1000000 ppm. In this case:

$$\Delta X_t = 20 [AQ / Mw]^{0.5} \quad (38c)$$

where:

AQ = airborne rate (kg/sec)

X = downwind distance (m)

T = release temperature (K)

ΔX_t = distance correction for initial dilution (m)

Mw = molecular weight

v_0 = release velocity (m/sec) – limited to sonic velocity

d_0 = discharge pipe diameter (m) – or equivalent diameter if discharge at sonic conditions

Vapor Dispersion Example – Estimate Distance to a Concentration

Estimate the distance to ERPG-3 concentration of 20 ppm by volume for a continuous 1 kg/sec chlorine release at 25 C (298 K) near ground elevation. Assume a very low velocity such that the initial dilution is zero. (The molecular weight for chlorine is 70.9)

$$\Delta X_t = 20 [AQ / Mw]^{0.5} = 20 [1 \text{ kg/sec} / 70.9]^{0.5} = 2.4 \text{ m}$$

a negligible correction which can be ignored in this case.

$$X = 20000 [AQ / (Mw C)]^{0.5} = 20000 [1 \text{ kg/sec} / (70.9 \{20 \text{ ppm}\})]^{0.5}$$

$$= 531 \text{ meter}$$

Vapor Dispersion Model Example – Estimate Concentration at a Distance

Estimate the concentration at a downwind distance of 100 m for a continuous 1 kg/sec chlorine release at 25 C (298 K) near ground elevation. Ignore the correction for initial dilution. Assume a very low velocity such that the initial dilution is zero. (The molecular weight for chlorine is 70.9)

$$C_C = 4.0 \times 10^8 AQ / [Mw (X)^2] = 4.0 \times 10^8 (1 \text{ kg/sec}) / [70.9 (100 \text{ m})^2]$$

$$= 564 \text{ ppm:}$$

Evaluation of Short Duration Release

For a short duration release, one needs to determine if a Continuous or Instantaneous dispersion model should be used. The Airborne Rate where transition occurs may be estimated by equating the continuous and instantaneous models for the same concentration at the distance of interest. This yields for 3 m/sec Class D weather:

$$AQ > 0.04 \text{ Total } AQ^{2/3} Mw^{1/3} \text{ for an Instantaneous Dispersion Model} \quad (39)$$

t_D is vapor release duration (sec) Mw = molecular weight
 AQ = airborne rate (kg/sec) Total AQ = 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 ER values. The exposure duration for a continuous vapor release is merely the total airborne quantity, Total AQ, divided by the vapor rate, AQ or

$$t_D = \text{Total AQ} / \text{AQ} \tag{40a}$$

For a liquid release, one might conservatively estimate dose based on the total airborne 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. As a very rough approximation, the correlations for continuous and instantaneous dispersion may be combined to estimate exposure duration at the transition from continuous to puff models at a very short distance from the release point. This appears to provide a reasonably conservative value. For Class D weather at 3 m/sec wind speed:

$$t_D = 25 (\text{Total AQ} / Mw)^{1/3} \tag{40b}$$

where:

t_D = estimated exposure duration (sec) Mw = molecular weight
 Total AQ = total airborne quantity (kg)

:

Correction for Elevation in Simple Vapor Dispersion Model

The release height significantly affects ground-level concentrations.

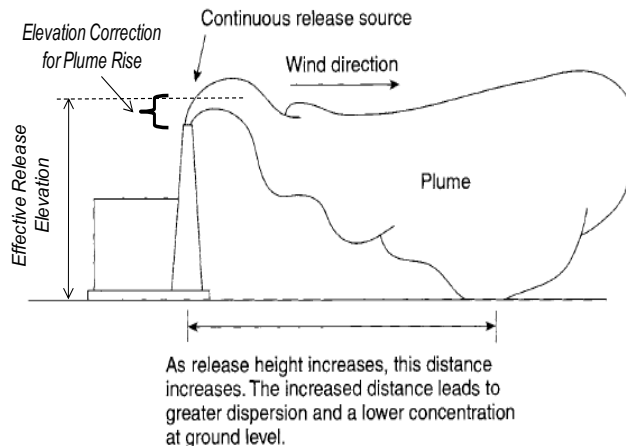


Figure 9.6 Elevated Vapor Release

Correction for release elevation due to vapor momentum and density may be approximated by⁷:

$$H = H' + 1.5 (v_0 / u) d_0 [\sin \Theta + 1.8 d_0 (1 - \rho_0 / \rho_{air})] \quad (41)$$

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 that at the center is approximately:

$$C / C_c = \exp[-0.5 (\Delta H / \{ 0.395 (X + \Delta X_t)^{0.701} \})^2] \quad (42)$$

where:

ΔH = effective release elevation minus reference or receptor elevation (m)

X = downwind distance (m)

ΔX_t = distance correction for initial dilution (m)

Estimation of Maximum Ground Level Concentration

For a ground elevation release, the maximum ground level concentration is the concentration at the release location. For release from an elevated location, the maximum ground concentration at any distance (for 3 m/sec wind and Class D atmospheric stability) may be conservatively estimated as:

$$C_{max} \sim 5.3 \times 10^6 \text{ AQ} / (\Delta H^{2.3} \text{ Mw}) \quad (43)$$

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)

Note that the reference elevation for "ground" level is typically assumed as 1.2 m (or 4 ft).

Example Correction for Elevation

Estimate the ground level concentration at 100 m downwind for a continuous 1 kg/sec chlorine release at 25°C (298 K) and 10 meter effective elevation. Assume a very low velocity such that the initial dilution and plume rise is zero. (The molecular weight for chlorine is 70.9)

$$X_t = 20 [AQ / Mw]^{0.5} = 15 [1 \text{ kg/sec} / 70.9]^{0.5} = 2.4 \text{ m}$$

a negligible correction which can be ignored

$$\Delta H = 10 - 1.2 = 8.8 \text{ meter using 4 ft or 1.2 m for "ground"}$$

$$C_c = 4.0 \times 10^8 AQ / [Mw (X)^2] = 4.0 \times 10^8 (1 \text{ kg/sec}) / [70.9 (100)^2]$$

$$= 564 \text{ ppm}$$

$$C = C_c \exp[-0.5 \Delta H / \{0.395 (X + \Delta X_t)^{0.701}\}^2] = 450 (0.677) = 382 \text{ ppm}$$

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 (overflow 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:

- 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

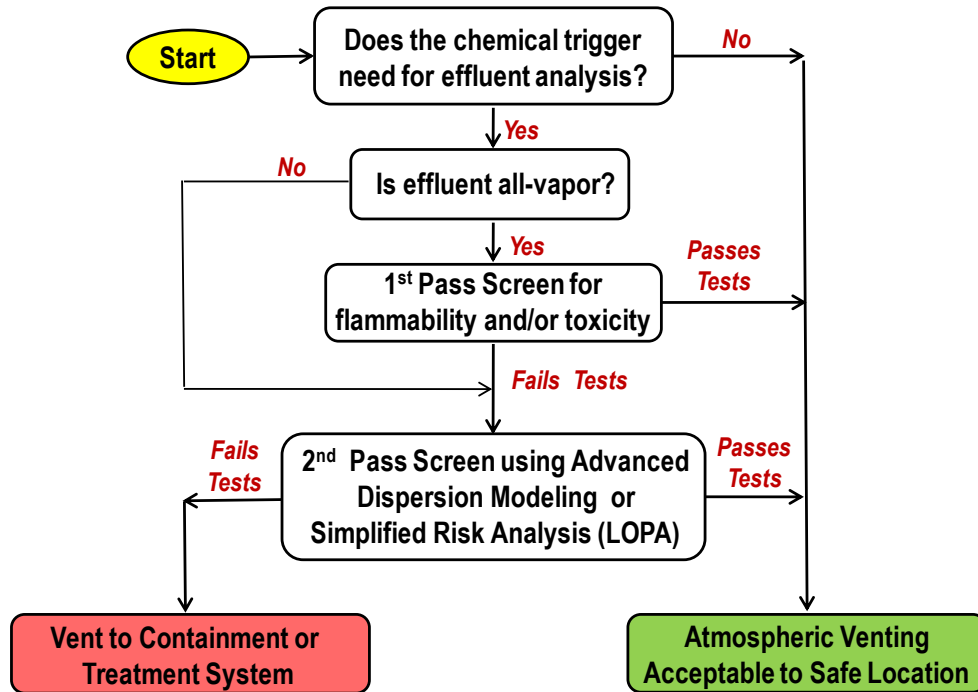


Figure 9.7 Example Relief Effluent Screening Flowchart

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.

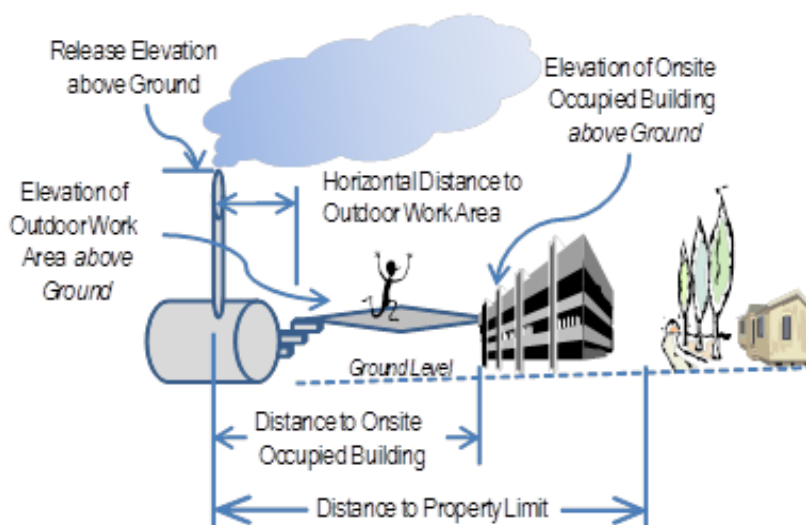


Figure 9.8 Depiction of Relief Device Effluent

Here are some example screening criteria:

- Offsite concentration less than ERPG-2* (at ≤ 4 ft elevation)
- Onsite concentration less than $\frac{1}{2}$ the Lower Flammable Limit at distance and elevation of nearest unrestricted work area
- Onsite concentration less than multiple times 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

**Alternately offsite concentration less than ERPG-3 using Class F atmospheric stability and 1.5 m/sec wind speed may be used.*

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 module. The tool, available in RAST, also:

- Addresses 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).

$$C_{\text{Indoor}} = 8.8 \times 10^{10} (AQ / Mw) / (VR V_B + 88020 AQ / Mw) \quad (44)$$

The average indoor concentration is limited to the total airborne release divided by the building volume for short duration releases or:

$$C_{\text{Limit}} = 2.45 \times 10^7 (Total AQ) / (V_B Mw) \text{ in ppm} \quad (45)$$

where:

AQ = airborne quantity (kg/sec) Total AQ_T = total release quantity (kg)

C = concentration (ppm by volume) V_B = building volume (m³)

Mw = molecular weight VR = ventilation rate (air changes/hour)

A typical 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. 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, by:

$$C_{\text{Indoor}}/C_{\text{Outdoor}} = 1 - e^{-VR t} \quad (46)$$

The above correlation 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.

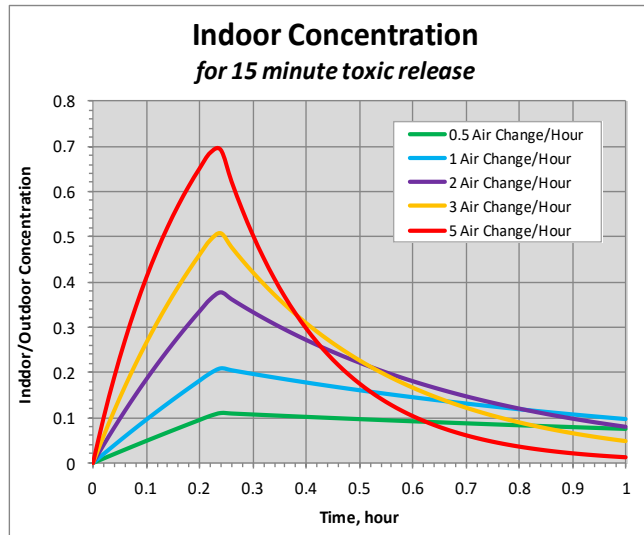


Figure 9.9 Ratio of Indoor to Outdoor Concentration vs Time

For very short duration releases within the typical range of ventilation rate, a practical upper limit for indoor concentration is $C_{\text{Indoor}}/C_{\text{Outdoor}} = 2 t'$ where t' is the release duration in hours.

Typical Ventilation Rates

The ventilation rate for occupied buildings is typically 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 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 9.1 Typical Ventillation Rate for Houses

10. 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.

Module Objectives

In this module you will learn:

- 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** – an explosion in which the reaction front advances into the un-reacted substance at greater than sonic velocity
- **Deflagration** - an explosion in which the reaction front advances into the un-reacted substance at less than sonic velocity.
- **Boiling-Liquid Expanding-Vapor Explosion (BLEVE)** – the explosive vaporization of material release that occurs upon rupture of equipment containing liquid above its normal boiling point.
- **Dust Explosion** – an explosion resulting from rapid combustion of fine solid particles.
- **Potential Explosion Site (PES)** - a congested or confined volume that can be occupied by a flammable vapor or dust cloud:

Damage and Blast Overpressure

The maximum pressure resulting from blast or shock wave is the Peak Overpressure which is correlated to damage.

| Overpressure (PSI) | <u>Damage per NFPA-921</u> |
|-------------------------------|---|
| 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 10.1 Blast Overpressure vs Damage

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 by⁷:

$$Q_{PV} = V P_B [\ln (P_B/P_A) + (P_A/P_B) - 1] \quad (47)$$

where V is the equipment volume (m^3), Q_{PV} is explosion energy (kJoule), and P_A , P_B are atmospheric and burst pressure (kPa) respectively.

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. Scaled pressure is merely 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 power².

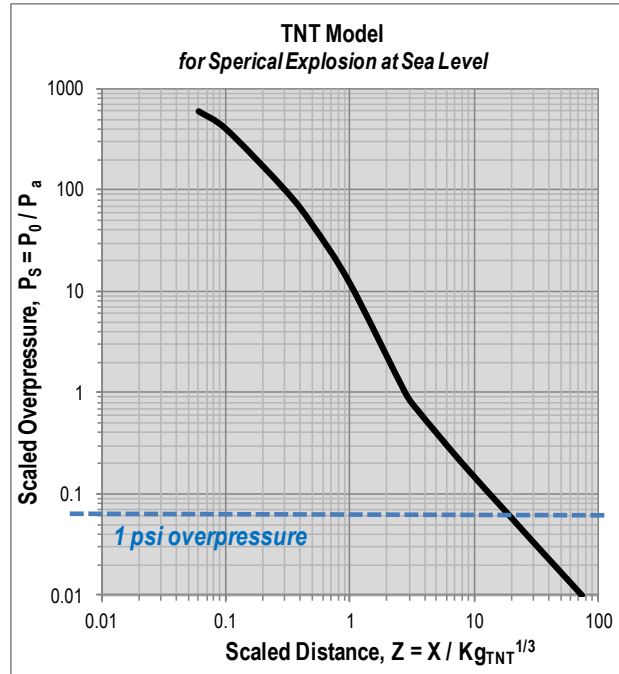


Figure 10.1 Scaled Overpressure vs Scaled Distance – TNT Model

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 above TNT Model graph.

TNT Model Example

Estimate the distance to 1 psi overpressure for rupture of a 10 m³ (2640 gal) vessel at 1000 kPa (145 psia).

$$Q_{PV} = V P_B [\ln (P_B/P_A) + (P_A/P_B) - 1]$$

$$= 10 (1000) [\ln (1000/101.3) + 101.3/1000 - 1] = 1.39 \times 10^4 \text{ kJoule}$$

$$\text{kg}_{\text{TNTeq}} = 1.39 \times 10^4 / 4600 = 3.0 \text{ kg}$$

From the TNT graph at 1 psi overpressure, Scaled Distance, $Z = 18 = X / 3.0^{1/3}$

$$X = 18 (3.0^{1/3}) = 26 \text{ m}$$

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 Model⁴ 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.

| High | Medium | Low |
|---|---|--|
| <i>Fundamental Burning Velocity > 75 cm/s</i> | <i>Fundamental Burning Velocity 45-75 cm/s</i> | <i>Fundamental Burning Velocity <45 cm/s</i> |
| 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 |

Table 10.2 Fuel Reactivity

The presence of obstacles within a flammable cloud generates turbulence and accelerates the flame front.

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 10.2 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.

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.

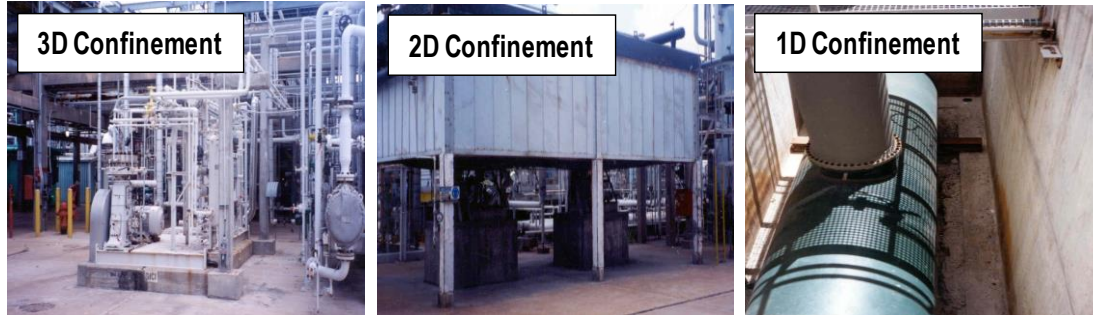


Figure 10.3 Examples of 1D, 2D, and 3D Confinement

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.

| Fuel Reactivity | Obstacle Density or Congestion | | |
|------------------------|---------------------------------------|---------------|-------------|
| | <u>Low</u> | <u>Medium</u> | <u>High</u> |
| High | 0.5 | >1 | >1 |
| Low-Medium | 0.35 | 0.5 | 1 |
| Class I Dust | | 0.35 | 0.5 |

Table 10.3 BST Mach Number at Common Congestion and Fuel Reactivity

Above 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).

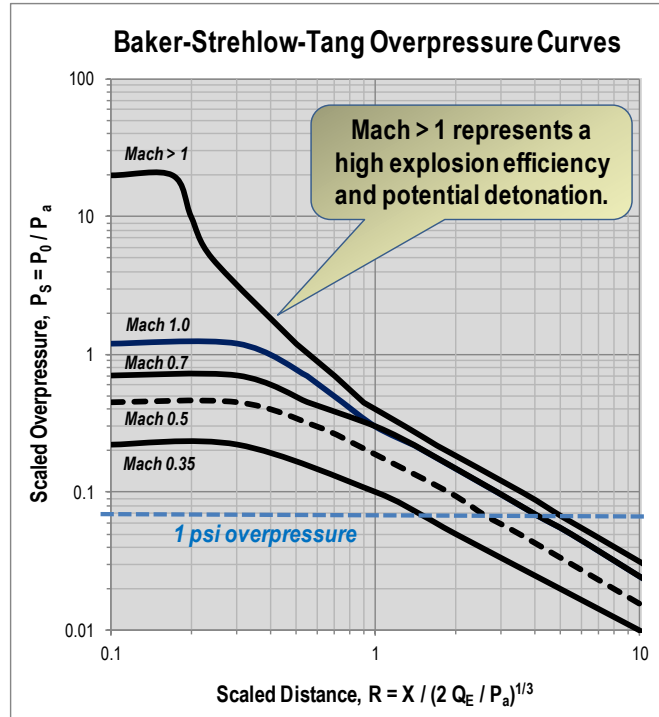


Figure 10.4 Scaled Overpressure vs Scaled Distance – BST Model

The Baker-Strehlow-Tang (BST) model is also a correlation of Scaled Pressure versus Scaled Distance. The Scaled Distance, R , is the distance from the Potential Explosion Site divided by $(2 \times \text{Explosion Energy in kJoule} / 101.3 \text{ kPa})^{1/3}$.

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.

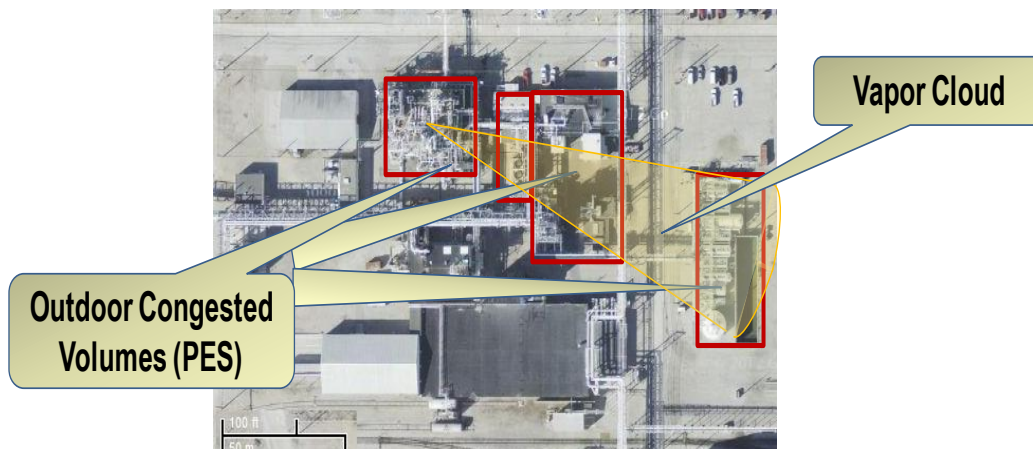


Figure 10.5 Potential Explosion Site

- 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 as²:

$$Q_E = 3500 V_{PES} \quad (48)$$

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.

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.

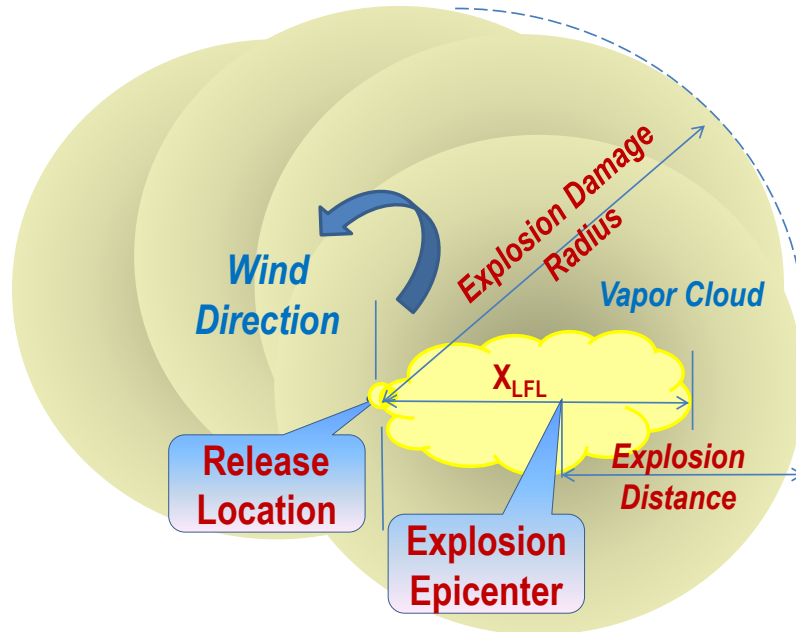


Figure 10.6 Simple Depiction of Vapor Cloud Explosion

The Potential Explosion Site volume is the expanded Cloud Volume to a maximum or limit of 30000 m^3 . The expanded vapor cloud volume is estimated as:

$$V_C \sim 0.08 X_{LFL}^{2.6} \text{ for Class D atmospheric stability} \quad (49)$$

where X_{LFL} is distance to the Lower Flammable Limit from the Dispersion Model

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 (medium reactivity fuel) airborne rate into a medium congestion process area. The distance to the lower flammable limit is estimated as 316 meter and cloud volume estimated as $V_C = 0.08 X_{LFL}^3 = 253000 \text{ m}^3$. 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 m^3 .

The explosion energy is roughly:

$$Q_E = 3500 V_C = 3500 (30000 \text{ m}^3) = 1.05 \times 10^8 \text{ kJoule}$$

The scaled pressure is $1 \text{ psi} / 14.7 \text{ psi} = 0.068$ where the Scaled Distance, $R = 2.5$ at Mach 0.5.

$$X_E = R [2 Q_E / 101.3]^{1/3} = 2.5 (2 \times 1.05 \times 10^8 / 101.3)^{1/3} = 319 \text{ m}$$

The epicenter is assumed at $0.5 X_{LFL}$ or 158 m such that the total distance is $319 + 158$ or 475 meter from the release point.

Class Exercise

Estimate the distance to 1 psi (6.9 kPa) blast overpressure from a 15 kg/sec butadiene (a medium reactivity fuel) leak into a low congestion outdoor process area. The distance to the lower flammable limit from dispersion modeling is estimated as 64 meter.

Share your 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* (such as 8 psi Hunter 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.

11. 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. 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.

Module Objectives

In this module you will learn:

- 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 μm 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 incident may have several outcomes. 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.

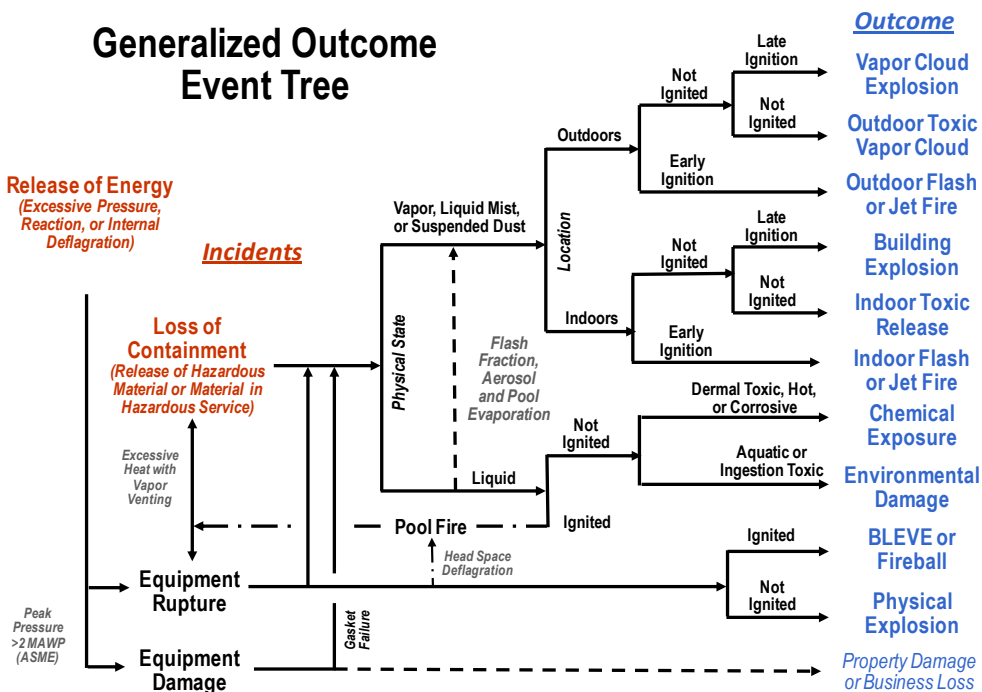


Figure 11.1 Generalized Outcome Event Tree

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: Personnel exposure to flammable cloud of a multiple of LFL
- Vapor Cloud Explosion: 1000 kg flammable (100 kg for high flame speed) released within 5 minutes.

- Building Explosion: Indoor average concentration exceeds a multiple of LFL
- Physical Explosion: Blast Overpressure exceeds a Threshold Distance
- Toxic Vapor Release (Indoor, Outdoor)
 - Off-site exposure to > ERPG-2 concentration
 - On-site exposure to > Multiple times ERPG-3 concentration for short duration (5-10 minutes) outdoors
 - 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 source². 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.*

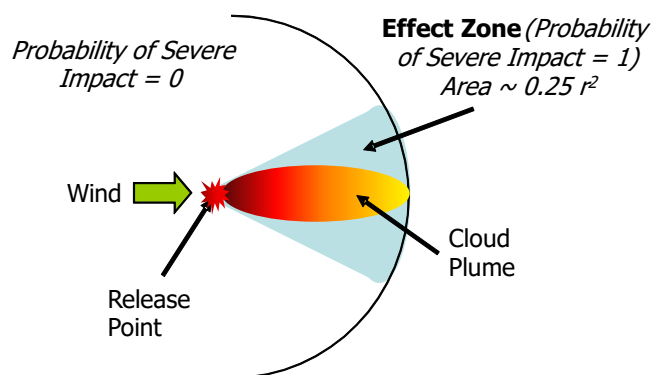


Figure 11.2 Example Effect Zone

$$\text{Impact Area} = 0.25 \text{ radius}^2 \text{ (for Class D weather)}$$

(50)

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 or:

$$\text{Impact Area} = 2 V_B^{2/3} C_{\text{indoor}} / \text{LFL} \quad \text{for flammable release} \quad (51)$$

$$\text{Impact Area} = V_B^{2/3} C_{\text{indoor}} / \text{LC-50} \quad \text{for toxic release} \quad (52)$$

Where V_B is the volume of the Enclosed Process Area and C_{indoor} is the average indoor concentration.

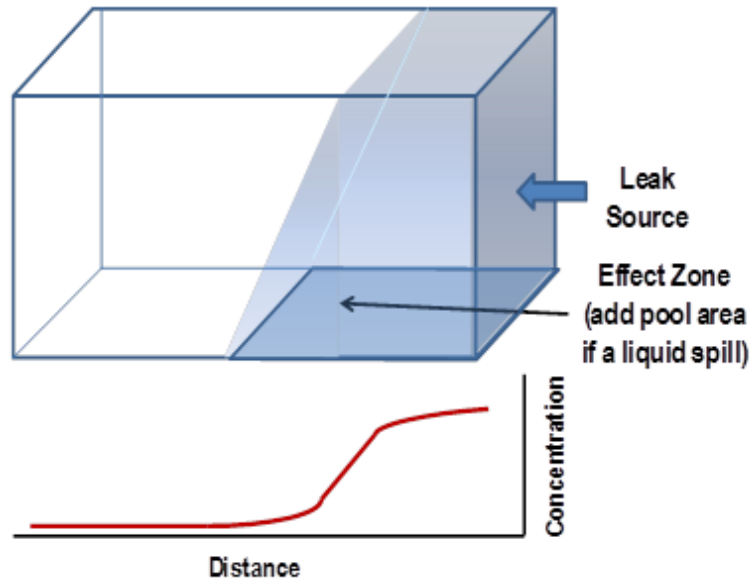


Figure 11.3 Indoor Effect Zone

For Explosions – the Impact Area (for Overpressure or Projectiles) a Hemispherical Effect Zone.

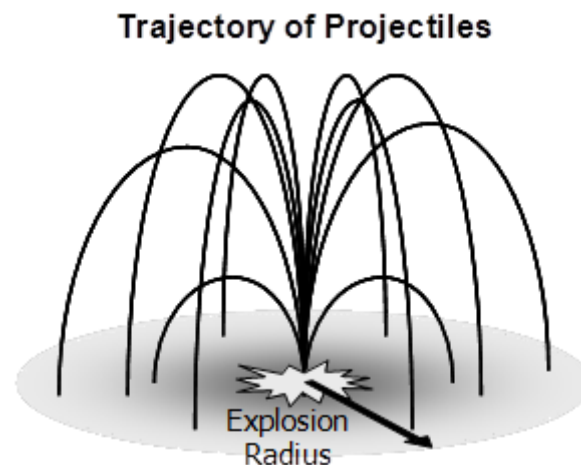


Figure 11.4 Projectile Effect Zone

$$\text{Impact Area} = \pi \text{ radius}^2$$

If the hazard distance or impact area is extremely small, a potential fatality is nearly impossible. The cross-sectional area of a toxic cloud less than 10 m distance to 10 times ERPG-3 is so small that a person would not be able to take 5-10 breaths while remaining within the cloud. The cross-sectional area of a flammable cloud less than 3 m distance to ½ LFL is so small that burns could not cover a sufficient fraction of body area to be a fatality. If the distance to 10 psi overpressure from a physical explosion (with no fragments) is less than 1 meter, a fatality is not feasible.

Example Screening Criteria for Levels of Concern

- **Flash (or Jet) Fire**
Personnel exposure to flammable cloud of a multiple of LFL (typically 0.5 to 1)
- **Vapor Cloud Explosion**
1000 Kg flammable (100 Kg for high flame speed) released within 5 minutes
- **Building Explosion**
Indoor average concentration exceeds LFL
- **Physical Explosion**
*Building Damage at >1 psi overpressure (>0.3 psi for fragmentation) for typical construction
to >10 psi for severe human impact*
- **Toxic Vapor Release (Indoor, Outdoor)**
 - *Off-site exposure to > ERPG-2 concentration to integration method for severe impact*
 - *On-site exposure to > ERPG-3 concentration for short duration outdoors (<10 minutes)
to LC-50 for severe impact*
 - *On-site exposure to > ERPG-3 concentration based on 60 min. exposure within an occupied
building to vulnerability model for severe impact.*

Table 11.1 Example Screening Criteria

Note that “severe human impact” represents human injury from the concussive force of a blast excluding thermal burns or being struck by fragments or debris.

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 fireball is a significant cause for damage or injury. The distance to a specific thermal radiation level may be estimated as²:

$$X_{\text{ThermRad}} = \{ 828 M^{0.771} / E_r - 18.9 M^{2/3} \}^{1/2} \quad (53)$$

A hazard distance and related impact area for severe burns from a fireball or BLEVE may be approximated by²:

$$X_{\text{Thermal}} = 3.6 M^{0.4} \quad (54)$$

where M is the total flammable mass in the fireball (kg) and hazard distance, E_r is radiation flux (Kw/m^2), at distance, X_{Thermal} , in meter.

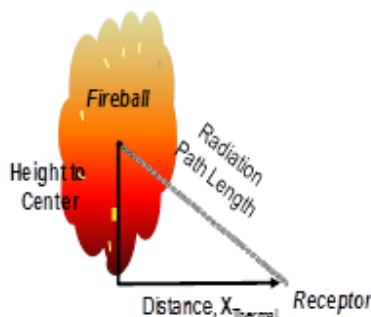


Figure 11.5 Radiation Fireball

A Boiling-Liquid Expanding-Vapor Explosion (BLEVE) may occur if a vessel containing liquid above its normal boiling point ruptures. This outcome is typically caused by 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 incident. 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 as¹⁴:

$$\text{Fireball Distance} = 3.1 \text{ Equipment Volume}^{0.402} \quad (55)$$

Fireball distance resulting from a vented internal explosion or deflagration from dust may be estimated as¹⁴:

$$\text{Fireball Distance} = 10 \text{ Equipment Volume}^{1/3} \quad (56)$$

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/m² 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:

- Not impacted if the hazard distance to flash fire (a multiple of LFL) is less than 1 meters - or - direct explosion impact 1 psi overpressure (0.3 psi if fragmentation) is less than 1 meters – or – hazard distance to multiple times ERPG-3 is less than 1 meter.
- Severely Impacted if the hazard distance to flash fire (a multiple of LFL) exceeds 3 meters – or - direct explosion impact 10 psi overpressure (1 psi if fragmentation) exceeds 1 meter – or – hazard distance to multiple of times ERPG-3 exceeds 3 meters.

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.

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.

| <u>Number Impacted</u> | <u>Probability of Exposure</u> |
|------------------------|--------------------------------|
| 0.1 to 1 | 1 |
| < 0.1 | 0.1 |

Table 11.2 Probability of Exposure

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/m² 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 X² in m².

Toxic Impact: 0.25 (100 m)² (0.0002 people/m²) = 0.5 people rounded to 1

Flammable Impact: 0.25 (25 m)² (0.0002 people/m²) = 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/m². For a “typical” facility covering 20000 m², 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 module - Multiple of ERPG-3 Concentration versus Vulnerability Models may be used to estimate the fraction of total Building Occupants impacted.

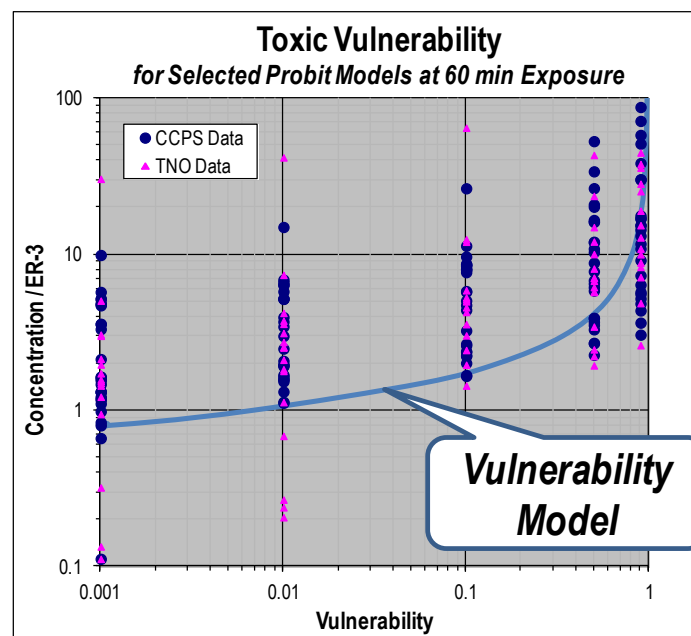


Figure 11.6 Toxic Vulnerability

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. Damage to blast resistant buildings are not well correlated by simple methods.

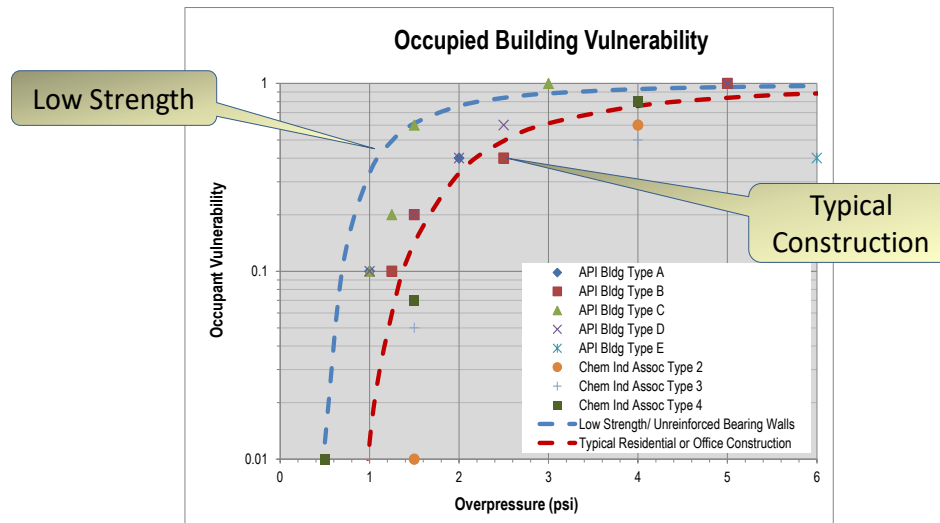


Figure 11.7 Occupied Building Vulnerability

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.

$$\text{Number of People Impacted} = 0.15 (20) = 3 \text{ people}$$

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.

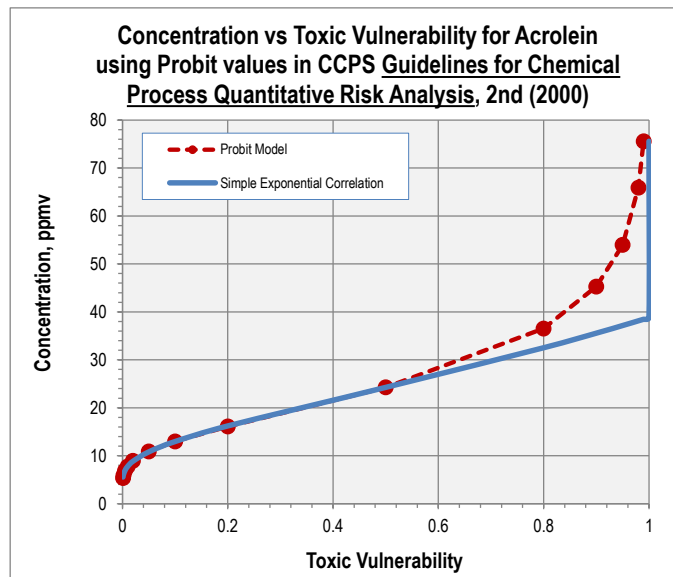
$$\text{Number of People Impacted} = 0.4 (10) = 4 \text{ people}$$

Offsite Toxic Impacts

A simple exponential function may be used to relate toxic vulnerability.

$$\ln(\text{toxic vulnerability}) = c + d / C^m \quad \text{or} \quad \text{vulnerability} = e^{c + d / C^m} \quad (57)$$

where c and d are evaluated at 2 points from a probit model (proposed as 1 and 50% lethality) and 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 distance².)



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.

Continuous Release:

$$\ln(\text{Lethality}) = c + d / C^m \quad \text{where } m = 2 b$$

$$\text{Concentration, } C = (a / X)^{1/b} Q / (Mw u) = a^{1/b} [Q / (Mw u)] / X^{1/b}$$

$$\ln(\text{Lethality}) = c + d [X^2 \{ (Mw u) / Q \}^{2b} / a^2]$$

$$\text{Lethality} = e^{c+d [X^2 \{ (Mw u) / Q \}^{2b} / a^2]} \tag{58a}$$

Instantaneous Release:

$$\ln(\text{Lethality}) = c + d / C^m \quad \text{where } m = 2 b$$

$$\text{Concentration, } C = (a / X)^{1/b} (Q^* / Mw)^{1/(3 b)} = [a^{1/b} (Q^* / Mw)^{1/(3 b)}] / X^{1/b}$$

$$\ln(\text{Lethality}) = c + d [X^2 (Mw / Q^*)^{2/3} / a^2]$$

$$\text{Lethality} = e^{c+d [X^2 (Mw / Q^*)^{2/3} / a^2]} \tag{58b}$$

where:

- C = concentration u = wind speed (distance/time)
- Mw = Molecular Weight X = downwind distance (including any correction)
- Q = release rate (mass/time) for initial dilution
- Q^* = release quantity (mass) 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, $dA / dX = 2 f X dX$.

$$\begin{aligned} \text{Number Impacted} &= 2 \eta P_D f x_0 \int X e^{c+d [X^2 \{ (Mw u) / Q \}^{2b} / a^2]} dX \\ &= \eta P_D f a^2 \{ Q / (Mw u) \}^{2b} \{ e^{c+d [X^2 \{ (Mw u) / Q \}^{2b} / a^2]} - e^{c+d [X_0^2 \{ (Mw u) / Q \}^{2b} / a^2]} \} / d \end{aligned} \tag{59a}$$

The lethality integral may also be written utilizing X_{Ref} as the distance to a concentration, C_{ref} , by substituting:

$$[Q / (Mw u)]^{2b} a^2 = C_{Ref}^{2b} X_{Ref}^2 \text{ for a continuous release}$$

$$[Q / (Mw u)]^{2/3} a^2 = C_{Ref}^{2b} X_{Ref}^2 \text{ for an instantaneous release}$$

$$\begin{aligned} \text{Number Impacted} &= 2 \eta P_D f_{X_0} \int X e^{c+d [X^2 / (C_{Ref}^{2b} X_{Ref}^2)]} dX \\ &= \eta P_D f C_{Ref}^{2b} X_{Ref}^2 \{ e^{c+d [X^2 / (C_{Ref}^{2b} X_{Ref}^2)]} - e^{c+d [X_0^2 / (C_{Ref}^{2b} X_{Ref}^2)]} \} / d \end{aligned} \quad (59b)$$

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, merely multiple 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 Incident 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 Case
 - Distance for Direct Explosion Impact
 - Distance needed for Off-Site Toxic
 - Concentration at Distance to Occupied Building for Toxic Infiltration
 - Overpressure at Distance to Occupied Building for Building Damage
- Estimate Impact Area for On-Site Cases. 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.

12. 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 incident 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. 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.

Module Objectives

In this module you will learn:

- 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). Between these two periods, the failure rate is reasonably constant for most components.

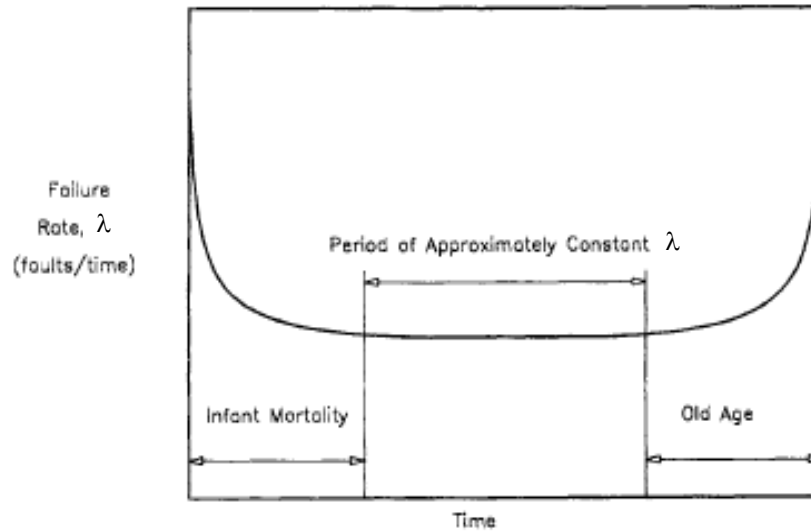


Figure 12.1 Failure Rate vs Time

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 as⁷:

$$R(t) = e^{-\lambda t} \quad (60)$$

where R is reliability over the time interval

The Failure Probability over this time interval, $P(t)$, assuming zero time for repair, is:

$$P(t) = 1 - R(t) = 1 - e^{-\lambda t} \quad (61)$$

The Mean Time Between Failures (MTBF) for constant failure rate is merely:

$$\text{MTBF} = 1 / \lambda \quad (62)$$

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.

$$P = \prod P_i = P_1 P_2 P_3 \dots$$

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).

$$P = \sum P_i = P_1 + P_2 + P_3 \dots$$

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: a flat tire on a car is immediately obvious to the driver. However, the spare tire may also be flat without the driver being aware until the spare is needed.



Figure 12.2 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 as⁷:

$$\text{PFD}_{\text{average}} \text{ for Unrevealed Failures} = \frac{1}{2} \lambda \tau \quad (63)$$

where τ is the inspection interval and λ is 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 as:

$$\text{PFD for Revealed Failures} = 1 - e^{-\lambda \tau} \quad (64)$$

The PFD for revealed failures that can be repaired may be estimated as:

$$\text{PFD} = \text{MTTR} / (\text{MTTR} + \text{MTBF}) \quad (65)$$

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 an incident 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 an incident, 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”.

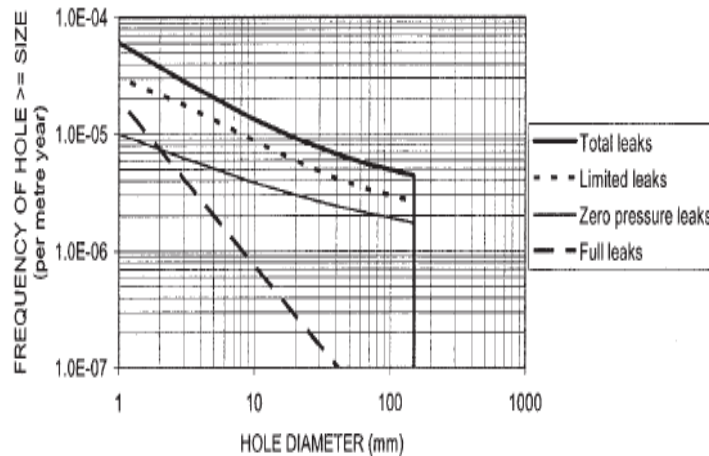


Figure 12.3 Leak frequencies for 150 mm diameter pipe - HSE offshore data

In many cases, the failure frequency is determined as the number of reported incidents 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 [Layers of Protection Analysis](#), Center for Chemical Process Safety, American Institute of Chemical Engineers, New York (2001) is tabulated below:

| 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} <i>per opportunity</i> |

Table 12.1 Common Initiating Event Frequencies

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).

Factor 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.

Enabling Conditions

An Enabling Condition is one that must be present for the event sequence to progress to the Loss Event or Incident.

- A proximity-based *Probability of Exposure* was covered under Impact Assessment.
- Some plant operations have potential for harm only during discrete periods of time. For example, a batch plant may manufacture a number of different products using the same equipment but only one product uses hazardous chemicals. The *Time at Risk* divided by the total time may represent an Enabling Condition that reduces the overall likelihood of a scenario.

- Ignition of a flammable release is another common Enabling Condition. For an outdoor release, the *Probability of Ignition* is based on the size of the cloud and likelihood the cloud reaches one or more unknown ignition sources. It is correlated with Airborne Rate or distance to ½ the Lower Flammable Limit concentration for short duration releases.

| Distance to ½ LFL Concentration based on Dispersion Modeling | Low Ignition Probability Vapor LOPA Credit for POI | Normal Ignition Probability Vapor LOPA Credit for POI | Elevated Ignition Probability Vapor LOPA Credit for POI |
|--|--|---|---|
| < 25 m or < 82 ft | 3 | 2 | 1 |
| 25 to 70 m or 82 to 230 ft | 2 | 1 | 0 |
| > 70 m or > 230 ft | 1 | 0 | 0 |

Note: The above table is based on an outdoor release into an electrically classified area and no strong ignition source (such as fired equipment, shop or hot work, electrical substation, high traffic roads or idled vehicles) within the ½ LFL cloud (including areas where liquid may travel). Excludes the probability of immediate ignition for releases above the autoignition temperature or static ignition of aerosol mists.

Table 12.2 Example of Probability of Ignition for Outdoor Releases

Unmitigated Risk

Unmitigated Risk represents an estimate of the consequence magnitude and expected frequency of an event if *no* Safeguards or Protective Layers were installed. The analysis team should consider unmitigated risk frequency and whether or not the sequence of events leading to the scenario is something that should be further analyzed. In Layers of Protection Analysis (LOPA), unmitigated risk consists of:

- The Tolerable Frequency
- the Initiating Event Factor
- Enabling Factors such as Ignition Probability or Probability of Exposure

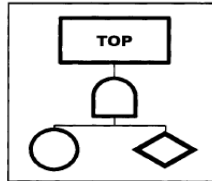
If these items are clearly defined and well documented, identification of appropriate controls and mitigations (existing or proposed to be added as an upgrade to close the gap), as well as subsequent reviews, of the case will be easier. The Chemical Hazards Engineering Fundamentals manual does not address Protective Layers.

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 incident.

Fault Tree Likelihood Modeling

Fault-tree is a technique that allows failure analysis teams to identify all potential causes of an undesired event.



- 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 event or incident. 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. 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.

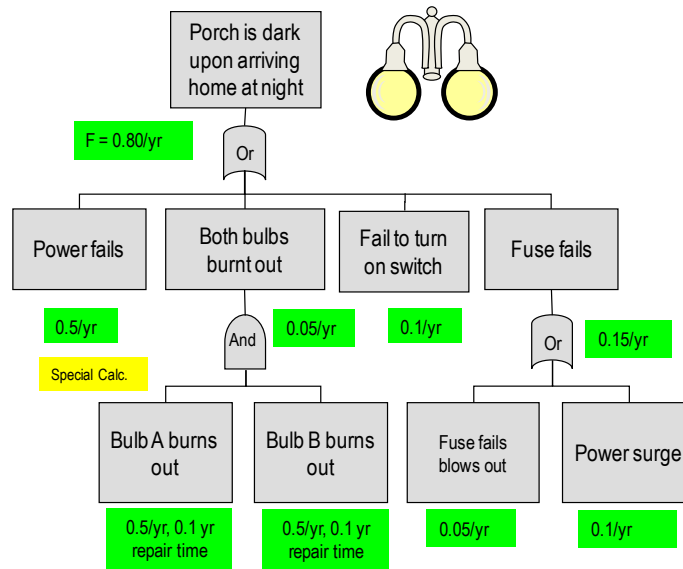
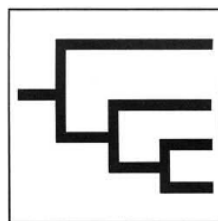


Figure 12.4 Example Fault Tree

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 you reach the desired stopping point or basic event level.

Event Tree Likelihood Modeling

The event tree is used to trace the initiating event through its various hazardous consequences. It will be simplest for incidents that have few possible outcomes (e.g., toxic releases or internal explosions). Releases that are both flammable and toxic may have many possible outcomes.



- 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 incident 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. 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).

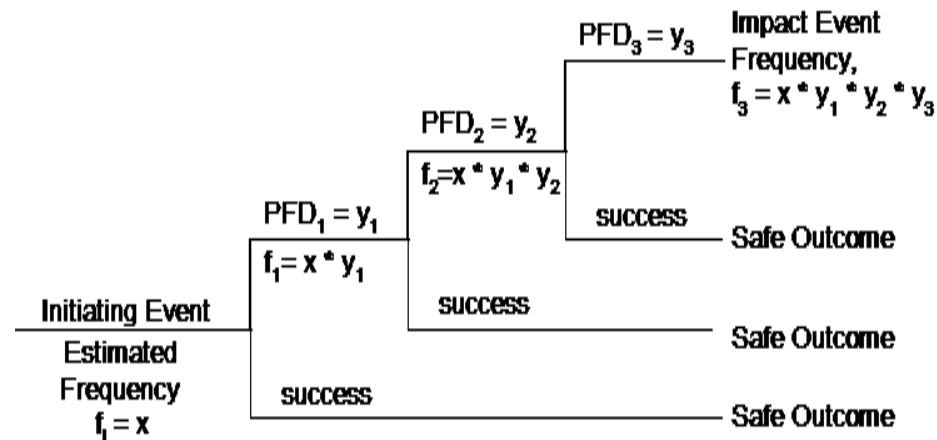


Figure 12.5 Example Event Tree

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 an 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.

We seldom evaluate incidents within one process unit that may affect another unit as the likelihood is very small. However, several situations with potentially catastrophic impacts are drawing 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.

Simplified Pool Fire Frequency Analysis

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. 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 merely the summation of all scenarios. As a simplification, common-cause failures are not included, so the final result for low frequency cases (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.

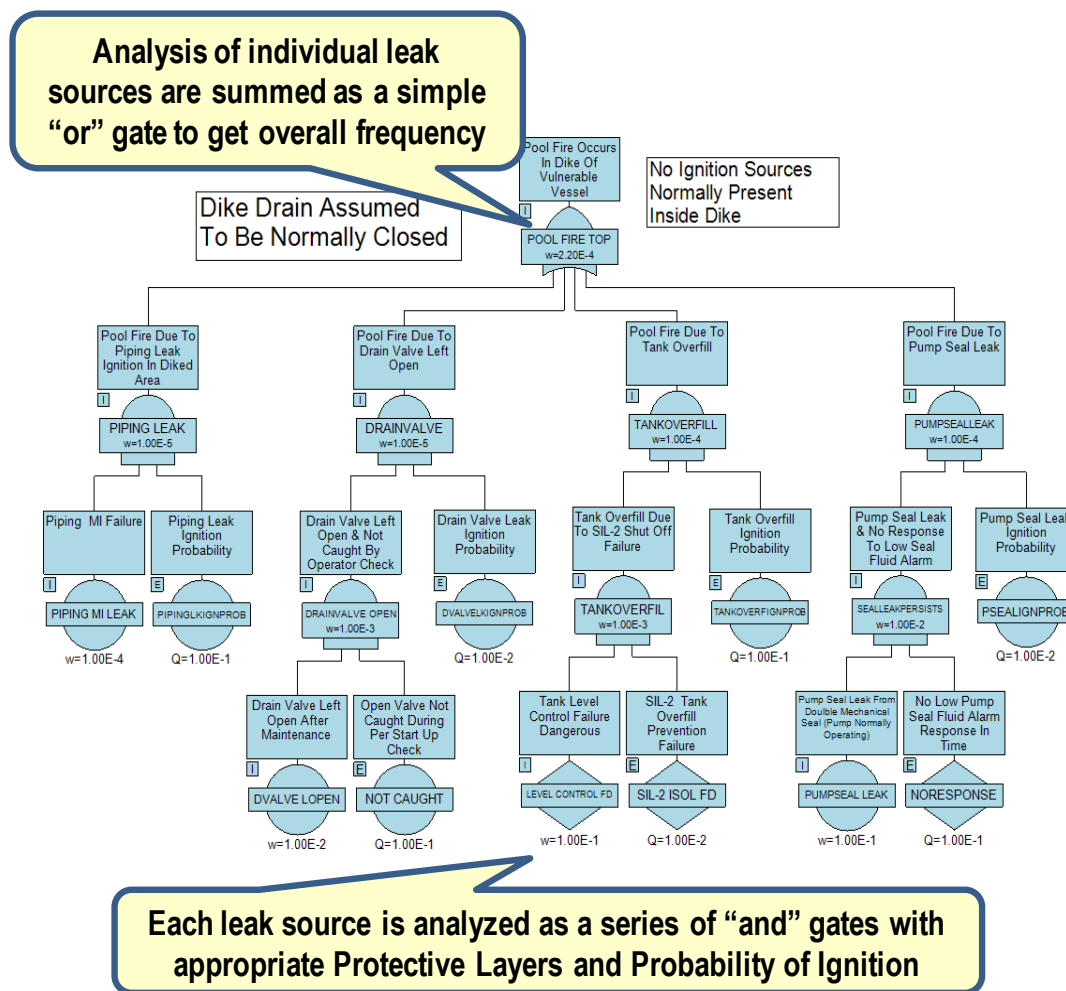


Figure 12.6 Example Fault Tree for Pool Fire Exposure to Equipment

Analysis of Protective Layers

Several techniques may be used for analysis of the effectiveness of Protective Layers in reducing the overall Likelihood of a hazard scenario. Two common approaches are Barrier Analysis and Layers of Protection Analysis (LOPA).

Barrier Analysis

Barrier Analysis is a form of simplified Risk Analysis. Having identified the hazards inherent in an activity, it becomes necessary to identify and evaluate barriers that provide control over these hazards. Barriers may be physical barriers, procedural or administrative barriers, or human action. The reliability of a barrier is its ability to resist failure. The objective of the process for identifying and evaluating barriers was to arrive at a set of optimum barriers, that is, a set of reliable and effective barriers. The expected failure frequencies of barriers provide a characterization of the reliability of the barriers.

Barrier Analysis is represented by a “Bow Tie Diagram”.

- The center of a “bow tie” diagram is the Top Event or incident.
- 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.

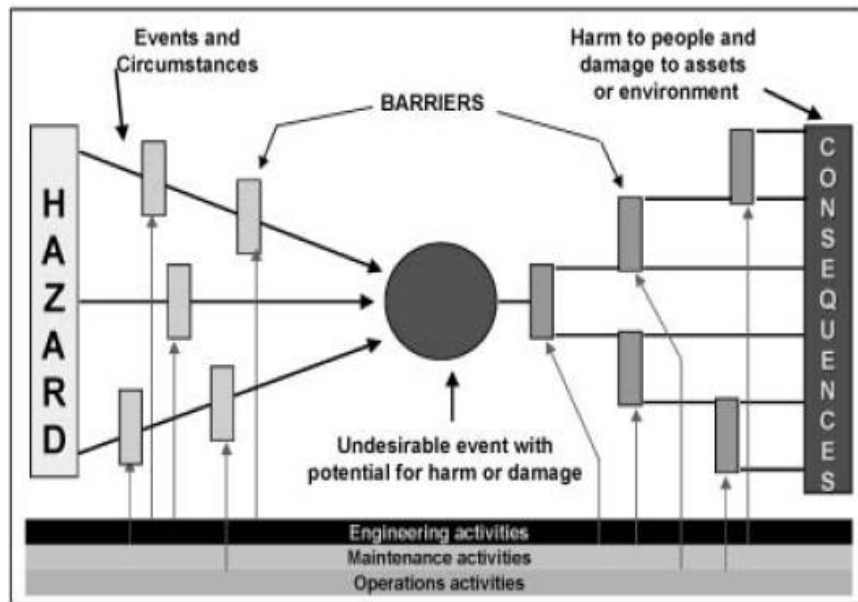


Figure 12.7 Example “Bow-Tie” Diagram

Layers of Protection Analysis

Layers Of Protection Analysis (LOPA) is a method for evaluation the effectiveness of Independent Protective Layers (or Barriers) in reducing the likelihood or severity of an undesired event (such as an incident) or consequence. It is based on a single Cause (Initiating Event) – Consequence (Incident Outcome) pair. LOPA is essentially a single “path” of Barrier Analysis.

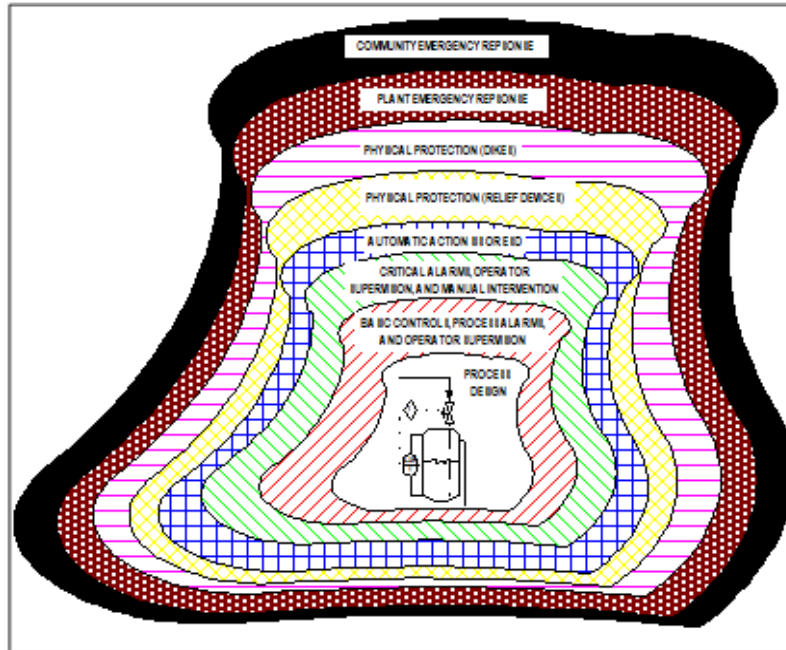


Figure 12.8 The LOPA Onion

LOPA assumes all events are in Series (AND gates) such that frequencies and probabilities are multiplied to obtain an overall frequency which is compared to a Tolerable Frequency. 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.

Tolerable Frequency

There are various risk criteria in use today. The uncertainty in these criteria are generally plus or minus one order of magnitude. Means to reduce risk below a targeted level are sometimes pursued if the cost for implementation is reasonable.

A single scenario case represents one of possibly many scenarios that could result in the same undesired consequence, so Process Risk for a manufacturing facility is often expressed graphically as “**cumulative**” **frequency versus severity** or an “FN” curve. Severity is expressed as N or more people severely impacted (potential fatalities). The technique is to plot the scenario case with the highest severity and associated frequency on the lower right-hand side of the graph. The following point is the next highest severity at the summation of frequencies of all cases of the same or higher severity. This procedure is repeated until all scenario cases are plotted. A line interconnecting these points is then compared to lines on the graph representing company or regulatory agency criteria.

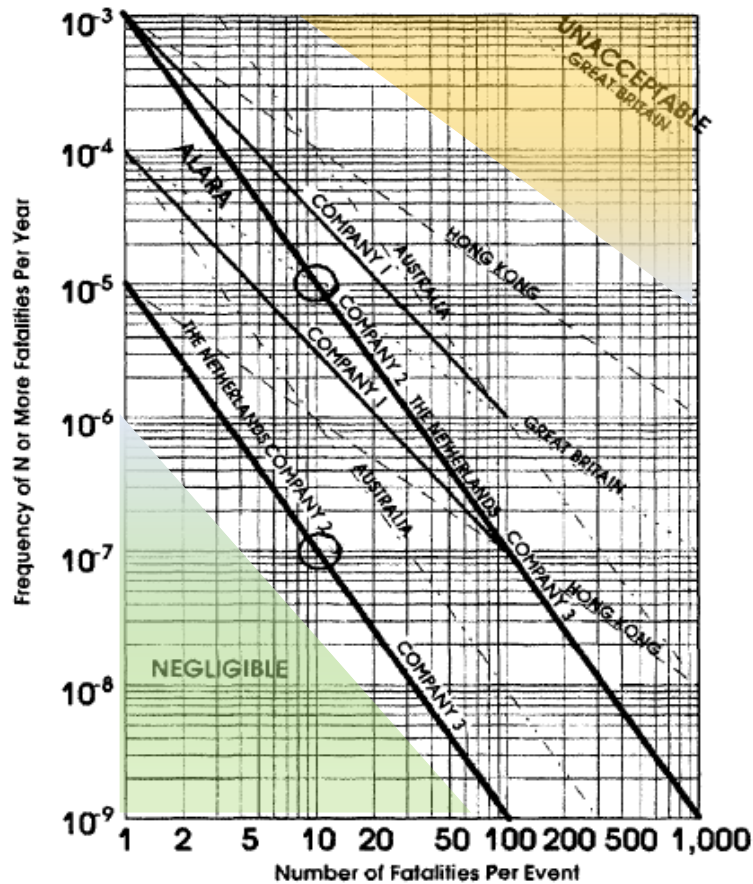


Figure 12.9 Example FN Curve

Tolerance criteria are based on a specific methodology (so comparisons are not always straight forward). An example is “ALARP” is short for “as low as reasonably practicable”. The concept of “reasonably practicable” lies at the heart of the British Health and Safety system. Other Regulatory Agencies have also established guidance for Broadly Acceptable and Unacceptable Risk.

13. SUMMARY

Hazard Evaluation and Risk Analysis

Hazard Evaluation and Risk Analysis are processes whereby hazards are evaluated by answering basic questions:

- What are the Hazards?
- What can go wrong?
- What are the potential consequences?
- How likely is it to happen? Is the Risk Tolerable?

Overall Work Process Steps for Hazard Evaluation and Risk Analysis

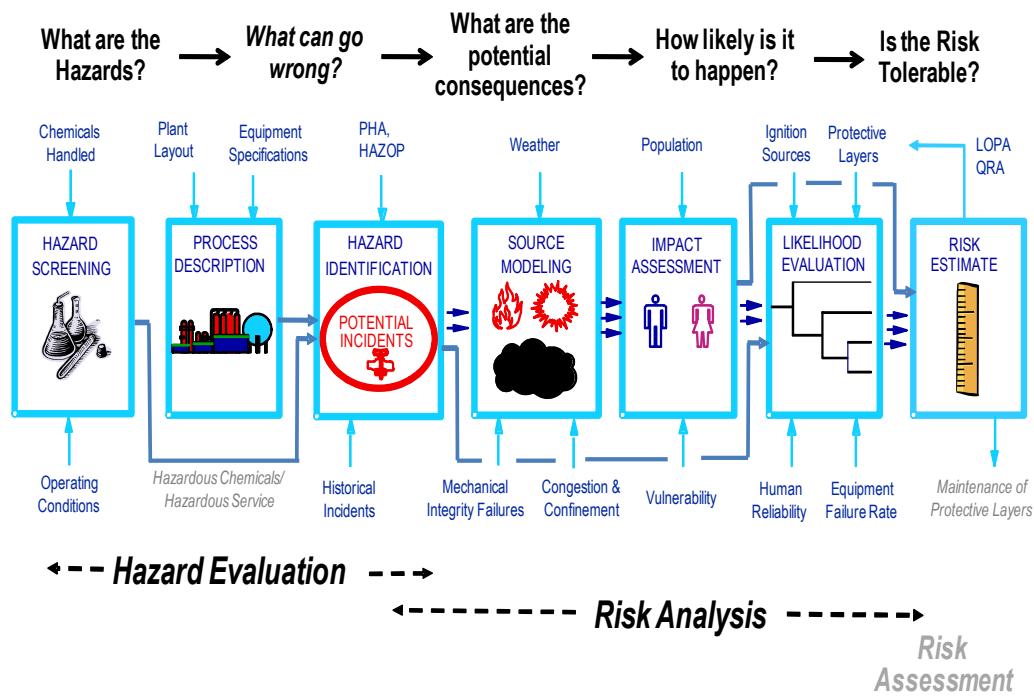


Figure 13.1 Hazard Identification and Risk Analysis Work Process

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REVISION HISTORY

| Version | Date | Description |
|---------|-------------|--|
| 1.0 | 2 Apr 2018 | Initial issue |
| 1.1 | 13 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 (pgs 79-80). Updated Vapor Cloud Explosion to reference Lower Flammable Limit (LFL) rather than $\frac{1}{2}$ LFL and updated cloud volume (pgs 104-105). Added section for Offsite Toxic evaluation. Minor formatting issues corrected. |