2

PREVENTION AND MITIGATION

2.1. INTRODUCTION

While preparing for an emergency is essential, preventing the event or mitigating its effects so that it never reaches emergency proportions is more desirable. Most incidents that lead to an emergency are caused by deviations from normal conditions. If these causes and their potential consequences are identified in advance, several measures can be taken to minimize the likelihood of events causing an emergency or to reduce an incident's impact on the plant or its surroundings. Industry and regulatory authorities recognize and promote the need to plan for unforeseen circumstances that may lead to emergencies.

Risk management in process industries handling hazardous materials has tended toward using a multilayered approach for protective systems. Minimization of risk due to process incidents is achieved by the independence of the layers of protection employed and the unlikelihood of simultaneous failure of several such layers. A diagrammatic presentation of the multiprotective layer concept was published recently by Drake and Thurston [15]. An adaptation of this diagram is presented in Figure 2.1. The diagram shows the protective layer concept where initial reliance is on the process operation itself followed as needed by various layers of protective systems. These protective layers include engineered process shutdown systems, followed by both active and/or passive release controlling systems.

Should the inner layers of safety protection fail to prevent or sufficiently mitigate the incident's effects, both on-site and off-site, then emergency response protection layers may be necessary. It is important to note that multiple layers may be damaged or fail in a single event (e.g., an explosion can damage process controls, engineered shutdown systems, and release protection systems).

The preceding chapter identified the PSM elements and components of process safety management employed in chemical process design, operations, and maintenance for prevention of incidents involving hazardous materials. Successful risk management is a blend of sound organizational practices and the use of basic

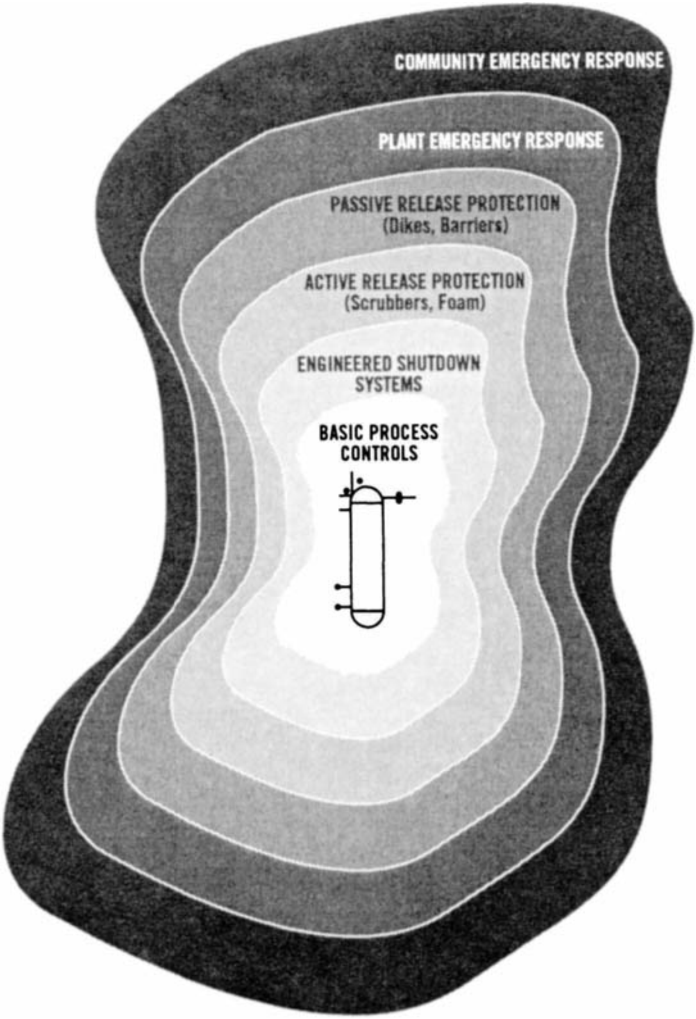


FIGURE 2.1. Typical layers of protection in a modern chemical plant. (Adapted from Drake and Thurston [15].)

safety-related technology. Sound organizational practices that prevent or mitigate incidents include documented operating procedures, operator training, preventative maintenance, management of change, and other human factor components. This chapter reviews some engineered plant and process design safety features that are used to prevent or mitigate hazardous material releases.

2.2. PRINCIPLES OF PREVENTION

2.2.1. Process Hazard Recognition

Preventing a hazardous release must start with recognition of the hazard, which has been defined as "a chemical or physical condition that has the potential for causing damage to people, property or the environment" [5]. Hazards can usually be identified by knowing the properties of the materials in question or knowing how they are used. In this book we are focusing on hazards in the use of chemicals in the process industries.

2.2.1.1. Identify Chemical and Physical Properties

Among the chemical and physical properties important to safety, we include such characteristics as toxicity, vapor pressure, flash point, autoignition temperature, flammable range, odor, corrosivity, solubility, and others. Toxicity must be understood in terms of acute versus chronic effects and the physiological results of possible alternate routes of exposure such as inhalation or absorption. The properties most important for emergency planning relate to fire, explosion, and acute toxicity. Planners must consider physical properties that affect mobility, volatility, fluidity, and vapor density. Other hazards such as corrosivity are also often considered in prevention as they may affect equipment integrity and personnel safety and health. Common information sources on these properties are Material Safety Data Sheets (MSDS) and commercially available references.

2.2.1.2. Identify Reactivity and Incompatibility Hazards

Less commonly recognized hazards are potential problems with chemicals involving their reactivity (i.e., self-reactive) or incompatibility with other substances. Self-reactive materials may include certain monomers that polymerize when not properly inhibited, thermally unstable materials like peroxides, and shock-sensitive materials. A search for potential chemical incompatibility hazards in a process system can be facilitated by use of an interaction matrix such as described in [6, pp. 45 and 242]. Chemicals incompatible with common materials such as water, oxygen, or iron can be extremely hazardous due to the availability of these reactants in the plant environment. Contaminating materials can sometimes act as catalysts for decomposition, such as copper in hydrogen peroxide solutions. Incompatible combinations of materials that are coprocessed or stored in close proximity may result in acid–base reactions releasing heat, toxic gases or mists; oxidizer/flammable reactions initiating fire and explosions; and many other reactions producing energy and possibly gaseous by-products. The sources noted in 2.2.1.1 should be supplemented by an examination of the *Guidelines for Chemical Reactivity Evaluation and Applications to Process Design* [7], *NFPA 491, Hazardous Chemical Reactions* [23], and others.

2.2.2. *Inherently Safer Plants*

A first step in risk management is to reduce or eliminate the hazard if possible. In his publication "Plant Design for Safety, A User-Friendly Approach," Trevor Kletz notes that "WHAT YOU DON'T HAVE CAN'T LEAK." Kletz presents many graphic and detailed examples that illustrate these concepts [20, 21]. Similarly, the second chapter of the *Guidelines for Engineering Design for Process Safety* [8] presents an excellent overview of the benefits and approaches to inherently safer plants. Usually one thinks of this approach for new plants; however, opportunities to improve inherent safety are also possible with existing plants. To achieve success, creative thinking and sound engineering judgment are needed to analyze and balance tradeoffs that may be introduced. Following are a few methods for developing inherently safer chemical processes and examples that typify their application.

2.2.2.1. Material Substitution and Attenuation

Hazard can be reduced simply through material substitution—using alternate chemical process routes that employ less hazardous materials, such as using sodium hypochlorite solution rather than pure gaseous chlorine for disinfection of water. Other substitutions might involve a change in the vehicle or carrier for a product such as using water-based paints or pesticide sprays versus using toxic and/or flammable carrier solvents. In plant auxiliary services, an example might be converting a process heating system from hot oil to steam resulting in a reduction in fire hazard. In most cases, the customer and the manufacturer will likely benefit from inherently safer products made by inherently safer processes.

Attenuation or dilution of a material can often be used to reduce hazards such as toxicity and high vapor pressure. Common examples include using aqueous solutions of hydrogen chloride or ammonia rather than the pure materials where possible.

2.2.2.2. Reduced In-Process Inventories

Enhancement of inherent safety is sometimes achieved by reducing quantities of intermediate hazardous materials in-process. A striking example of not reducing such inventories occurred in Bhopal, India, where a hazardous intermediate, methylisocyanate (MIC), was produced and put in protected storage for later use in herbicide production. Other plants have utilized closely coupled reaction steps where the product from one stage is fed directly into the next reaction stage, thereby eliminating the need to store a high hazard material like MIC. Eliminating large inventories of intermediates may introduce process inefficiencies since process interruptions can reduce final product output. It has often been necessary in such cases to improve the availability or on-stream time for the segments of the processes closely connected in this manner. As a result, in such cases safety and economy can be served.

2.2.2.3. *Reduced Storage Capacities*

Reduction of storage inventories of hazardous raw materials has become more common in the chemical process industry. Large inventories are often carried as a defensive measure to protect against the effects of a supply interruption, even when the risk of interruption is low. In such cases, inventory reduction can be very successful. Before proceeding, engineers should carefully examine the patterns of use and the reliability of supply to ensure that plant shutdowns due to raw materials shortages will not occur. This concept also applies to hazardous finished products.

In other cases, tank and container size have been reduced, thereby lowering the risk of huge leakage. For example, to reduce a potential leak's impact area, chlorine cylinders have been used in place of tank car quantities. While this reduces the magnitude and impact of a larger release, a trade-off is the likelihood of a higher frequency of small leaks and associated worker exposure due to the increased number of material transfers. Minimizing storage in such cases may require greater attention to training plant operating personnel and instituting system safeguards to prevent an increased risk to individuals who may still be affected in a smaller release.

2.2.3. Process Design Modifications

Process engineering has long involved scale-up of processes to achieve needed production capacity and product quality while ensuring safe and reliable plant operation. As part of their scale-up procedures, engineers normally determine in theory the effect of possible scale-up parameters on all these desired results. At this stage, several process options may be available that have different implications for efficiency, cost, environmental releases, and safety. Process design modification to enhance safety works best when starting with a new process because flexibility is greatest and the cost of a change is lowest; however, opportunities can often be found for modifying existing processes with attendant benefits such as reduced likelihood for releases or a reduced consequence. A more complete discussion of process design modifications can be found in the *Guidelines for Engineering Design for Process Safety* [8].

2.2.3.1. *Continuous versus Batch Reactions*

Chemical processes are generally more tightly controlled in continuous processes that operate under steady-state conditions within a narrow band of desired parameters (e.g., temperature, flows, pressures). Continuous processes generally require fewer operating steps for normal operations and involve lower material quantities in the reaction stage. These characteristics often make continuous processes inherently safer than batch processes, particularly for large capacity plants; however, continuous processes do not operate at steady-state conditions during startup and shutdown and are, therefore, more prone to accidents during these operational phases than during normal operations.

Continuous processes usually require high production rates and a high capital expenditure in specialized equipment; therefore, batch processes are quite common in the chemical process industry since a great variety of process conditions can be achieved while producing even small quantities of material in more general purpose equipment. Scaling up to continuous process operations is desirable, but not always practical or economically feasible, particularly for small capacity plants. Batch processes involve greater potential for human error largely because of the sequenced steps and varied process operations needed.

Many techniques, however, exist for enhancing batch process safety. For example, batch reactors can run more safely by gradually adding a limiting reactant to avoid accumulating unreacted materials. Additionally, operational methods that utilize heat balance or utilize tests on the properties of the batch itself can offer a higher degree of control assurance for batch operations. Batch reactors can be built in a robust manner with corrosion-resistant materials capable of withstanding elevated pressures that enhance their integrity. Some other common features that improve safety of batch reactor systems include agitation/feed interlocks, catch tanks for collecting emergency emissions, runaway reaction inhibitors, and high-cooling capacity for excess heat removal.

2.2.3.2. Pressure versus Vacuum Operation

The pressure of a process sometimes depends on required temperatures and reaction kinetics. Safety considerations often govern the selection of operating pressures. Some processes that utilize toxic gases are operated under partial vacuum conditions so that a loss of containment results in leakage into the process stream rather than into the atmosphere. This is true in many continuous chlorinated hydrocarbon manufacturing processes and also in water treatment using chlorine. Vacuum conditions are also commonly used in the process industry to reduce the temperature needed for distillation where decomposition and residue formation may be serious issues. In the case of flammable materials, on the other hand, positive pressure is generally maintained because air leakage into the process streams could result in potentially explosive conditions.

2.2.3.3. Gas versus Liquid

In some process applications, a choice exists whether a material can be introduced as a liquid or as a gas in the process. Where practical, plants should reduce the total inventory of materials in equipment by conveying or processing the materials in the gaseous state. The maximum release quantity will be effectively reduced in this portion of the system. This applies when selecting a site for liquefied gas vaporization equipment in a plant where the material is unloaded from rail cars and eventually fed to the process in gaseous form. Many plants have located the vaporization equipment near the unloading location and convey gaseous material to the points of use. This system reduces the inventory in the transfer line and the release rate, which is limited by the heat input to the vaporizer.

2.2.3.4. Control System Strategy

The CCPS addressed the role of process control systems in its *Guidelines for Safe Automation of Chemical Processes* [11]. Although not a substitute for inherent process safety, using well-designed control interlocks is a good way to prevent incidents. The Guideline advice includes separating safety interlock systems from the basic process control system (BPCS) and paying careful attention to the interface of the operator and control instrument systems. There are many choices to be made in controlling a chemical or petrochemical process, and the close coordination of process and control engineering specialists is essential to minimize introducing hidden hazards and to identify failure modes introduced by control system hardware and software.

2.2.3.5. Refrigeration

There is a special hazard associated with the leak of a superheated liquid (i.e., a material held above its normal atmospheric pressure boiling point) when storing and transferring liquefied gases. This type of liquid leak will rapidly atomize and become airborne if there is sufficient superheat, resulting in a possibly toxic and/or flammable cloud containing gas and aerosol material. Additional atomization may be caused by a pressure drop across the leak aperture in the vessel or pipeline of superheated liquid. Both vapor and aerosol production can be reduced by refrigerating the liquefied gas to near or below its normal boiling point. This technique has been practiced at some facilities with materials such as natural gas and ammonia. Further information on this technology is presented in *Guidelines for Postrelease Mitigation Technology in the Chemical Process Industry* [10].

2.3. PRINCIPLES OF MITIGATION

Mitigation in this book differs from prevention in that it focuses on dealing with the hazardous material after it is released from its primary containment. This section briefly outlines passive and active means to limit the amount released or to reduce the consequences of a release.

2.3.1. Plant Siting/Buffers

A passive means to mitigate the effect of a release is to establish maximum distances between the possible release point and sensitive zones. This technique is somewhat more effective for fire and explosion than for toxic releases because significant acute toxic effects can sometimes occur even at the low concentrations present at significant distances from the leak. Buffers of several hundred feet can be useful for fire hazards; for toxic hazards, thousands of feet may be needed. Barriers that enhance the effect of distance on toxic releases include trees, hills, or structures that can either trap or disperse airborne material. The role of models for estimating dispersion of toxic releases will be covered briefly in Chapters 3, 6, and 9 of this book. Further insight can be gained from the *Guidelines for Postrelease Mitigation Technology in the Chemical Process Industry* [10], *Guidelines for Chemical Process Quantitative Risk Analysis* [5], and other sources, including those from air pollution regulatory agencies.

The mitigating effect of risk buffer zones in plant siting will be influenced by the type of occupied area that may be impacted. For example, hospitals and tunnels are particularly vulnerable impact areas, while an adjoining industrial plant may be less vulnerable since the occupants should be prepared for emergency action when needed.

2.3.2. Unit Siting in Plant Design

Many published recommendations exist on unit layout within plant sites that help reduce the chances for propagation of a release, especially where a fire or explosion is involved. The *Guidelines for Evaluating Process Plant Buildings for External Explosions and Fires* [12] is especially helpful for development of building design as influenced by the risk of possible fire or explosion in the vicinity.

In general, chemical or petrochemical plants group storage systems away from process operations since storage systems, although experiencing low frequency of serious releases, have the potential for greater area impact accidents, while process systems might have more frequent releases but of generally more local area impact. Special site isolation is usually given to boiler houses, flares, other direct-fired systems, and electrical switch rooms, all of which can cause ignition of flammable releases. The overall layout of large plants is usually designed with multiple access routes for the approach of emergency teams and their equipment.

Among other references especially valuable on unit siting in plant design are those supplied by NFPA [18], IRI [19], API's RP 752 [24] and the earlier *Guidelines for Safe Storage and Handling of High Toxic Hazard Materials* [3] and on *Guidelines for Vapor Release Mitigation* [4].

2.3.3. Principles of Mitigating Chemical Releases

Accidental releases of hazardous materials usually have their root causes in some combination of human and mechanical failure. Process design principles for mitigating releases using countermeasures rest on (1) use of consensus safety codes representing industrial experience, (2) safety experience with the specific process in question, and (3) prospective hazard analysis studies such as those described in the *Guidelines for Hazard Evaluation Procedures* [6]. Learning about accidents from experience allows us to apply the lessons learned to eliminate causes or to reduce consequences. Modern hazard analysis attempts to anticipate situations or scenarios that can result in injury or damage before they actually occur.

2.3.3.1. *Release Causes*

The *Guidelines for Vapor Release Mitigation* [4] note four general categories to which most releases can be assigned. These include: (1) "open end" routes to the atmosphere; (2) imperfections in, or deterioration of, equipment integrity; (3) external impact; and (4) operating deviations from design conditions. Some examples are:

- Overfilling a vessel
- Leaving a drain valve open
- Pipeline rupture
- Failure of a vessel nozzle
- Overpressuring a process vessel due to loss of process control or external heating.

As noted above, the root causes of releases will usually be some combination of events, both human and mechanical, leading to the loss of containment.

2.3.3.2. *Design to Mitigate Releases*

Many methods exist to mitigate chemical releases, depending on the nature of the process and the environment in which it exists. A plan to mitigate releases might start with assurance of physical plant integrity, including careful attention to materials of construction, testing during construction and installation, management of change procedures, and sometimes the use of double-containment systems. Critical instrument controls usually have backup features in the event of failure to help assure process integrity. Another typical safety-related backup feature is the use of emergency relief valve systems that ensure physical plant integrity by preventing vessel or pipeline failure caused by overpressure. For nonreactive systems, API 520 [1] provides valuable information on relief systems. The AIChE's Design Institute for Emergency Relief Systems (DIERS) gives attention to the proper design of relief systems [13] for special circumstances such as reactive systems or systems involving two-phase flow. Relief systems may include relief discharge treating systems such as catch tanks, quench tanks, flares, or stacks, as mentioned under the section on postrelease Mitigation below.

2.3.4. Postrelease Mitigation Systems

The purpose of a postrelease mitigation system is to reduce the impact area and the ultimate consequences of an uncontrolled release of a hazardous material. Such systems can be either passive (i.e., requiring no operational action) or active (requiring some mechanical or human action). The releases may be vapor or gas, liquid (with or without significant vaporization), or aerosols (i.e., mists of fine liquid droplets). Releases of chemicals reactive with common environmental materials such as water or air are a special case. Chemicals reactive with water often result in the evolution of gases, whereas chemicals reactive with oxygen (i.e., pyrophoric chemicals) often give off flame and combustion products. Another special case might be protection provided for the release of projectiles from a system that includes the risk of explosion such as blast curtains surrounding an oxygen–hydrocarbon mixing system. Postrelease mitigation systems are in the last layer of protection before emergency response. The *Guidelines for Vapor Release Mitigation* and *Guidelines for Postrelease Mitigation Technology in the Chemical Process Industry* [4, 10] offer considerable insight into the variety of mitigation techniques that have been used by industry (depending on the material) and on the state-of-the-art for several of the techniques. Some examples of postrelease mitigation technology follow.

Several ideas for preventing the spread of contamination after a release are discussed in Chapter 14, Section 14.3 on Cleanup of Facilities.

2.3.4.1. Secondary Containment for Storage, Handling, and Fire Situations

Secondary containment techniques such as berming and diking have long been used for above-ground combustible and flammable liquid storage tanks. Such contained areas are usually graded or sloped to keep a liquid spill away from the storage vessel in case the material ignites. For volatile toxic materials, the contained area may be designed to minimize exposed surfaces and thus limit airborne

PHOTO 1. Storage Tank with Containment Dike.

evaporation. A good practice is to provide berming and containment for transport filling or unloading areas where connections must be made and broken frequently. The principles of spill separation and of exposed area minimization similarly apply in these cases. Berming and containment areas are examples of passive mitigation.

Diked containment areas have sometimes been installed to retain fire water runoff from such areas as process areas or warehouses storing hazardous materials. The desirability of adequate design of this type of retention was exemplified as a result of the 1986 warehouse fire in Switzerland that contaminated the Rhine River. A good summary of this incident was written by H. H. Fawcett [17]. In the absence of runoff control to a sensitive area, responders may at times consider allowing the material to burn to extinction.

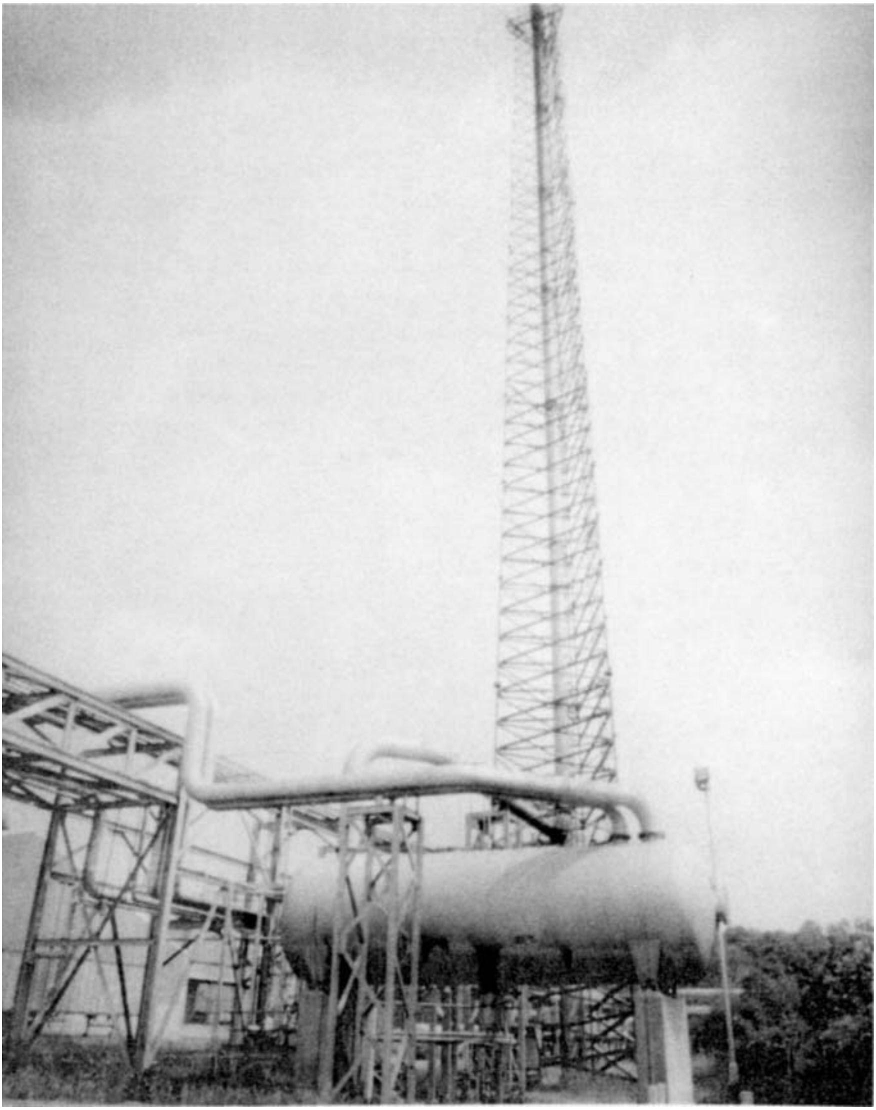
Secondary containment has also sometimes been used in the form of a structural enclosure where volatile acute toxics are handled. Such enclosures can be monitored by detectors, and any exhaust air may be scrubbed, dispersed (e.g., steam dispersion), or incinerated to mitigate releases.

2.3.4.2. Remote Shutoff, Flow Limitation, Transfer

Remote shutoff systems are widely used in the event of a pipe break in a transfer system. A notable example is a remotely operated valve on the unloading dip pipe of a vessel unloaded by pressure (e.g., chlorine tank car under dry air). Simple flow-limiting devices such as orifices and excess flow valves are often included in piping transfer systems to reduce the maximum release rate of spill from a damaged line. Sometimes an alternative empty storage vessel is installed for a hazardous liquid in the event of a leak in the original vessel so that the liquid can be safely transferred to minimize release from the damaged vessel. A variation of this concept is a dump tank system (sometimes also referred to as a deinventory system). An example is the hydrofluoric acid (HF) storage tank and HF settler in the Phillips™ alkylation process. The storage tank directly under the settler is nearly empty and can be used to rapidly receive the HF from the settler in the event of a release in the settler or associated piping [10].

2.3.4.3. Absorbents/Foam and Other Covers

Evaporation of vapors from spilled liquid pools may be significantly reduced by the appropriate application of absorbents, foam, or other suitable covers. Foams or other covers must be selected considering the reactivity of the spilled material. Foams have been used in some installations as the preferred mitigation measure for fire situations where management of water runoff can be a serious problem (e.g., a hazardous material warehouse). A table showing a variety of cover choices made in industry for 22 hazardous materials is presented in *Guidelines for Vapor Release Mitigation* [4]. Most of the mitigating techniques mentioned in this section are of the active type requiring a signal to be initiated.



2.3.4.4. *Catch Tanks, Scrubbers, Flares, Stacks*

Dealing with discharges from relief devices designed to prevent vessel overpressure is sometimes necessary. Typically, catch tanks or knockout pots are used as passive controls to trap liquids, while scrubbers and flares are used as active controls to destroy vapor emission. Sometimes the catch tanks can also serve as a condenser or passive scrubber for an emergency relief system. Stacks are commonly used to dilute residual vapor emissions. Any of these systems must be carefully designed for the particular process, taking into account quantities and rates of release involved, process conditions, critical physical/chemical properties, and the area to be protected from the emission [10]. Such postrelease mitigation systems include both active and passive types.

2.3.4.5. Water Sprays and Steam Curtains

Water sprays are sometimes installed to absorb highly water-soluble toxics such as ammonia or hydrogen chloride. Steam curtains find an application in the dilution of heavier-than-air flammables by both thermal and kinetic effects. Obviously these systems are active and require considerable detailed design study. The state-of-the-art in using these techniques in postrelease mitigation is also reviewed by CCPS in Chapters 4 and 5 of [10].

2.3.4.6. Detectors

Detectors for identifying and measuring the presence of flammable and certain toxic materials have been used in industry and are now widely available. Their value in activating postrelease mitigation treating systems or alerting emergency response teams is also noted in Chapter 6 of this book. A review of various detectors, their applicability and sensitivity to 22 types of materials is presented in *Guidelines for Vapor Release Mitigation* [4, Chapter 5], whereas *Guidelines for Postrelease Mitigation Technology* [10] provides much valuable detail on design principles of the various units. Detectors and their sampling systems are active systems that have become increasingly valuable for early warning of chemical releases to accelerate the application of mitigation and emergency response measures; however, these systems require carefully planned maintenance to be effective and may be subject to local environmental conditions (e.g., winds, snow), depending on their location.

2.3.5. Principles of Mitigating Fires and Explosions

Fire and explosion protection has long been a feature of plant and process design for chemical or petrochemical facilities to minimize injuries, loss of property, or business loss. Moreover, according to insurance reports, the severity of the largest such incidents has tended to increase over time. One reason is the trend toward construction of larger plants. Other suggested reasons include more remote operation and more plant congestion. Furthermore, in addition to the fire and explosion injuries and the property damage suffered from high temperature and overpressure, environmental concerns have arisen with regard to liquid and vapor discharges.

This discussion will only briefly touch on the principles of mitigating fires and explosions in view of the wide literature on the topic. Recent applicable CCPS

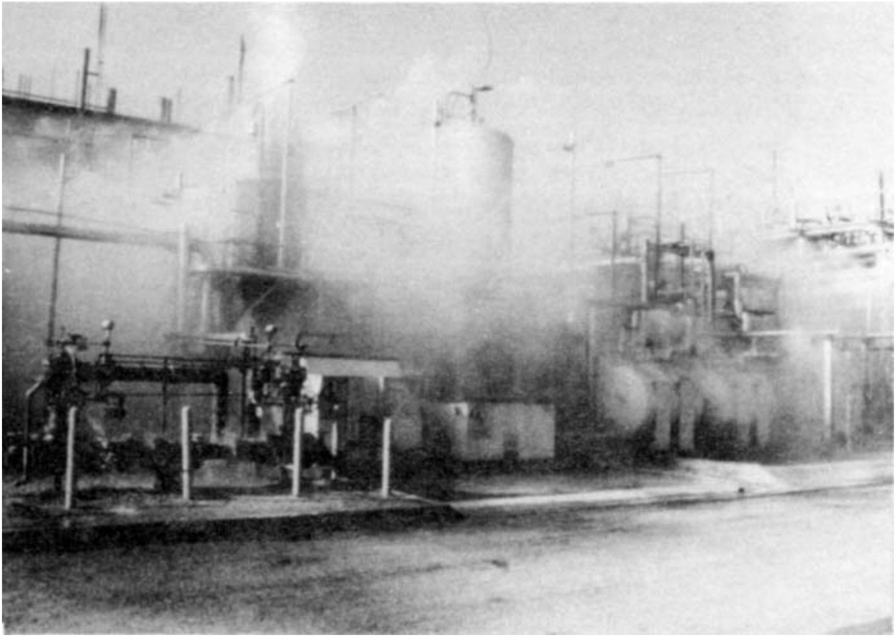


PHOTO 3. Polyethylene Plant Gas Dispersion Sprinkler System—At Start.

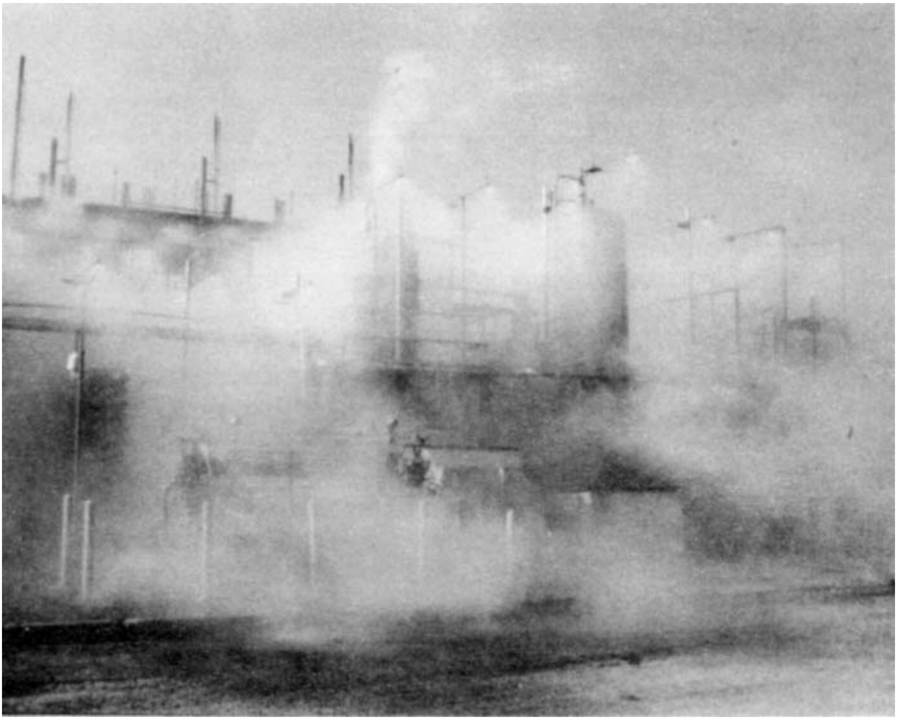


PHOTO 4. Polyethylene Plant Gas Dispersion Sprinkler System—Fully Developed.

publications include the *Guidelines for Engineering Design for Process Safety* [8], the *Guidelines for Evaluating the Characteristics of Vapor Cloud Explosions, Flash Fires, and BLEVEs* [9], and the *Guidelines for Evaluating Process Plant Buildings for External Explosions and Fires* [12]. Many National Fire Protection Association standards, insurance guides, and municipal codes may apply. A particularly valuable industry reference is Dow Chemical Company's Fire and Explosion Index now in its seventh edition via AIChE publication [14]. One of the best general references on loss prevention is that by Frank Lees [22]. Several other special references are also listed at the end of this chapter.

2.3.5.1. Fire and Explosion Causes

The basic cause for a fire or explosion is the simultaneous presence of a fuel, an ignition source, and an oxidant (usually oxygen from air) forming the well-known fire triangle. Since chemical and petrochemical processes frequently deal with flammable materials, ignition sources are widespread, and air is our common environment, it takes the utmost care to guard against fire and explosion in process operations. Eliminating at least one of the elements of the fire tetrahedron is necessary and, where appropriate, eliminating two elements would be preferable.

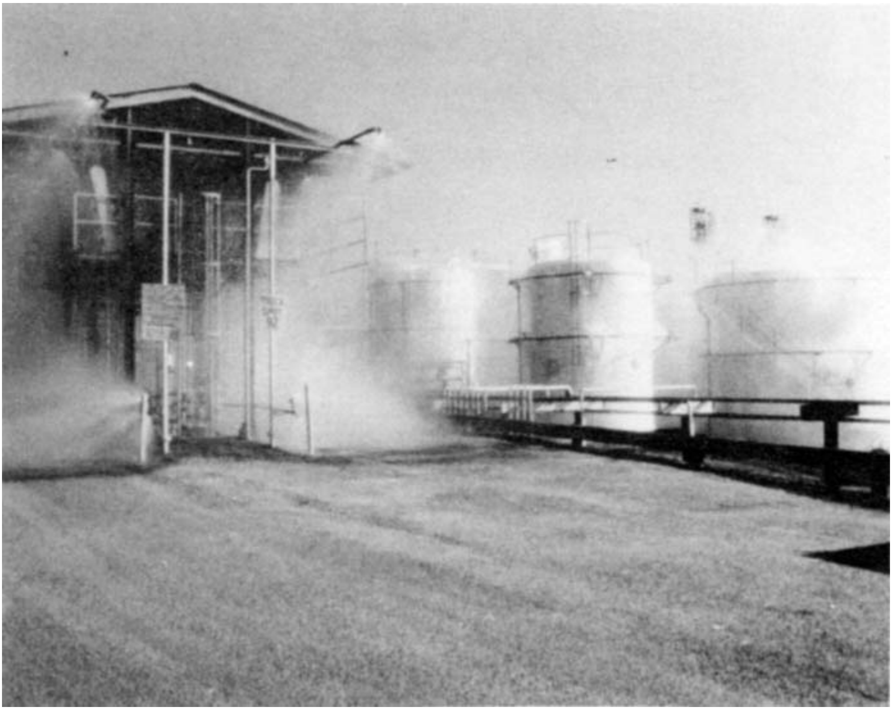


PHOTO 5. Truck Loading Rack for Flammable Liquid with Sprinkler System Activated.

A special fire case can be the result of a BLEVE or boiling liquid expanding vapor explosion. Such an explosion can occur from the sudden loss of containment of any superheated liquid. Where the superheated liquid is flammable and an ignition source is present, a highly dangerous elevated fire ball can result.

Explosions can occur either in confined vessels or in the open air. Confinement in a vessel can result in damage due to flying equipment projectiles as well as an overpressure blast wave. Open air explosions can be minor, such as in a flash fire, or major where there is sufficient fuel and mixing of air. The violence of a nominally unconfined explosion has been shown to be enhanced by structures within the fuel–air vapor cloud. The *Guidelines for Evaluating the Characteristics of Vapor Cloud Explosions, Flash Fires, and BLEVEs* [9] provides an update on explosion technology and includes some of the best recent research.

The complex type and location impacts resulting from a simple release of a flammable material are shown on the incident event tree in Figure 2.2. The position of ignition sources and local weather conditions are important variables for this event tree. The possible outcomes of this event tree are fire or explosion at the source of release, fire or explosion remote from the release, or safe dispersion. A specific evaluation for a given site can help provide input, not only on risk estimating, but also on the potential benefits of possible countermeasures and emergency response.

2.3.5.2 Design to Mitigate Fires and Explosions

First of all, every effort should be made to prevent flammable mixtures in the workplace. Equally important is the elimination of ignition sources by such

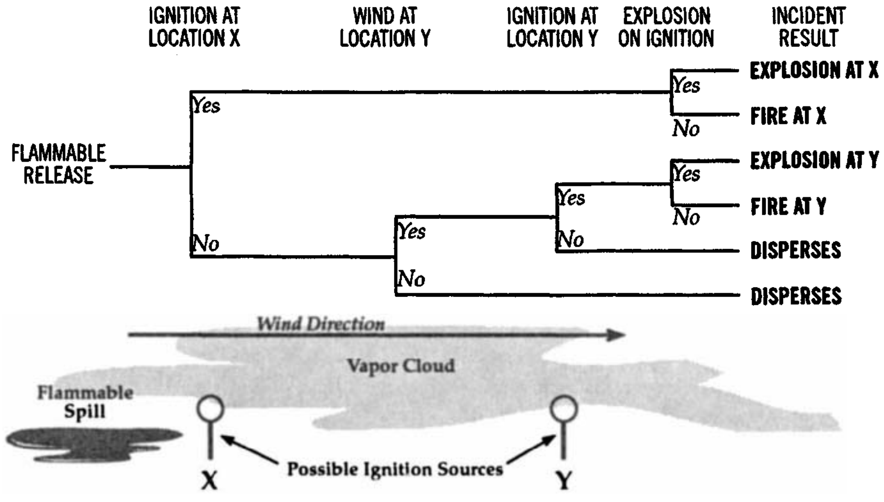


FIGURE 2.2. Event tree for possible outcomes of a flammable release.

measures as the use of area-classified electrical systems, control of hot work in the area, control of static electric buildup by proper bonding and grounding, and control of process flow velocity, the use of flame arresters on vents, and by installation of suitable lightning protection.

Elimination of oxygen within process or storage vessels containing material above its closed cup flash point is often achieved by padding or purging (blanketing) with an inert gas such as nitrogen. Controlled mixtures of low oxygen and nitrogen can also be used where the material needs oxygen for stability (e.g., some monomers) since most hydrocarbons require 8–12% oxygen for combustion. In this case oxygen gas analyzers are commonly used. A useful reference on this subject is to be found in NFPA 69.

Eliminating the fuel for most processes is essentially impossible, but it is helpful to handle a flammable material below its flash point if air can be present and certainly below its autoignition temperature in the presence of air. In some cases it may be possible to dilute with enough air to get below the lower flammable limit (LFL) to prevent ignition.

The controls of releases of fuel to the atmosphere are similar to the controls previously mentioned for chemical releases. Installing tanks either underground or earth covered above ground for highly flammable materials requires special protection to eliminate possible environmental impact due to any leakage. The alternative of locating tanks of highly flammable material above ground necessitates careful review of provisions for fire and explosion protection. Features for such protection include fire-resistant insulation, special venting, inerting, floating roof and weak seam roof/tank hold-down systems where internal explosion is possible.

Some other special precautions for processing flammables include minimizing confinement due to equipment structures where accidental emission and ignition of a heavy gas can occur. A less complicated equipment arrangement has sometimes been an effective countermeasure. Factors influencing gas mixture explosions are covered with extensive examples in *Guidelines for Evaluating the Characteristics of Vapor Cloud Explosions, Flash Fires, and BLEVEs* [9].

The use of countermeasures for possible dust explosions in process equipment or storage bins is another important consideration. Where inerting is not practical and control of ignition sources is not assured, explosion suppression systems are sometimes used. Among the expert studies on dust explosion are those by Bartknecht [2].

Methods to deal with the risk of occupied plant buildings on a site containing flammables are discussed in the *Guidelines for Evaluating Process Plant Buildings for External Explosions and Fires* [12]. Various levels of risk are developed as a function of siting, building design, and overpressure from possible vapor cloud explosions. The methodology, in fact, might be applied to selection processes for any of the foregoing mitigation or prevention features where standards and codes may not be entirely applicable and high process hazards exist.

Some special cases of countermeasures where explosions are possible are the use of bunkers for storing peroxides or the use of three walled barrier systems for high pressure equipment. In both cases, the enclosures are intended to knock down flying projectiles and/or relieve explosion overpressure into a safe path.

The general needs and techniques for emergency fire suppression and for fighting fires with fixed or portable systems will be discussed in Chapters 5 and 6 in this book.

REFERENCES CITED

1. API (American Petroleum Institute) 520. *Relief Systems for Non-Reactive Materials*, Washington, D.C.
2. Bartnecht, W. 1989. *Dust Explosions: Cause Prevention, Protection.* Berlin and New York: Springer-Verlag.
3. CCPS (Center for Chemical Process Safety). 1988. *Guidelines for Safe Storage and Handling of High Toxic Hazard Materials.* New York: American Institute of Chemical Engineers (AIChE). ISBN 0-8169-0400-6.
4. CCPS. 1988. *Guidelines for Vapor Release Mitigation.* New York: AIChE. ISBN 0-8169-0401-4.
5. CCPS. 1989. *Guidelines for Chemical Process Quantitative Risk Analysis.* New York: AIChE.
6. CCPS. 1992. *Guideline for Hazard Evaluation Procedures*, Second Edition with Worked Examples. New York: AIChE. ISBN 0-8169-0491-X.
7. CCPS. 1993. *Guidelines for Chemical Reactivity Evaluation and Applications in Process Design*. New York: AIChE.
8. CCPS. 1993. *Guidelines for Engineering Design for Process Safety*. New York: AIChE. ISBN 0-8169-0565-7.
9. CCPS. 1994. *Guidelines for Evaluating the Characteristics of Vapor Cloud Explosions, Flash Fires, and BLEVEs.* New York: AIChE. ISBN 0-8169-0474-0.
10. CCPS. 1995. *Guidelines for Postrelease Mitigation Technology in the Chemical Process Industry*. New York: AIChE.
11. CCPS. 1993. *Guidelines for Safe Automation of Chemical Processes*. New York: AIChE.
12. CCPS. 1995. *Guidelines for Evaluating Process Plant Buildings for External Explosions and Fires*. New York: AIChE.
13. DIERS (Design Institute for Emergency Relief Systems). 1992. *Emergency Relief System Design Using DIERS Technology, DIERS Project Manual.* New York: AIChE.
14. Dow Chemical Company, 7th Ed., 1994. *Fire and Explosion Index Hazard Classification Guide.* New York: AIChE.
15. Drake, E.M. and C.W. Thurston. 1993. *A Safety Evaluation Framework for Process Hazards Management in Chemical Facilities with PES-Based Controls, Process Safety Progress,* Vol. 12, No. 2, New York: AIChE.
16. *NFPA 69, Explosion Prevention Systems.* 1992. Quincy, MA: National Fire Protection Association.

17. Fawcett, H.H. 1988. "What We Learned From the Rhine," in *Hazardous and Toxic Materials; Safe Handling and Disposal*. New York: John Wiley and Sons, pps. 421-428.
18. NFPA. 1994. *Fire Protection Guide to Hazardous Materials*. Eleventh Edition, Quincy, MA: National Fire Protection Association.
19. IRI (Industrial Risk Insurers). March 1992. *Plant Layout and Spacing for Oil and Chemical Plants*. IRI Manual 2.5.2. Hartford, CT: Industrial Risk Insurers.
20. Kletz, T.A. 1984. *Cheaper, Safer Plants or Wealth and Safety at Work*. Rugby, Warwickshire, UK: Institution of Chemical Engineers.
21. Kletz, T.A. 1991. *Plant Design for Safety*. New York: Hemisphere Publishing Company.
22. Lees, F.P. 1980. *Loss Prevention in the Process Industries*. Vols. 1 and 2, London: Butterworth's.
23. *NFPA 491, Hazardous Chemical Reactions*. 1991. Quincy, MA: National Fire Protection Association.
24. API, 1994. *Recommended Practice (RP) 752, Management of Hazards Associated with Location of Process Plant Buildings*, Washington, D.C.

Other References

Bartknecht, W. 1989. *Dust Explosions; Cause, Prevention, Protection*. Berlin and New York: Springer-Verlay. ISBN 0-387-50100-2.

Bodurtha, F.T. 1990. *Industrial Explosion Prevention and Protection*. New York: McGraw Hill.

Bretherick, L. 1990. *Handbook of Reactive Chemical Hazards,* 4th Ed., London and Boston: Butterworth's.

CCPS, 1989. *Guidelines for Technical Management of Chemical Process Safety,* New York: AIChE.

Fawcett, H.W. and W.S. Wood. 1982. *Safety and Accident Prevention in Chemical Operations,* 2nd Ed. New York: John Wiley & Sons.

Hatayama, H.K. et al. 1980. *A Method of Determining the Compatibility of Hazardous Wastes*. EPA-600/2-80-076, Municipal Environmental Research Laboratory, U.S. EPA, Cincinnati, OH.

Kutcha, J.M. 1985. [Bulletin 680] *Investigation of Fire and Explosion Accidents in Chemical, Mining, and Fuel Related Industries - A Manual*. Washington, D.C.: U.S. Department of Interior, Bureau of Mines.

Nagy J. and H.C. Verakis. 1983. *Development and Control of Dust Explosions*. New York: Marcel Dekker.

NFPA, 1992. *Hazardous Materials Response Handbook*. Quincy, MA: National Fire Protection Association [Contains NFPA 471, 472, and 473].

NFPA 704, Identification of the Fire Hazards of Materials. 1990. Quincy, MA: National Fire Protection Association.

Sax, N.I. and R.J. Lewis. 1984. *Dangerous Properties of Industrial Materials*, 6th Ed. New York: Van Nostrand Reinhold. ISBN-0442-28304.