SAFETY

1. Introduction

Health and safety of personnel and loss prevention are paramount concerns of the chemical industry. Several industry groups encourage members to improve the management of safety and improve manufacturing procedures and practices to minimize hazards. Moreover, state and federal authorities have legislated improvements for the safety of both employees and the public. Particular emphasis has been given to process safety in the legislation and in industry guidelines. Chemical manufacturers are required to follow detailed steps in ensuring adequate training, comprehensive operating procedures, thorough analysis of processes for hazards and investigation of accidents, diligent maintenance of facilities, well-developed emergency plans, and self-audits for compliance. Process safety management, including process production hazards and the various engineering and administrative controls, is emphasized in this article. The role of plant location, design and operation of facilities, and hazard prevention are presented, as are safe work practices and hazard analysis.

Injuries and property damage have high costs, not the least of which are business interruption and loss of trained personnel or equipment. Over the years, worker fatalities have decreased and lost time has leveled, but property losses have increased. Of particular concern are explosions that involve combustible dusts; during the period February 2003 to October 2003, there were three dust explosions that resulted in 14 fatalities and 80 injuries, with multimillion-dollar losses in each incident.

Annual worker fatalities are ~3/100,000 employees; and annual lost-time disabling injuries are ~900/100,000 employees (1). Annual property losses have increased fourfold from the 1970s to the present (2). The trends in fatalities and property losses can probably be ascribed to the increasing complexity and productivity of the highly automated chemical plants, where personnel are isolated from processes. Whereas exposure to health and safety hazards may be reduced, the ability of experienced operating personnel to sense process problems and to correct these problems frequently is decreased. Another aspect of process management that has tended to increase hazards is the effort to reduce the formation of wastes and undesired by-products. This effort requires close approach to temperature and pressure limits, at which point loss of control can be catastrophic (see PROCESS CONTROL). Process and plant safety issues have been discussed frequently in the open literature (3–8).

Safety assessments of entire processes began with quantification of overpressure potential and flammability hazards, by measurements of vapor pressure and of flash points and flammability limits, respectively (9–12). Process designers make use of data pertaining to reaction rates and energies for exothermic reactions and unstable chemicals; temperature limits beyond which explosive decompositions or other undesirable behavior can occur; rates of gas or vapor generation for proper design of emergency pressure-relief devices; recommended limits for exposures to toxic materials (13), radiation, noise, and heat; and strengths and corrosion rates of materials of construction. The application of fault-tree analysis to chemical processes provides a means for quantitatively combining characteristics of process hazards with component and human failure rates to obtain a safety assessment of a process (14,15) (see Hazard analysis and risk assessment).

Many changes have occurred in the requirements for safety in the chemical and petrochemical industries during the period from 1974 (Flixborough) to 1984 (Bhopal) to 1994 (Lodi, N.J.). Some of these changes were presented as consensus guidelines initiated by industry groups, such as the Center for Chemical Process Safety (CCPS), established by the American Institute of Chemical Engineers; the Chemical Manufacturers Association (CMA, now the American Chemistry Council); and the American Petroleum Institute (API). Other changes were legislated by individual states (particularly New Jersey) and by the U.S. Government (through OSHA and the EPA). The objective of these changes is to raise the design, operating, and maintenance standards of all members of these industries to as high a level as is economically possible.

2. Protection of the Public and the Environment

The responsibility of chemical process managers for preventing air, water, and soil pollution has indirectly influenced plant safety in the United States by requiring better control of plant processes to prevent releases of hazardous materials. Regulatory legislation was introduced by the Health, Education, and Welfare Department (Health and Human Services) and the U.S. Environmental Protection Agency (EPA) to require (*1*) improvements in air quality (1955 Air Pollution Act; 1963 Clean Air Act and its amendments in 1970, 1977, 1990, and 1999; the 1967 Air Quality Standards and National Air Pollution Acts; and 1970 National Environmental Policy Act); (*2*) better waste disposal practices (1965 Solid Waste Disposal Act; 1976 Resource Conservation and Recovery Act) (see Wastes, industrial; Waste treatment, hazardous wastes); (*3*) reduced noise levels (1972 Noise Control Act); (*4*) improved control of the manufacture and use of toxic materials (1976 Toxic Substances Control Act); and (*5*) assignment of responsibility to manufacturers for product safety (1972 Consumer Product Safety Act) (16,17).

3. Process Safety Management

Several incidents occurring in the latter part of the twentieth century indicated that a significant improvement in the management of process hazards was needed. Those incidents that provoked the greatest industrial and legislative response are listed in Table 1. Standards and guidelines, intended to improve the management of process safety, have since been developed and their implementation required. These standards and guidelines are presented herein in chronological order.

3.1. Health and Safety at Work Act. The Health and Safety Executive (HSE) in the United Kingdom was the leading authority among industrialized nations in establishing standards for process-hazards control (8). Starting in 1974, following the explosion at Flixborough (see Table 1), and empowered by the Health and Safety at Work Act (18), the HSE required registration of processes according to the type or quantity of chemical used or produced. The HSE also submits recommendations concerning plant design and maintenance functions, operator training, and methods for evaluating process hazards (see PLANT LAYOUT; PLANT LOCATION).

3.2. Occupational Safety and Health Act: Protection of Employees.

Prior to 1985, the U.S. Occupational Safety and Health Administration generally limited its activity to enforcement of codes or consensus standards concerning toxicity and flammability; after 1985, OSHA began applying the "general duty clause" (in its enabling legislation) more broadly to management of hazardous chemical processes (19).

The U.S. Occupational Safety and Health Act (OSHA) enacted in 1970, establishes standards for several types of occupational hazards, including toxicity, noise, equipment guarding and protection against falling, and electrical shock (20). It also promulgates other consensus standards for exit facilities and fire and explosion control. Employers are obliged to keep records concerning occupational injuries and illnesses, and OSHA inspectors are authorized to inspect places of employment for violations of the standards as part of its program for inspection of high risk industries or as the result of an accident or employee complaint. Penalties are assessed for violations, and appeal procedures are established. Employers may apply for variances from the Act, based on equally effective protection, ie, a permanent variance, or inability to comply readily, ie, a temporary variance. Personnel from OSHA and the National Institute for Occupational Safety and Health (NIOSH) are available for consultation to identify, evaluate, and correct workplace hazards (21).

In 1986, shortly after the Bhopal disaster, OSHA contracted to develop a federal standard on process hazards management. A proposed standard was issued in 1990, and the Process Safety Management (PSM) of Highly Hazardous Chemicals standard was issued and implemented in 1992 (22).

The regulation lists 137 toxic and reactive substances and a threshold quantity for each. The regulation also applies to flammable liquids and gases in quantities of 10,000 lb ($\geq$4.5 metric tons) or more, except hydrocarbon fuels and liquids stored in unpressurized, ambient-temperature tanks, as well as to the manufacture of any quantities of explosives (see EXPLOSIVES; PROPELLANTS) and pyrotechnics (qv).

There are 14 elements in this OSHA legislation: Employee Participation; Process Safety Information; Mechanical Integrity; Hot Work (and other) Permits; Process Hazards Analysis; Operating Procedures; Training; Contractors Safety; Pre-Startup Safety Review; Management of Change; Incident Investigation; Emergency Planning and Response; Compliance Audits; Trade Secrets.

Whereas no quantitative consequence analysis is required by this legislation, the process hazards analysis must include a qualitative evaluation of the possible effects of failure of controls on employees. Details concerning development and implementation of programs for these subjects are available (23–25).

The original PSM standard has not been significantly amended since 1992, although many questions have been raised concerning the meaning of several sections of the standard, and OSHA has issued letters of interpretation (26).

3.3. Clean Air Act Amendments: Protection of the Public.

In 1990, the Clean Air Act of the U. S. Environmental Protection Agency (EPA) was amended to include Section 112(r), Prevention of Accidental Releases, and Section 304, Chemical Process Safety Management (27). Section 112(r) states that “operators producing, processing, handling, or storing extremely hazardous substances have a general duty to identify hazards which may result from releases and to design and maintain a safe facility.” This section applies to facilities handling any of an initial list of at least 100 chemicals. Section 304 directed OSHA to regulate process safety management and listed the 14 elements of a safety standard required by the EPA legislation: Management System; Hazards Analysis; Process Safety Information; Process Hazards Analysis; Standard Operating Procedures; Training; Mechanical Integrity; Management of Change; Pre-Startup Safety Review; Compliance Audits; Incident Investigation; Employee Participation; Hot Work (and other) Permits; Contractor Safety; Emergency Response Program; Risk Management Plan (Report).

In response to the requirements of Section 112(r)(7)(B), the EPA developed a proposed standard for a Risk Management Program (RMP) (27). This program was to be established by all stationary sources having a regulated substance present in a process in more than a threshold quantity. The list of regulated toxic substances and threshold quantities (28) contains 77 chemicals; the list of regulated flammable substances contains 63 chemicals. This standard also applies to the handling of explosive materials, by reference to the U.S. Department of Transportation requirements (29), and thus applies to the handling of 43 explosive chemicals, commercial explosives, fireworks, flares, igniters, ammunition, and ordnance (30).

The hazard assessment is to include the identification of a worst-case scenario and other more likely scenarios for release of a regulated substance, and analyze the off-site consequences of such releases. The release and consequence assessment is to include the rate, duration, and quantity of the release, the distances for exposure or damage (using specific atmospheric conditions: “F” stability and a 1.5-m/s wind, or the most-often-occurring conditions), populations that could be exposed, and environmental damage that could be expected.

The EPA adopted a three-tiered approach, with Program 1 applying only to processes that do not pose a substantial threat to the surrounding area, with Program 2 applying to processes at small, simple businesses that are not part of the petrochemical industry, and with Program 3 applying to processes covered by the OSHA PSM standard and the specific NAICS (formerly SIC) codes: 32211 (paper pulp), 32411 (refineries), 32511 (petrochemicals), 325181 (chlorine), 325188 (inorganic chemicals), 325192 (cyclic chemicals), 325199 (organic chemicals), 325211 (plastics), 325311 (fertilizers), and 32532 (agrichemicals).

The EPA RMP standard has not been significantly modified since its enactment in 1994, except that the Threshold Quantities for several materials have been changed, and explosives are not now included in the scope of the Program.

3.4. State Acts and Regulations. The New Jersey Toxic Catastrophe Prevention Act (NJTCPA) was developed following the Bhopal disaster in 1984, an incident in Institute, West Virginia in 1985, and several chemical-release incidents in New Jersey during 1986. This act and its program regulations became effective in 1988 (31,32). A registration quantity was specified for each of the 109 materials that were listed in the regulations, based on attainment of an acute toxicity concentration at a distance of 100 m from a potential source of a 1-h release (33). This act was readopted and amended, effective in 1993 and 1999, with this latter revision to include the requirements of the EPAs RMP, as discussed in Section 3.9, below. The 1988 and 1993 versions of this act did not include the handling or storage of flammable or explosive materials, unless such materials are also toxic and are included in the lists of Extraordinarily Hazardous Substances (EHS).

A California statute requiring hazardous materials management was passed in 1985 (34), but guidance for compliance for industries covered by the act was not issued until 1988 (35). A revised standard, which became effective in January of 1994 (36), applied to facilities handling any of 128 toxic materials; flammable liquids and gases in quantities of 10,000 lb (4.54 t) or more, except where used as fuel or when contained in atmospheric pressure, ambient temperature tanks; and explosives. In 1997, the California statute was modified to include the EPAs RMP.

In Delaware, the Regulation for the Management of Extremely Hazardous Substances Act, developed in response to the Bhopal disaster and several chemical-release incidents in Delaware, became effective in 1989 (37,38). The regulations listed 88 toxic substances, 32 flammable substances, and 50 explosive substances. A “sufficient quantity” for coverage by the regulation was specified for each of these materials, based on potential for a catastrophic event at a distance of 100 m from a potential source of a 1-h release. In 1999, the Delaware statute was modified to include the EPAs RMP.

As of December 2001, the following States had adopted the EPAs RMP as state programs, with a few modifications that were prompted by incidents that had occurred within its borders, with the dates of the initial legislation in parentheses: Florida (1998), Georgia (1998), Kentucky (1999), Louisiana (1992), Mississippi (1994), Nevada (1991), North Carolina (1995), Ohio (1999), and South Carolina (1995). The state of Texas controls chemical process hazards through its statute that established the Texas Air Control Board in 1965. In 1985, guidelines were established for evaluations of community impact of releases of 46 toxic chemicals, if Texas decides that a disaster potential exists (39). However, all states are required to comply with the Federal RMP standard.

3.5. U.S. Community Right-to-Know Act. In 1986, the U.S. Congress enacted the Emergency Planning and Community Right-to-Know Act, often called Title III of the Superfund Amendments and Reauthorization Act. This act requires facilities to notify State Emergency Response Commissions when any of 366 [as of 1988 (40)] extremely hazardous substances are present in quantities at or above the threshold planning quantities. The act also requires facilities to participate with local emergency planning committees (LEPC) to plan and prepare for chemical emergencies. Moreover, facilities are required to provide critical information on the identities, quantities, and on-site locations to the community.

3.6. Chlorine Institute. Starting in 1986, members of the Chlorine Institute are required to reaffirm their commitment to the Institute’s safety pledge, including prevention of chlorine releases. The safety pledge also includes annual safety audits, annual emission and hazard evaluations of chlorine operations, periodic emergency-response test drills, and coordination with local officials for protection of the community (41).

3.7. American Chemistry Council Process Safety Code.

In 1988, the Chemical Manufacturers Association (CMA, now known as the American Chemistry Council) adopted an initiative called Responsible Care: A Public Commitment (42). Members of the ACC commit themselves, as an obligation of membership, to improving performance in response to public concerns about the impact of chemicals on health, safety, and environmental quality.

One of the six elements of Responsible Care is the Codes of Management Practice, and one of the codes is the Process Safety Code of Management Practices (43). This code emphasizes management commitment and accountability, information sharing, and community relations, but also includes 11 of the 14 specific elements of the legislated process safety management standards developed later.

3.8. American Petroleum Institute Recommended Practice.

In 1990, the American Petroleum Institute issued a recommended practice on Management of Process Hazards (44). The stated objective was to help prevent the occurrence of, or minimize the consequences of, catastrophic releases of toxic, flammable, or explosive materials.

This recommended practice is intended to apply to facilities that (*1*) handle or store flammable or explosive substances in such a manner that a release of ~5 tons of gas or vapor could occur in a few minutes, and (*2*) handle toxic substances. The threshold quantity for the toxic materials would be determined using engineering judgment and dispersion modeling, based on a potential for serious danger as a result of exposures of <1 h.

3.9. U. S. Chemical Safety and Hazard Investigation Board: Protection of Employees and the Public.

The U. S. Chemical Safety and Hazard Investigation Board was authorized by the Clean Air Act Amendments of 1990, but did not become operational until 1998. The principal role of this Board is to investigate chemical-related incidents to determine the conditions and circumstances that led to the event and identify the cause(s) so that similar events might be prevented. The Board is an independent organization, similar to the National Transportation Safety Board and the Department of Transportation. It collaborates with the EPA and OSHA, but does not issue fines or penalties.

The board’s first report concerning process incidents was issued in 1995, and several additional reports that concerned other incidents have been issued since that date. Of particular interest to the board are runaway reactions and dust explosions. A report that concerned runaway reaction and reactive chemicals was issued in 2002 (45), and the CSB has recommended that OSHA and the USEPA take steps to include reactive chemicals in the Process Safety Management and Risk Management Program standards.

4. Process and Production Hazards

There are several steps that individuals and corporations can and should take to prevent process-related incidents and minimize the consequences of incidents, thereby minimizing the risks to employees and the public (46,47). Much of the legislation has adopted a hierarchy of controls that essentially fall into two categories, ie, engineering and administrative (47,48).

Engineering controls may be subdivided into those providing inherent safety and those involving process equipment and conditions. Those providing inherent safety controls include (*1*) intensification: minimizing the amount of hazardous material or hazardous operations; (*2*) substitution: using inherently safer materials or inherently safer processing or production methods; and (*3*) isolation: barricading or distancing to minimize personnel exposure.

Design and operating controls include (*1*) containment: designing for plant and process integrity; (*2*) attenuation: using less severe operating conditions of pressures and temperatures; (*3*) consequence reduction: designing to minimize accidental release rates and quantities; (*4*) simplification: avoiding complexities in equipment and control systems; (*5*) use of passive safeguards: explosion vents, rupture disks, relief devices, excess flow valves, and dikes; (*6*) use of active safeguards: alarm and interlock systems, scrubbers, and remote-operated valves; and (*7*) risk minimization: ventilation, leak-stopping, dump or drown systems, spill control, and toxic and flammable-vapor sensors and alerting systems.

The administrative controls include (*1*) operating procedures for startup, shutdown, response to upsets, and emergencies; (*2*) maintenance programs: maintaining plant integrity through inspections and testing; (*3*) process hazards analysis: maintaining and upgrading process integrity; (*4*) limiting personnel exposure, ie, limiting access and providing personal protective equipment; and (*5*) emergency procedures for escape and evacuation.

4.1. Chemical Hazards.

Chemical manufacturers and employees contend with various hazards inherent in the production of even commonplace materials. For example, some catalysts used in the manufacture of polyethylene ignite when exposed to air or explode if allowed to become too warm; the basic ingredient in fluorocarbon polymers such as Teflon, can become violently self-reactive if overheated or contaminated with caustic substances (49,50); one of the raw materials for the manufacture of acrylic fibers (see FIBERS, ACRYLIC) is the highly toxic hydrogen cyanide (see CYANIDES).

Table 2 lists some of the physical, toxicity, flammability, and reactivity properties of common chemicals (10,13,30,51–56). Also given are some of the quantities specified for reporting spills and for compliance with legislated requirements. The OSHA regulations require that material safety data sheets (MSDS) be developed for all process materials, so that the hazard data can be communicated to employees (57). Characteristics of toxicity, flammability, chemical instability, reactivity and reaction energy, operating conditions, and corrosive properties of construction materials must all be considered in analyzing hazard potentials of chemicals and chemical operations.

Toxic Materials. Individuals can come in contact with materials by ingestion, inhalation, skin irritation, skin absorption, and subcutaneous injection (58) (see INDUSTRIAL HYGIENE). If employees are careless about washing before eating, chemical substances on the hands may contact the eyes, nose, or mouth or be ingested after contaminating food, drinks, cigarettes, or other materials. For most substances, a single event (acute exposure) does not cause serious effects. The continuous daily ingestion of small amounts (chronic exposure) may, however, result in harmful accumulation. Inhalation of gases and vapors also may cause toxicological effects. Also, toxic dusts such as beryllium (see BERYLLIUM AND BERYLLIUM ALLOYS), silica (see SILICA, INTRODUCTION), and lead compounds (qv), can cause acute or chronic symptoms (59).

Strong acids and alkalies can severely burn the skin, chromium compounds can produce skin rashes, and repeated exposure to solvents cause removal of natural oils from the skin. Infection is always a concern for damaged skin. Absorption through the skin is possible for materials that are appreciably soluble in both water and oil, eg, nitrobenzene, aniline, and tetraethyllead. Other materials can be absorbed if first dissolved in extremely good solvents, eg, dimethyl sulfoxide. Subcutaneous injection can occur accidentally by direct exposure of the circulatory system to a chemical by means of a cut or scratch or inadvertent penetration of the skin with a hypodermic needle.

The eyes are particularly susceptible to liquids, gases, and some solids. The conjunctival membrane surrounding the eye is easily irritated. Alkaline materials, eg, hydroxides and amines, destroy the eye tissues rapidly and can cause partial or complete loss of vision.

Physiological Classifications of Contaminants. The physiological classification of air contaminants is difficult, because the type of action of many gases and vapors depends on concentrations (60). For example, a vapor at one concentration may exert its principal effect as an anesthetic but, at a lower concentration, the same vapor may injure the nervous system, the hematopoietic (blood-forming) system, or some visceral organ (see TOXICOLOGY).

Irritants. Irritant materials are corrosive or vesicant, ie, cause blisters, and may inflame moist or mucous surfaces. These have essentially the same effect on animals as on humans. The concentration is far more significant than the duration of exposure. Some representative irritants, eg, aldehydes (qv), alkaline dusts and mists, ammonia (qv), hydrogen chloride (qv), hydrogen fluoride, sulfur dioxide, and sulfur trioxide, chiefly affect the upper respiratory tract (61). Other irritants, eg, bromine, chlorine, dimethyl sulfate, fluorine (qv), ozone (qv), sulfur chlorides, and phosphorus chlorides, affect the upper respiratory tract and lung tissues. Irritants that primarily affect terminal respiratory passages and air sacs include arsenic trichloride, nitrogen oxides, and phosgene (qv). Lung irritants are similar to the chemical asphyxiants in that the effects frequently result in asphyxial death.

Asphyxiants. Asphyxiants interfere with oxygenation of tissues and may be classified as simple or chemical. Simple asphyxiants are physiologically inert gases that act principally by dilution of atmospheric oxygen below the partial pressure required to maintain an oxygen saturation of the blood sufficient for normal tissue respiration. These include ethane, helium, hydrogen, methane, nitrogen, and nitrous oxide. Chemical asphyxiants either prevent the blood from transporting oxygen from the lungs or prevent normal oxygenation of the tissues even if the blood is well oxygenated. Among the chemical asphyxiants, carbon monoxide combines with hemoglobin; cyanogen, hydrogen cyanide, and nitriles inhibit tissue oxidation by combining with cellular catalysts; and aniline, *N*-methylaniline, *N*, *N*-dimethylaniline, and toluidine cause formation of methemoglobin. Nitrobenzene, characterized by the nitrite effect, also causes methemoglobin formation, lowers blood pressure, and disturbs breathing. Hydrogen sulfide causes olfactory and respiratory paralysis.

Anesthetics and Narcotics. Anesthetics (qv) and narcotics exert their principal action as painkillers without seriously affecting systemic processes. Their depressant action on the central nervous system is governed by their partial pressure in the blood supply to the brain (see PSYCHOPHARMACOLOGICAL AGENTS). In the order of decreasing anesthetic action are acetylenic hydrocarbons, olefins, ethyl ether and isopropyl ether, paraffins, aliphatic ketones, and aliphatic alcohols.

Systemic Poisons. Some systemic poisons, the majority of which are halogenated hydrocarbons, cause organic injury to one or more of the visceral organs. Benzene, phenols, and, to some degree, toluene, xylene, and naphthalene, damage the hematopoietic (blood-forming) system. Nerve poisons include carbon disulfide, methanol, and thiophene. Some of the toxic metals are lead, mercury, cadmium, antimony, manganese, and beryllium. Toxic nonmetal inorganics include fluorides and arsenic, phosphorus, selenium, and sulfur compounds.

Particulate Matter Other Than Systemic Poisons. Silica and asbestos dust produce fibrosis of the lungs, reducing their elasticity and also can cause cancer. Silicon carbide, carbon (other than exhaust emissions), and emery are inert dusts. Many organic dusts, eg, pollen, wood, and resins, cause allergic reactions. Acids, alkalies, fluorides, and chromates are irritants.

Carcinogens. Special rules for 17 specific carcinogenic materials have been formulated by OSHA (62). Cancers are thought to be the result of changes in or damage to the deoxyribonucleic acid (DNA) material in the chromosomes (see NUCLEIC ACIDS). Carcinogenic materials include nitrogen mustards and other direct alkylating agents and some forms of electromagnetic and atomic particle radiation. It appears that metabolic activation may be needed before most carcinogens, eg, benzopyrene or vinyl chloride, are effective. Some compounds act as promoters that speed the development of tumors, and other substances, eg, asbestos (qv), appear to act through physical damage to the cells.

Reproductive-hazard materials act by (*1*) reducing the amount or viability of sperm, eg, as spermatotoxins, eg, dibromochloropropane; (*2*) by crossing the placenta and thereby injuring the developing embryo, eg, as fetotoxins, or by altering the development of the embryo, eg, as teratogens like thalidomide; or (*3*) by damaging germ cells so that faulty sperm or ova are produced, eg, as mutagens. Several governmental and private agencies (such as the Center for Disease Control, the American Cancer Society, and the National Cancer Institute) are compiling and studying data concerning the role of chemicals in causing cancer, with the goal of cancer prevention.

The long latent periods involved in development of cancers make correlation of chemical exposures and disease extremely difficult. This can be countered partly with tests on naturally short-lived animals, such as mice and rats. Tests on bacteria, eg, the Ames test, may permit rapid detection of cancer potential, although there apparently is no direct relationship between the results of bacterial tests and the effects of the tested chemicals on humans (63).

Threshold Limit Values. The American National Standards Institute (ANSI) has published standards regarding the maximum acceptable concentration for certain gases and vapors in the air at work locations. A list of threshold limit values (TLVs), published annually by the American Conference of

Governmental Industrial Hygienists (ACGIH), provides the concentrations of dust, mist, or vapor believed to be harmless to most workers when exposed for five 8-h days/week (13). The 1970 TLVs were adopted by OSHA as a consensus standard for Permissible Exposure Limits (PEL), which were to be used as time-weighted averages (TWA) or as ceiling limits. The NIOSH has documented concurrence with some of these values or has recommended different and usually lower values in a few cases (64). The American Industrial Hygiene Association (AIHA) has carefully evaluated the effect of many toxic vapors [114 as of 2005 (65)] and has developed Emergency Response Planning Guidelines (ERPGs).

There are several other guidelines for exposures to toxic materials. They include Workplace Environmental Exposure Level (WEEL) guides for healthy workers; Emergency Exposure Limits (EEL) for short-term exposures of emergency responders; Emergency Exposure Guideline Levels (EEGL) and Continuous Exposure Guidance Levels (CEGL) for military personnel; Short-Term Public Emergency Guidance Levels (SPEGL) for short-term exposures of the general public; and Emergency Exposure Indices (EEI) and Community Emergency Exposure Levels (CEEL) for the general public.

There also are guidelines for biological exposures and hazards. Biological Exposure Indices (BEI) are developed to provide quantitative measures of the uptake by workers, as determined from analysis of urine, blood, or exhaled air. As of 2001, BEI values for 40 materials had been developed. Biological Environmental Exposure Limits (BEEL) have been defined for healthy workers, but no BEEL values for materials had been established as of 2005.

The American Conference of Governmental Industrial Hygienists also have established Threshold Limit Values for physical agents (66), including noise, ergonomics (including hand activity, lifting, hand–arm vibration, whole-body vibration), ionizing radiation, lasers, nonionizing radiation, light and near-infrared radiation, ultraviolet radiation, and thermal stress (cold, including wind-chill effects, and heat, including temperature–humidity effects). The ACGIH also plans to develop Threshold Limit Values for bioaerosols, such as bacteria, fungi, molds, and infectious agents, such as germs and viruses.

Control of Exposure Potential. Exposure to toxic materials can be controlled by a number of methods, eg, substitution, removal, enclosure, and personal protection. The best method of protecting workers is by substituting a less toxic material for a more toxic substance having equal effectiveness, eg, the use of 1,1,1-trichloroethane for carbon tetrachloride, and toluene for benzene. Ventilation at the work location is much more effective in removing undesirable contaminants than general room ventilation (67). Suitable exhaust hoods or flexible ducts should be utilized to draw off contaminated air as near to the point of chemical release as is feasible. Some operations can be completely enclosed, eg, continuous processing in contrast to batch operation, where process vessels are opened occasionally. Personal protection, the last point of defense, sometimes is the only way in which a worker can be protected from exposure. Such protection includes a hard hat, face shield or goggles, apron, coat, gloves, pants, and boots or rubber shoes. Respiratory protection may be provided by a dust respirator, canister gas mask (if sufficient oxygen is always present), or self-contained breathing equipment or airline respirators (68) (if the atmosphere contains $<19.5\%$ oxygen). OSHA requirements for breathing apparatus specify special fit-testing of masks and positive-pressure face masks, so that any air contaminants present are not drawn inward through gaps at the edges of the mask.

Specially designed impervious, completely sealed suits, and positive-pressure, eg, Level A suits (69), are utilized by workers responding to leakages of toxic materials, particularly where there is a skin-absorption hazard, and when handling highly hazardous compounds, such as rocket fuels (see EXPLOSIVES; PROPELLANTS). Level B suits provide splash resistance and are worn with positive-pressure breathing apparatus. Level C suits provide splash resistance and are worn with cartridge respirators when the concentrations of airborne substances are known. Level D suits are worn for protection against exposure to nuisance gases, vapors, liquids, and dusts.

Where it is necessary to use known cancer-causing substances in industry, OSHA has promulgated rigorous standards for regulated areas that include and surround the place of use (62). These standards include analysis of processes for adequate engineering controls to prevent releases, strict control of access to potentially hazardous facilities, and high standards for ventilation and personal protective equipment, special work practices, training, health monitoring of employees, and control of used clothing and waste disposal.

Starting in 1994, employers are required by OSHA (68) to perform hazards assessments to determine if workplace hazards are present that require personal protective equipment (PPE). This could include hard hats, safety glasses, respirator masks, gloves, safety shoes, and also may include long-sleeve shirts, long pants, and nets over long hair. Also, the hazards assessment may require the removal of wristwatches and rings. If such hazards are present, the employer is to document the hazards assessment, select appropriate PPE, and require that employees properly use the PPE and conform to other requirements. The OSHA standard does not require that the employer purchase and provide employees with the needed PPE, but many employers have accepted a responsibility for furnishing the PPE to employees.

Flammability. Engineering and operational controls are usually effective in preventing fires involving flammable materials. Modern continuous processing is characterized by retention of such materials in closed inerted systems, thus preventing access to air or ignition sources. However, in batch processing or under some emergency conditions, flammable materials may be released and can be ignited. The basic method of fire prevention is to avoid situations in which flammable materials, air, and ignition sources are in the same place at the same time. The pertinent properties describing the fire hazards of a flammable material have been defined by the National Fire Protection Association (NFPA) (70), as follows:

The flash point is a measured temperature at which vapors above the surface of a liquid are just sufficiently concentrated to propagate a flame (10). In practice, materials of concern may be in closed or open containers or may have spilled. Generally, the chosen flash point method should be related to the problem as well as to the type of material; ie, open-cup methods are more significant for open containers or spills, whereas closed-cup methods give more significant information for closed containers, eg, process vessels. A number of commercial flammable liquids contain a moderate amount of noncombustible components, eg, chlorinated hydrocarbons, in order to elevate the closed-cup flash point and thus gain a more favorable classification. When the same material is analyzed by an open-cup method, the flash point may not be elevated, ie, after a spill, the noncombustible material would soon be lost and the residue may be highly flammable.

The regulations of the U.S. Department of Transportation (DOT) for the shipping of hazardous materials specify the use of the Tag open-cup test (ASTM D1310) and the Tag closed-cup apparatus (ASTM D56) (9). The Tag closed-cup method is used for liquids with flash points <80°C, except No. 4 and heavier fuel oils; the Tag open-cup method is for liquids with flash points of −18 to 163°C. Because the flash points of many petroleum products exceed 163°C, the Cleveland open-cup method (ASTM D92) is used for all petroleum products, except fuel oils, with flash points >80°C. Many fuel oils and other mixtures are excluded from the scope of the above three methods; such materials usually are tested in the Pensky Martin closed-cup test (ASTM D93), which is intended for fuel oils, lubricating oils, viscous materials, and suspensions of solids having flash points of −7 to 370°C. Two other methods that have been developed are for drying oils (ASTM D1393) and for waxes and similar products (ASTM D1437). The test methods are revised frequently by the ASTM.

The ignition temperature or autoignition temperature is the minimum temperature of a flammable mixture that is required to initiate or cause self-sustained combustion without ignition from an external source of energy such as a spark or flame (ASTM D2155).

The lower flammable limit (LFL) or, equivalently, the lower explosive limit (LEL) is the minimum concentration of vapor in air below which a flame is not propagated when an ignition source is present (71–74). Below this concentration, the mixture is considered too lean to burn. The lower flammable limit and the flash point of a flammable liquid are closely related to the liquid's vapor pressure. Usually, the temperature that corresponds to the LFL is a few degrees lower than the flash point, because the former is for upward propagation of flame, while the latter is for downward propagation.

The upper flammable limit (UFL) or, equivalently, the upper explosive limit (UEL) is the maximum vapor concentration in air at which a flame can propagate. Above this concentration, the mixture is too rich to burn, ie, the oxygen is consumed in the combustion of one particle and there is insufficient oxygen to burn the adjacent particle of fuel. Products of combustion surrounding the first particle tend to quench the flame. The flammable range or explosive range consists of all concentrations between the lower flammable limit and the upper flammable limit. Flammable limits usually refer to flowing materials; explosive limits usually refer to confined or stagnant mixtures. Values for LFL and LEL, or UFL and UEL, are identical.

The values for LFL and UFL, are usually determined at room temperature (∼25°C) and atmospheric pressure, and the flash point is usually determined at atmospheric pressure. Higher temperatures and pressures usually lower the LFL and raise the UFL. Also, combustible liquid that is heated to a temperature at or above the flash point should be considered to be a flammable liquid. Mists or aerosols may behave as flammable liquids at temperatures below the flash point.

The stoichiometric concentration is that mixture of fuel and oxidant, usually air, that produces fully oxidized combustion products, chiefly water and carbon dioxide, following ignition. Such mixtures typically are the most easily ignited and produce the highest temperature and pressure at the greatest rates. The stoichiometric concentration is readily calculable for most organic compounds and is not affected by temperature or pressure.

The limiting oxygen concentration (LOC) or minimum oxygen concentration (MOC) is that concentration below which combustion, usually in air diluted with an inert gas, such as nitrogen or carbon dioxide, does not propagate in a mixture of gases or vapors. The value of the LOC is important in establishing the quantity or flow of inert gas that would be required to prevent combustion of a flammable gas or vapor.

The characteristics of flammable and combustible materials can be displayed on a ternary (triangular) graph. The characteristics of several common flammable and combustible materials are presented in Table 2.

Water solubility sometimes is important in determining whether water can be used to dilute or flush away flammable liquids. However, a water solution of some flammable liquids can give off sufficient vapors to burn, eg, a 30 vol% solution of ethyl alcohol in water (60 proof) has a flash point that is only 16.6°C above that of pure ethyl alcohol (29.4 vs. 12.8°C).

Storage and Transfers of Flammable Materials. The preferred storage for flammable liquids or gases is in properly designed tanks. Floating roof tanks frequently are used in the petroleum industry for flammable crudes and products (see TANKS AND PRESSURE VESSELS). The vents on cone roof tanks should either be equipped with flame arrestors, or the vapor space above the contents should be inerted with a nonflammable gas or vapor, unless the flash point is above the maximum ambient temperature or the contents are not heated above the flash point, and the tank is not exposed to other tanks containing flammable liquids.

Flammable materials in drums should be stored away from processing and operations buildings and should be protected by sprinkler systems or other automatic fire-extinguishing devices. High vapor pressure liquids should not be subjected to high temperature and direct exposure to the sun during hot weather. Plastic drum plugs (to replace the steel plugs) are available to minimize the likelihood of drum rupture during fire exposure.

Flammable liquids used in indoor workplaces and laboratories should be contained in approved safety cans having self-closing spouts and flash arrestors whenever possible. Other flammable or combustible materials may be kept safely in metal containers fitted with fusible-link automatic closures. Floor-level and local ventilation of indoor areas where flammable vapors may be present can greatly reduce the probability of flash-fire or explosion.

The transfer of flammable liquids from tanks or plant streams into drums or other containers and from drums into smaller vessels has resulted in many fires, with ignition caused by static electricity. Bonding and grounding cables must be used to equalize charges and thus prevent ignition from electrostatic discharges. Also, because static electricity can be generated by free fall of liquid, lines into vessels should discharge below the surface or with no more than a 15-cm free fall to the bottom of the tank.

Plant Fireproofing. There is a growing practice in the chemical industry of locating principal equipment out of doors and to enclose only a control room where all instruments and control equipment are centered. The control room should be located and/or designed to be resistant to potential explosion and fire, and pressurized to minimize the entry of toxic gases and vapors. Prompt and orderly shutdown of processes following a serious incident is essential in order to minimize injuries and property losses (75,76).

Steel structures should be protected by approved fireproofing treatment, eg, concrete or insulating, intumescent, or ablative materials. Untreated steel should be protected by some method of cooling, eg, a water-spray system.

Electrical equipment that is installed or used in areas where there is a fire hazard should be in accordance with the NFPA National Electrical Code, eg, the equipment should have explosion-proof motors, switchgear, lights, wiring, instrumentation (77). However, it may be more practical to enclose and purge-ventilate such equipment, particularly instrument panels, when a dependable source of clean air is available. Intrinsically safe equipment that uses extremely low voltages and currents may be used in some hazardous locations because any sparks produced do not have enough energy to ignite vapors (78). This equipment typically is much less expensive than instruments in explosion-proof housings.

Waste facilities should be designed to prevent explosions in sewer systems and typically are comprised of suitable traps, vents, clean-outs, collecting chambers, etc. Flammable gas detectors are installed in sewers to warn of hazardous concentrations, and inert gas blanketing of closed process sumps is generally advisable.

Vapor Cloud Explosions. The Flixborough, England, disaster in 1974 demonstrated the potential hazards of flammable vapor releases. In this incident, tons of liquid cyclohexane heated above its atmospheric-pressure boiling point escaped through a damaged expansion bellows. Delayed ignition at a furnace caused a violent explosion that demolished the existing plant and damaged many of the surrounding buildings and residences; 28 fatalities resulted, including 26 in the nearby control building. There were no fatalities away from the plant. Flammable fluid releases and vapor cloud explosions also occurred in Norco, Louisiana, on May 5, 1988 (7 fatalities); in Pasadena, Texas, on October 23, 1989 (23 fatalities) (79), and in Texas City, Texas, on March 23, 2004 (15 fatalities).

Theories are being developed to account for the high flame speeds that occur in vapor cloud explosions and to explain the blast effects, which differ from those of high explosives in that the far-field damage indicates a higher trinitrotoluene (TNT) equivalent than the damage close to the explosion center (80). Where flammable liquids are processed at temperatures above their boiling points and thus at high pressure, special precautions are required: limiting the storage quantities and flow rates of such materials; providing isolation valves that are operable from the control room, to limit the quantity released in an incident; providing a system that will allow remotely controlled deinventorying to a vent stack or flare; isolating the process by placing it at a distance from occupied buildings; providing blast resistance for occupied buildings; eliminating ignition sources close to potential release points and providing procedures and controls for prompt shutdown of ignition sources downwind from the release; and providing alarms actuated by flammable vapor detectors to alert personnel in local and downwind areas. Use of the Dow Fire and Explosion Index (81) can aid in determining the hazard range of explosions.

Boiling Liquid Expanding Vapor Explosion. A phenomenon that has developed upon use of increasingly large storage tanks and railroad tank cars is explosive vaporization of superheated liquid as a result of fire exposure, runaway reaction, or physical expansion of superheated liquid (82). Although this can occur with nonflammable liquids, it is more likely that a container of flammable liquid is involved. Usually, a boiling liquid expanding vapor explosion (BLEVE) is caused by heat from surrounding fire or flame from a relief device or a leak at the top of the tank. As the liquid level decreases, direct flame impingement and heat transfer to the wall area above the liquid level in the tank causes this portion of the vessel to weaken and fail (83). The result is release of the hot, compressed vapor from the vapor space and, in some materials, an explosive flash vaporization of the superheated liquid remaining in the tank. For flammable liquids, the further result is, in addition to the shrapnel and blast effects (84), an extremely dangerous fireball (85). Cooling the container walls with water via an unattended or remotely controlled water monitor is a practical countermeasure.

Reactions. Certain reactions are difficult to control, particularly if there is a failure of instrumentation or cooling water, agitation, reflux, recycle through a heat exchanger, or other such systems. The conditions of many chemical reactions often are extreme, eg, temperatures well above 500°C or well below 0. Changes in metal properties at these temperatures can be dramatic. Ordinarily, steel loses much of its tensile strength with increasing temperature and becomes quite brittle at moderately low temperatures. Stainless steel or other special alloys may be used at elevated temperatures, and nonferrous materials usually are needed for very low temperature conditions. Pressures range from high vacuum (near zero psia) to dozens of megapascals (of the order of 10,000 psig) in both laboratory and commercial reactions. Choice of metals and proper design commonly must be in accordance with standards (86). Stresses, eg, from temperature cycling, vibrations, load bearing, wear, and earthquakes, also must be considered.

Reaction rates typically are strongly affected by temperature (87,88), usually according to the Arrhenius exponential relationship (89). However, side reactions, catalytic or equilibrium effects, mass-transfer limitations in heterogeneous (multiphase) reactions, and formation of intermediates may produce unusual behavior (87,88). Proposed or existing reactions should be examined carefully for possible intermediate or side reactions, and the kinetics of these side reactions also should be understood and accounted-for in the process design. Usually, semibatch operation (with one reactant fed slowly into the other, at the normal operating temperature) is inherently safer than a batch reaction (where all of the ingredients are placed in the reactor, followed by heating to the reaction temperature). In all semibatch exothermic reactions, accumulation of the continuously fed reactant must be avoided, by ensuring the presence of catalyst (if needed) and by ensuring the proper reaction temperature (with a low temperature interlock) and providing reliable agitation. Continuous reactions (through a pipe reactor, or with flow through a well-stirred reaction vessel) are inherently safer than either semibatch or batch reactions.

Laboratory or pilot plant work does not always provide accurate prediction of a reaction hazard (90). Impure raw materials may, eg, replace pure chemicals in a full-scale plant. Temperature gradients may be quite appreciable in large equipment, and local temperatures can be much higher than indicated by the usual sensing devices. For large reactors, the ratio of cooling surface to reaction mass may be much smaller, as compared to pilot-plant reactors, and processing times often are longer. The use of metal instead of glass apparatus may also exert profound effects upon the course of the reaction, through catalytic effects. Also, the mass of material may change the ratio of undesired to desired products because of heat absorption.

Certain molecular groups, eg, nitrates; primary and secondary nitramines; aliphatic and aromatic nitro compounds; and organic salts of perchlorates, chlorates, picrates, nitrates, bromates, chlorites, and iodates have explosion potential (91). Less powerful, but often more sensitive compounds, include azides, nitroso groups, diazo groups, diazosulfides, peroxides, haloamines, and acetylides. The presence of one or more of these groups in a molecule indicates compound instability. Another safety evaluation is consideration of the oxygen balance if the molecule contains combined oxygen. Usually, the closer the molecule approaches stoichiometry (sufficient oxygen for complete combustion), the more powerful the explosive. For example, three nitro groups on an aromatic ring, or in TNT and trinitrophenol (picric acid), provide a source of readily available oxygen for the explosive oxidation of much of the carbon and hydrogen in the molecule. Many unstable chemicals require inhibitors to minimize self-reaction.

It is often difficult to decide when exhaustive and expensive investigations should be undertaken to develop safety data for a new compound. Much depends on the amount of compound available, the forecast for production, the end use, and the potentially exposed population. Several instruments are available to assess quantitatively the stability of chemicals as functions of temperature, time, and pressure (9). They are based primarily on heat effects, eg, vent-sizing package (VSP), accelerating rate calorimeters (ARC), differential thermal analyzers (DTA), and differential scanning calorimeters (DSC), or on weight loss, eg, thermogravimetric analyzers (TGA). Some of these devices can be used to analyze the thermal behavior of mixtures, including reaction masses.

A process plant typically consists of a charging system, a reactor system, purification operations, and a product-formulation step. All reactants must be introduced in the correct order, and the reaction must be well understood. Provision should be made for controlling instability or excessive pressure or temperature. Highly viscous materials, or those in which solids are present, may cause fouling, poor agitation, and local overheating, with possible decomposition. Some hazardous reactions must be blanketed with an inert gas for safety and quality control. In any reaction system, relief devices should be installed with well-designed vent systems. For extremely hazardous processes, it may be necessary to provide emergency dumping, dilution, or other emergency controls. Withdrawal or removal of products from closed-system operations can also be hazardous. Such locations should be monitored with suitable sensing and alarm devices.

Identifying the hazards of the contents of in-plant bulk storage tanks, warehouses, etc, is important to fire-fighters and may be achieved by a system developed by the NFPA (52). The system makes use of three diamond-shaped areas, which are marked with numbers 0, 1, 2, 3, or 4 indicating increasing hazards of toxicity (blue, left), flammability (red, top), and instability (yellow, right), respectively. The fourth (white, bottom) diamond can be used to indicate water reactivity, biological hazard, radioactivity, or strong-oxidizer hazard. The "0" classification indicates essentially no hazard, and the "4" classification indicates extreme hazard.

Combustion. The burning of solid, liquid, and gaseous fuels as a source of energy is very common. This process seldom causes serious problems, provided that sufficient and reliable combustion controls are provided. However, some combustion processes are deliberately carried out with an inadequate oxygen supply in order to obtain products of incomplete combustion. Explosive mixtures sometimes occur, and then flashback is a serious problem. Modern combustion controls should be provided, to ensure safe startup, operating, and shutdown conditions.

Oxidation. There are 10 types of oxidative reactions in use industrially (92). Safe reactions depend on limiting the concentration of oxidizing agents or oxidants, and on maintaining a safe (usually low) temperature. The following should be used with extreme caution: salts of permanganic acid; hypochlorous acid and salts; sodium chlorite and chlorine dioxide; all chlorates; all peroxides, particularly organic peroxides; nitric acid and nitrogen tetroxide; and ozone (qv).

Nitration. All nitration reactions are potentially hazardous because of the explosive nature of the products and a strong oxidizing tendency, which is characteristic of the nitrating agent. Further, both the nitration reaction and the oxidation side reaction are highly exothermic. Therefore, these reactions may be extremely rapid and become uncontrollable. Close temperature control must be maintained (93,94), typically with semibatch operation. Sensitivity is enhanced by the presence of impurities, and rapid autocatalytic decompositions, ie, fume-offs, may be violent (see NITRATION).

Halogenation. Heats of reaction are highly exothermic for halogens, particularly fluorine (qv), and chain reactions can result in explosions over broad concentration ranges. Halogens also present severely challenging corrosion problems.

Hydrogenation. Except for the difficulties of using hydrogen under very high pressures and at moderately high temperatures, hydrogen reactions are not particularly hazardous. Moderately exothermic, uncontrollable conditions are rarely encountered, except where hydroxylamine intermediates can be formed.

Polymerization. Chain reactions may proceed quickly following slow initiation. Heat effects can be sudden, especially where catalysts are used, and may become uncontrollable, particularly as the visocosity of the reaction mixture increases (94). In reactors intended to contain exothermic reactions, a maximum differential of 10°C should be maintained between the reactants and the cooling surface. Sufficient surface cooling and auxiliary cooling, eg, refluxing liquid, should be provided. An adequate, dependable supply of coolant is essential for control of exothermic reactions. Instrumentation for control of chemical processes is extremely complex as temperature and pressure limits are approached. However, most instrument-control systems can be designed to "fail safe" upon failure of the computer, electric power, or the instrument air supply.

Corrosion. Proper attention should be given to the corrosion of all chemical processing equipment, both internal and external, at the maximum expected operating temperature. Special alloys that are resistant to stress corrosion induced by chloride ions in stainless steel vessels should be employed where necessary (95,96). Hydrogen can induce similar stress corrosion cracking and blistering. Lining vessels with glass preserves the purity and color of the product and prevents corrosion which would weaken the process vessel. Fumes, such as hydrogen chloride, can cause stress corrosion on external piping, valves, and other critical pieces of equipment. Periodic inspection and testing of all process vessels is an essential aspect of preventive maintenance (qv).

Assessment of Reactive-Chemical Hazards. In December of 2002, the Chemical Safety and Hazard Investigation Board issued a report (45) that presented a history of reactive-chemical incidents (primarily explosions) during the period 1980–2001. Particular emphasis was given to nine incidents that occurred from 1995 to 2001 that took 33 lives. One of the Board's recommendations was that the OSHA Process Safety Management standard require assessment of reactive chemical hazards by chemical-plant owners and operators, with a similar recommendation to the EPA for the RMP standard.

In response to reactive-chemical incidents that occurred in New Jersey, the New Jersey Department of Environment Protection amended the Toxic Catastrophe Prevention Act to require special attention to reactive chemicals (96). The standard now requires assessment of the hazards involved in handling and processing 30 listed chemicals (including 14 nitro compounds and 8 organic peroxides) and chemical reactions that could yield an exothermic heat of 100 cal or more per gram of mixture. Threshold quantities are based on an energy-release equivalent of 1000 lb (453.59 kg) of TNT; thus, the threshold quantity for mixtures that could release 1000 cal/g is 2400 lb, and the threshold quantity for mixtures that could release 100–200 cal/g is 13,100 lb.

5. Design of Facilities

5.1. Plant Site and Layout.

The choice of a location for a chemical plant depends on a number of factors, including effects on plant personnel and the surrounding community and topography (see PLANT LAYOUT; PLANT LOCATION). The assessment of hazards, based on the flammability of materials, reaction energy, and presence of highly toxic materials, is important (76,97). Consideration also should be given to possible effects on plant personnel and the community from the worst possible incident (see HAZARD ANALYSIS AND RISK ASSESSMENT). An adequate water supply for process cooling and fire fighting is a vital necessity. Prevailing winds should also be considered.

Open areas around the operating units of a plant act as buffers within the plant and to the surrounding community. Sufficient clearance should be allowed so that, if tall structures collapse, other on-site buildings or equipment, or off-site properties are not affected. Adequate roadways providing entry to the plant are extremely important, and multiple entries and exits are advisable.

An overcrowded plant can lead to damage or shutdown of adjacent units and may impede the movement of vehicles and materials in case of emergency (98). Another consideration is access for community fire-fighting assistance, police, first aid, and medical facilities.

Operations having potential for fire and explosion should be segregated from nonhazardous operations, such as offices, cafeterias, laboratories, maintenance shops, and warehouses, to minimize evacuation hazards and victim toll in a fire or explosion incident. When administrative facilities are located on the periphery of the plant, visitors are less likely to be exposed to operational dangers. Tank–car and tank–truck loading and unloading facilities should be adequately separated from other operating areas as well. Elevated flares or ground-level burning pits must be carefully located and designed to minimize the possibility of igniting flammables in case of spills. Tankage areas should be isolated as much as practical from operating areas. Adequate roadways should surround every process unit and principal building, for access of maintenance and construction vehicles and fire-protection equipment.

The practice of building single-line processing units as compared to small parallel facilities is growing rapidly. Although the latter may be somewhat more expensive to build and may require somewhat greater manpower to operate, the possibility of a costly total shutdown resulting from a disaster is much less likely to occur (as compared to a large single unit). Physical separation of such parallel lines is essential to prevent transmission of explosive or other effects to neighboring units. Some attention should be given to fire and business interruption insurance programs when a choice is being made between a large single-line plant and multiple units.

Plant security may be an important factor in siting the operating equipment, storage tanks, railcar holding locations, truck operations, vehicle parking locations, and office buildings. Access to all parts of a plant, including office buildings and operating units, should be strictly controlled, with fences, card-access or guard-controlled gates, photo-ID badges, frequent patrols of all areas of the plant, and closed-circuit television coverage of infrequently occupied areas. Special attention should be given to the control of access through railroad and truck gates and from adjacent waterways. Special protection in the form of walls or shielding by buildings should be provided for storage tanks that contain liquefied toxic and/or flammable gases, since rupture could result in a large cloud of hazardous vapor and aerosol.

All processes should be designed so that interference with, or deliberate misoperation of, a control system cannot result in a catastrophe. Ability to interact with computer systems within the plant, from outside the plant, should be prohibited or tightly limited to essential personnel, with a well-devised and secure system of passwords.

5.2. Utilities. *Services and Facilities.* Preferably, principal electric power lines should be run underground to reduce the probability of damage from exterior causes (eg, weather or vehicles). Transformer stations and switchgear need to be accessible only to authorized personnel. Repair work on electrical circuits should occur only when circuits are not energized. No work on active lines should be permitted if it is reasonably possible to arrange for shutdown.

If shutdown is not possible, work should commence only upon written direction, signed by the top level of management.

Each plant or laboratory should adopt definite rules and procedures for electrical installations and work. All installations should be in accordance with the National Electrical Code (NEC) for the type of hazard, eg, Class I: flammable gas or vapor; Class II: organic, metallic, or conductive dusts; and Class III: combustible fibers; and the degree of process containment, eg, Division 1: open; and Division 2: closed (77). Any significant changes in procedures or methods of handling such materials should result in reevaluation of electrical installations.

Generally, it is more economical to prevent explosive atmospheres in rooms than to provide explosion-proof electrical equipment. The areas where electrically classified equipment is required can be reduced when reliable ventilation is provided. Also, personnel should not be allowed to work in a hazardous atmosphere. Where such an atmosphere cannot be avoided through control of flammable gases or vapors, or combustible dusts, access to the area involved should be limited and the area segregated by walls or other barriers, with special exhaust ventilation. Electrical equipment on open, outdoor structures >8 m (25 ft) above ground usually is considered free from exposure to more than temporary, local flammable mixtures near leaks (99). Electrical equipment should be grounded to protect personnel from shock hazards and to prevent extraneous sparking, ground currents, and electrical fault heating. Portable tools should be grounded or double-insulated. All electric motors, appliances, lighting fixtures, and other electrical equipment should be similarly grounded by internal wiring or external wire or cables (100).

All steel buildings and outdoor structures and all tanks, drums, transfer hoses, tank cars, trucks, and chemical equipment associated with the handling or use of flammable liquids or gases should be grounded as recommended in the National Electrical Code (77). Flexible grounds should be connected to large water pipes or to metal rods driven into the ground, but never to electrical conduits, branch sprinkler lines, or gas, steam, or process piping. These grounds should be properly maintained, and the electrical resistance to ground should be measured periodically. Lightning protection should be achieved through the use of arresters on top of tall structures or equipment, with large grounding conductors.

Electrical switches should be labeled with the name and equipment number of the process equipment that they control, and all switches should be designed to permit lockout. Pins and chains should be provided at all butterfly switches, where such switches interrupt power to a device, as opposed to breaking a control circuit to a remote power interrupter. Extension cords should be three-wire and limited to 8-m (25-ft) lengths.

Water. Water mains should be connected to plant fire mains at two or more points, so that a sufficient water supply can be delivered in case of emergency. The plant loop and its branches should be adequately valved, so that a break in any main can be isolated without affecting a principal part of the system. If there is any question of maintaining adequate pressure, suitable booster pumps should be installed. Fire mains, fire pumps, isolation valves, and fire protection systems should be tested at a frequency that would ensure their reliable operation if needed.

Any connection made to potable water for process water or cooling water must be made in such a manner that there can be no backflow of possibly contaminated water; check valves alone are not sufficient. The municipal supply should fall freely into a tank from which the water is pumped for process purposes, or commercially available and approved backflow preventers should be used.

For large plants located at natural water sources, special water mains can be used to supply untreated water for emergency use as well as for cooling, process water, or general plant uses other than human consumption and emergency washing facilities. Extreme care must be taken to prohibit any cross-connection of the two systems. Untreated water usually is supplied by pumps (qv) which, preferably, are driven by two unrelated sources of energy, eg, steam (qv) pumps may be installed parallel to diesel pumps. If the equipment is only on standby use, it should be test-run frequently enough to make sure that it operates when needed.

Compressed Air. Explosions have occurred in air compressors as a result of rapid oxidation of oil deposits in the piping between stages of multiple-stage compressors. Use of proper lubricants prevents deposition of oxidizable materials in high pressure piping (see LUBRICATION AND LUBRICANTS). High maintenance standards are required to detect and avoid the hazards associated with broken valves and other sources of hazardous recompression.

Compressor systems for respirators should be completely separate from other uses. Special air compressors that are designed to produce breathing-quality air are required. In smaller systems, it may be preferable to use bottled air rather than a compressor. The contents of bottles, however, should be analyzed to ascertain that they do contain air (particularly if suppliers produce “manufactured” air, from oxygen and nitrogen) and to assure that the concentrations of any contaminants are acceptably low.

Safety Showers. Safety showers and eyewash fountains or hoses should be installed where corrosive or toxic materials are handled. A large-volume, low velocity discharge from directly overhead should effect continuous drenching, ie, a minimum flow of 200 L/min (50 gal/min). Water to outside showers may be heated to a maximum temperature of 27°C by an electric heating cable. The valve handles for all safety showers should be at the same height and position, relative to the shower head, and they should operate in the same way and direction. The shower station should be identified by paint of a bright, contrasting color or a light on a reliable power supply. In areas where chemicals harmful to the eyes may be encountered, an eyewash fountain or spray should be available in case of splash accidents.

Ventilation. When plant equipment is located outdoors, there usually is little need for mechanical ventilation. Many operations must be done indoors, however, and it may be necessary to remove toxic or flammable gases or vapors or process-generated atmospheric heat (58,66). Ventilation and heat-stress standards are intended to avoid hazards associated with high body temperature, heat exhaustion, heat stroke, or discomfort in processes generating high ambient temperatures, eg, glass and steel manufacturing.

Most flammable vapors are heavier than air; thus they tend to flow to the floor or ground level and then travel appreciable distances. However, appreciable diffusion takes place, and the entire atmosphere in the building may be contaminated. The removal of flammable and toxic contaminants is best achieved by local exhaust ventilation as near the source of discharge as possible, to minimize the amount of air removed from a building, the energy losses resulting from exhausting conditioned air, and the exposure of personnel to the contaminants (66,101). General room ventilation, which is expressed as the number of air changes per hour, requires the removal of much air and exposes the entire population in the room to materials that may have been released. Suction should be within 30 cm of the floor, particularly for dispensing operations.

Local ventilation is accomplished by ductwork, either rigid or flexible, which conveys the vapor through the wall or roof of the building. The blower, preferably a high suction type, should be on the outside of the building so that all ductwork inside the building operates at less than atmospheric pressure; thus leakage does not cause contamination (see FANS AND BLOWERS) (67).

Discharge from blowers is usually directly to the atmosphere unless this presents a pollution problem; if so, scrubbing of vapors or collection of dusts may be required. Atmospheric discharge should be at a sufficient height to obtain the desired amount of dispersion, and the exhaust should be straight up with no weather cap or any other obstruction. Where suction must be at numerous points, the system should be designed with (*1*) many blowers, ie, one for each point, or (*2*) a large blower with a manifold system collecting from many points. The latter is very difficult to balance aerodynamically and, although less expensive to install, may be less effective and more costly to operate and maintain.

5.3. Pressure Vessels and Piping.

Some of the most critical components of a chemical plant involve pressure vessels. A thorough knowledge of the American Society of Mechanical Engineers (ASME) Pressure Vessel Code (86) is essential for the design and maintenance of chemical plants. Some states have their own codes, which usually conform closely to the ASME version (see HIGH PRESSURE TECHNOLOGY; TANKS AND PRESSURE VESSELS).

Of particular importance in the design of pressure-control instrumentation and overpressure-protection devices is the design pressure of a process vessel. The Maximum Allowable Working Pressure (MAWP) is essentially equal to the design pressure, and relief devices must not be set higher than the MAWP. For ASME Code Section VIII, Division 1 pressure vessels, the design pressure is about one-quarter of the burst pressure, since the tensile strength that is used for vessel design typically is one-quarter of the ultimate tensile strength (102,103). For piping, the design pressure is about one-third of the burst pressure (104).

Relief Devices. Overpressures in process equipment usually can be prevented by automatic or manual controls, in response to pressure sensors (qv) and alarms (see PRESSURE MEASUREMENT). In event of pressure-control failure, overpressure relief can be provided by spring-loaded relief valves or rupture disks. Rules for the setting, sizing, and location of pressure-relief devices are described in the ASME Pressure Vessel Code (86), in API standards (105), by the NFPA (106), and by governmental agencies (107). In general, the set pressure must not exceed the design pressure of the vessel. Special consideration, calculations, and tests may be required for two-phase flow through the relief device, eg, liquid and vapor or gas, or foam or flashing liquid. Study of two-phase relief was sponsored by the American Institute of Chemical Engineers (AIChE) through the Design Institute for Emergency Relief Systems (DIERS) (108).

Relief valves are preferred for use on clean materials, because automatic reclosure prevents excessive discharge once excessive pressure is relieved. Rupture disks are less susceptible to plugging or other malfunctions but may allow complete emptying of the vessel, thus creating a safety or environmental hazard. Where fluctuating pressures or very corrosive conditions exist, or where polymerizable materials could prevent proper operation of a relief valve, some designers install two safety devices in series, ie, either two rupture disks or an upstream rupture disk followed by a relief valve. With either arrangement, it is imperative that the space between the two relief devices be monitored (eg, with a pressure gauge), so that perforation or failure of the relief device closest to the vessel may be detected (109). Where polymerization of a flammable material can be initiated by oxygen (eg, tetrafluoroethylene), it would be necessary to maintain an inert atmosphere between the safety devices, because compression of air in this space could result in explosion (110).

The internal passageways of relief devices must not become obstructed, and the discharge piping must be sized to transport the effluent to a safe place and with minimum pressure drop. Blow or catch tanks may be provided for liquid discharges, and gases can be exhausted to stacks or flares. Discharge piping must be anchored to resist discharge reaction and shock effects. Passing inert gas into piping, ducts, blow tanks, and knockout drums or use of flame arrestors in vents is advisable where flammable vapors could form explosive mixtures with air (111) (see PIPING SYSTEMS). Special precautions, eg, heating devices, may be required if condensation or other forms of pluggage could occur in flame arrestors.

Flame detectors should be installed at the downstream side of flame arresters where the flow of gases and vapors through the arrester could be within the flammable range, and a flame could stabilize on the arrester (112). Where pressure–vacuum valves are installed on storage tanks, it usually is not advisable to install a flame arrestor on the outlet from the pressure/vacuum valve (112).

5.4. Materials Handling. *Liquids.* Liquids usually are moved through pipelines (qv) by pumps. Special alloys, plastic pipe and liners, glass, and ceramics are widely employed in the chemical industry for transport of corrosive liquids. Care is required in making the connections, to prevent exposure of unprotected metal such as flanges and bolts to the corrosive material inside the piping.

Piping design requires consideration of the maximum pressures, temperatures, and flows that might be attained, the corrosive and erosive nature and the viscosities of the materials passing through the piping, the distances between the inlet and discharge points, and the external force and vibrational stresses to which the piping might be subjected. Tests under simulated conditions may be required to define material specifications and maximum flow velocities (and minimum flow velocities for slurries). The results of such tests may determine the materials of construction, the diameter and length of the piping sections, and the pressure resistance of the piping. Other considerations include the location of the piping, ie, underground or above ground, and supporting methods;

exposure to vehicle traffic; and stresses created by fluctuations in temperature and pressure.

Valves used to isolate sections of piping and to control the flow of materials through piping must be compatible with the materials being handled. Similarly, pumps used to develop motive pressure must be constructed of materials which resist the corrosive or erosive properties of the materials. Centrifugal pumps are widely used in the chemical industry. Precautions are required to prevent operation when suction or discharge valves are closed, particularly when using heat-sensitive materials. Positive-displacement pumps should have relief valves on the discharge or an alternative method of preventing dead-head operation. Pump failures commonly occur at the packing gland and can result in the release of toxic or flammable materials.

Drainage valves should be provided at the low points of the plant piping and vessel systems, and all piping should slope downward toward them. The specification of safe valving arrangements is required. Double-block valves having intermediate bleed valves should be used for dependable shutoff of hazardous materials flow. Bypasses should be provided around control valves only in coolant or diluent lines, not in lines where inadvertent opening could defeat the process-control system or create a hazard. Check valves prevent inadvertent backflow of nuisance materials into feed systems and backflow through parallel pumps, but check valves need to be inspected frequently. They should not be relied on alone to maintain isolation of reactive, corrosive, flammable, or toxic materials. For liquids having high coefficients of expansion, such as liquefied gases, pressure-relief valves or expansion chambers must be provided between block valves.

Solids. Equipment for transporting and feeding solid materials include belt, flight, and screw conveyors (see CONVEYING), and pneumatic systems. Common hazards associated with solids handling are dust explosions and the escape and dispersion of noxious or combustible dusts (see POWDERS, HANDLING). Two items are of critical importance in designing pneumatic conveying systems. First, if the material is combustible, inert gas should be used as the conveying fluid, or blowout panels or vents should be provided to avoid explosion damage. Pressure systems are preferred over vacuum systems, because these preclude air infiltration. Second, where poisonous or noxious materials are being transported, special attention must be given to recovery of fines from the exit air. A complete recycle of the carrier gas may be desirable. Special guarding of belt and screw conveyors is required to restrict access during start-up, unclogging, and maintenance.

Electric or fuel-powered means of transporting solid materials, eg, forklift trucks, should be employed only when full consideration has been given to any hazardous atmospheres in which these might be used. Such transport must be properly maintained to preserve the integrity of built-in safety devices. Operators must be trained to operate transportation equipment safely, avoiding even the possibility of puncturing drums or packages containing hazardous materials. Overhead guards should be provided on all riding trucks intended for operation in areas where materials are stored above head height. Lighting not obstructed by the load should be provided if trucks are to operate after dark or in poorly lighted areas (113).

5.5. Plant Construction. Construction of a chemical plant most often is the responsibility of a construction company, although a few large manufacturers carry out their own construction work. Regulations regarding some construction hazards are described in the OSHA Construction Standards (20,114). Considerable responsibility is placed on the plant owner to evaluate the safety performance and to monitor the operations of construction contractors (22). During construction, the client should gather information that may help in the start-up and operation of the plant. Frequent field checking of dimensions and locations during construction can lead to helpful but relatively inexpensive changes compared to postconstruction alterations. Prior to start-up of new facilities, a prestart-up safety review should confirm that (*1*) construction, equipment, piping, and controls are in accordance with design specifications; (*2*) the equipment is suitable for the process application and has been installed properly; (*3*) operating procedures have been developed, and operators have been adequately trained, and (*4*) maintenance materials are on hand, and procedures and inspection-and-test frequencies have been developed. A checklist should be used to evaluate the readiness of new facilities for start-up.

6. Operation of Facilities

6.1. Start-Up. Often key personnel from the design and construction organizations remain at the plant during start-up. Depending on the hazards of the process and materials involved, it may be advisable to use less hazardous materials under working conditions before going ahead with the actual process. For example, a distillation column might be operated on water or high flash-point liquid prior to introduction of a volatile process material. In this way, leaks may be detected without serious consequences, and operating and control problems may be identified and corrected. Furthermore, such initial testing provides training for operators under stable and safe conditions.

It frequently is necessary to charge vessels with inert gases before introducing flammable or reactive materials. The hazards of entering vessels that have been filled with inert atmospheres that do not support life must not be overlooked. Start-up procedures should be written in detail well ahead of actual start-up.

6.2. Normal Operation. The designer of a chemical plant must provide an adequate interface between the process and the operating employees. This is usually accomplished by providing instruments to sense pressures, temperatures, flows, etc, and automatic or remote-operated valves to control the process and utility streams. Alarms and interlock systems provide warnings of process upsets and automatic shutdown for excessive deviations from the desired ranges of control, respectively. Periodic interruption of operations is necessary to ensure that instruments are properly calibrated and that emergency devices would operate if or when needed (see FLOW MEASUREMENT; TEMPERATURE MEASUREMENT).

6.3. Shutdown. Written procedures for normal, as well as for emergency, shutdowns should be prepared, rehearsed, and kept up-to-date. Operating supervisors must be responsible for leaving the process equipment in a safe condition or preparing plant equipment for maintenance work.

6.4. Maintenance. Good plant maintenance (qv) obviates the crash shutdowns that could follow failure of critical components. Maintenance in the chemical industry differs from that in other industries because of the nature of the materials, processes, and types of equipment used. Because much chemical work involves the movement of fluids, gases, and powdered solids from one piece of equipment to another, many pipelines (qv), conveyors, forklift trucks, and other material-handling devices are used. Containers are more likely to be tanks, drums, or some form of closed container than in other industries. Prior to maintenance inside equipment, all lines and equipment containing hazardous materials need to be effectively separated, disconnected, or blanked, to prevent entry of harmful materials into the equipment. Maintenance personnel must make sure that all equipment and piping is so prepared.

6.5. Safe Work Practices. *Locking and Tagging.* Safe maintenance requires that no one works on or be exposed to energized or power-driven equipment without positively disconnecting the source of power beforehand (115). This may be done by locking the electric switch on the power circuit in the off position, disconnecting the motor electrically or mechanically, removing the belt drive, or locking feed valves to prime movers (pneumatic or hydraulic) in the closed position, and by blocking the movement of pistons, crank arms, or flywheels. Any exceptions, such as adjusting glands and seals on moving equipment, must be approved by supervisors.

Written procedures should be prepared and thorough training given. In general, these procedures stress that operating supervisors must first identify the equipment and equipment controls. Operating supervisors and each person who is to work on the equipment must individually place their locks on the controls after the controls have been placed in the off position. Each person keeps the key to their own lock. The equipment should be rechecked to be certain that it cannot be started; work then can begin. When the work has been completed, the procedure is reversed before control of equipment is relinquished to the operating supervisors.

Entry into Confined Spaces. In 1993, OSHA adopted a confined space entry rule (116) requiring employers to evaluate the workplace to (*1*) determine if it contains any confined spaces, (*2*) mark or identify such confined spaces, and (*3*) develop and implement a permit program for entry into such spaces. The program must include a permit system that specifies the steps to be taken to identify, evaluate, control, and monitor possible electrical, mechanical, and chemical hazards; select and use equipment; institute stand-by attendance; and establish communications. The reference standard (116) should be studied for details.

Hot Work. The objective of a hot work standard is to prevent fires, explosions, and other causes of injury which might result from workplace ignition sources such as welding (qv), cutting, grinding, and use of electrically powered tools. The OSHA standards have specific requirements (22,117) for fire prevention and protection and a permit system, including a requirement that a fire watch remain in attendance for at least 30 min following welding and cutting operations.

Opening Process Equipment or Piping. A procedure for opening process equipment or piping that could contain hazardous materials is required by the OSHA Process Safety Management standard (22). The procedure requires appropriate isolation of equipment and flows; draining of hazardous materials, use of personal protective equipment; observance of emergency preparedness; obtaining proper authorizations; and employment of specific opening methods. Equipment or piping that cannot be adequately drained requires protection against possible unanticipated events, including large spills, sprays, and fire.

7. Product Handling

7.1. Labeling. The Federal Hazardous Substance Labeling Act (118) requires that all containers sold to consumers be labeled with appropriate precautionary wording to protect the user and employees from injury resulting from contact with the chemical. The capacities and contents of all packages, up to and including 208-L (55-gal) drums, customarily are indicated by labels. The information includes identification of the material, notification of principal hazards and precautions for use, antidotes or first-aid measures if applicable, name and address of the supplier and, typically, a telephone number to call in an emergency.

7.2. Sampling. The first consideration in sampling (qv) is protection of the person performing the sampling. Eye and face protection, gloves, and respiratory equipment may be needed. Line sampling usually is carried out at a suitable valve, preferably equipped with a self-closing or fusible-link device. The sampler should be aware of the possibility of a sudden increase in flow or of the flow of high pressure or high temperature material when the valve is opened. Operating personnel should always be told that a sample is being taken.

For toxic materials, it usually is advisable to provide ventilated sampling hoods or breathing-air stations and masks, to assure that the sampler is adequately protected from toxic or flammable vapors and dusts. Special provision for access to and exit from sampling points also may be needed at elevated locations and to avoid tripping or bumping hazards and to ensure that the sampler does not transverse areas not intended as walkways, eg, tank covers or roofs.

Safe sampling facilities are needed at railroad tank car and truck unloading areas to avoid falls, particularly in winter or wet weather. Installation of a well-designed loading rack with an adjustable platform reduces this hazard. Care should be taken so that the car is not jolted by a switching engine or other vehicle during sampling. The same precaution should be taken with tank trucks: the truck should be chocked, and the driver should be aware that the sampler is on the truck and be sure not to attempt to move it.

7.3. Storage. Liquid products may be stored in tanks at isolated tank farms, or in drums or cans in warehouses (see TANKS AND PRESSURE VESSELS). Smaller packages, eg, glass bottles, usually are placed in protective cases or carriers. Large quantities of solid materials typically are stored in bins or silos; smaller amounts are packaged in steel or fiber drums, paper boxes, or plastic bags. A source of danger in bulk storage occurs when workers enter tanks or silos to clear blockages, for maintenance, or other duties. Gases or vapors above the stored materials can cause intoxication, asphyxiation, or explosions, and collapse of the stored materials could cause engulfment and suffocation.

In any warehousing operation, it is essential that incompatible substances be isolated to avoid a reaction in case of a spill or fire. Where highly hazardous materials are stored, it may be advisable for them to be segregated in masonry enclosures protected by suitable fire extinguishing or ventilation equipment. Shock-sensitive or extremely heat-sensitive materials should be stored in separate buildings, and rules for maximum contents should be well-defined and rigidly observed. Scrupulous attention to housekeeping, shelf life, and inventory control helps to minimize storage hazards. For some highly hazardous materials, minimum distances between storage areas are recommended (50,70).

In the design of warehouses in which flammable or combustible materials are to be stored, consideration should be given to the installation of fire walls, fire doors, and duct shut-off dampers. Automatic sprinklers are standard equipment in such locations. Developments in warehousing include high piling of palleted material by computer-controlled handling equipment. However, there is concern about the large size of these warehousing installations and the high value of the contents. For example, fire involving drummed, flammable liquids stacked four or five tiers high would be exceedingly difficult to control using customary sprinkler designs. The use of aqueous film-forming foam has been proposed for control of fire in these warehouses (11). Fire-detection devices, such as flame-sensing or ionization-interference types, operate much more rapidly than sprinkler heads and are used extensively both as alarms and to activate fixed fire- extinguishing systems.

7.4. Disposal. Disposal of hazardous waste must be carried out in accordance with precautions against fire and explosion hazards, severe corrosion, severe reactivity with water, toxic effects, and groundwater pollution. Several methods are available, but each has drawbacks. Burning in the open is becoming less acceptable because of the air pollution (qv) that may result from incomplete combustion. Incineration controls the pollution problem somewhat by assuring complete combustion, but care must be taken that the heat release is not so rapid as to damage the incinerator and its auxiliary parts (see INCINERATORS). Disposal through industrial sewers must be in accordance with good waste-disposal practices, and it must observe the restrictions imposed by the receptor and authorities. Volatile, flammable materials may generate explosive vapors in sewers, causing flashbacks that can damage the plant. Suitable separators or treatment facilities usually are necessary to treat waste entering a sewer system. Reactive wastes should be treated to make these wastes relatively harmless before disposal (119). For example, sodium can be treated with alcohol, and the resulting alkaline solution can be neutralized. Explosive materials usually are taken to safe areas and burned in controlled quantities.

Methods of waste disposal that were previously used are now generally prohibited. This includes burying of wastes and disposal at sea. The alternatives now are incineration (to decompose and oxidize chemicals) and chemical treatment (to detoxify hazardous chemicals). The manufacturer should ascertain that disposal agencies are adequately aware of chemical hazards and can responsibly handle and dispose of the waste materials (see WASTES, INDUSTRIAL).

Minimization of wastes—through (*1*) recovery and recycling, process improvement to minimize the generation of undesired by-products and products that do not meet specifications, and (*2*) use of by-products or waste materials for other uses—has become an important part of process design. Sometimes byproduct generation can be reduced by adjustment of temperatures, pressures, or residence times in reactors, and minimizing process upsets by improved control systems. However, reducing the safety margin in operating temperature and reducing the frequency of equipment cleaning and area cleanup, can introduce safety hazards, and compensating improvements in process control may be required.

7.5. Transportation of Chemicals.

Feed materials and finished products are frequently transported by tank truck and railroad tank cars. Design, construction, and movement of these vehicles are regulated by the U.S. Department of Transportation (DOT) (120). The DOT regulations require placarding of material-transport vehicles to alert the public and emergency personnel to the nature of their contents.

Assistance following an accident involving hazardous chemicals during transport can be obtained 24 h/day from CHEMTREC, which is an industry-supported information network, by telephone at 1-800-424-9300 (see TRANSPORTATION).

When loading or unloading a tank truck or car, static bonding lines must be attached between the vehicle and the fixed piping system. Tank truck drivers may be inexperienced in the handling of chemicals and, therefore, it is essential that the plant personnel be alert in checking the driver's operations and in correcting any possible deficiencies (see TRANSPORTATION).

During the loading or unloading of tank truck and cars, the brakes should be set and the wheels must be chocked. Warning signs should be in place to prevent unintended movement. During the loading or unloading of tank cars, derails should be locked in place to prevent contact between a switching engine or other cars during the transfer of materials. The DOT regulations require that the loading and unloading of tank trucks and cars be attended. As an alternative to stationing an employee at the transfer operation, this objective can be accomplished by leak detectors, television monitors, and remote-operated shutoff valves installed on the tank car or tank truck.

In the United States, regulation of barge shipments is overseen by the U.S. Coast Guard. It is essential that the barge be bonded by a cable to the pipe system on shore whenever loading or unloading takes place, in order to minimize the hazards of differences in voltage and static electricity.

8. Human Relations

8.1. Personnel Selection and Training.

The quality of operating personnel is of paramount importance to the safe operation of a chemical plant. Operators must be intelligent and emotionally stable. Excessive use of alcohol and drugs (*1*) affects reliability and decision making, (*2*) can render workers more susceptible to toxic exposure and other hazards, and (*3*) can endanger other workers. Thorough medical screening is essential to avoid damaging exposures to susceptible individuals, eg, people with respiratory ailments should not be employed in areas where corrosive atmospheres could occur.

Training effort has assumed significant proportions in some larger companies. A great deal of attention has been given to the development of standard training procedures, including a liberal amount of safety training. A successful method involves the preparation of a manual of standard operating procedures for each unit or plant, and personnel are trained in complete adherence to these procedures. Another method involves job-safety analysis: careful study is made of what an operator is expected to do under normal conditions and how they might be trained to react in emergency situations. Discussions assist operators in recognizing hazardous situations, reacting correctly and promptly, and contributing ways of handling such conditions.

Proven steps for on-the-job training include (*1*) preparing the workers by describing the job and discussing the important points; (*2*) presenting the operation, encouraging questions, and stressing key points; (*3*) working under close supervision, with errors being corrected as they occur; and (*4*) then working alone with frequent follow-up by supervisory personnel.

8.2. Medical Programs. Large chemical plants have at least one full-time physician who is at the plant 5 days a week and on call at all other times. Smaller plants either have part-time physicians or take injured employees to a nearby hospital or clinic by arrangement with the company compensation-insurance carrier. When part-time physicians or outside medical services are used, there is little opportunity for medical personnel to become familiar with plant operations or to assist in improving the health aspects of plant work. Therefore, it is essential that chemical-hazards manuals and procedures, which highlight symptoms and methods of treatment, be developed. A full-time industrial physician should devote a substantial amount of time to becoming familiar with the plant, its processes, and the materials employed. Such education enables the physician to be better prepared to treat injuries and illnesses and to advise on preventive measures.

Clinical tests can and should be made prior to employment or work assignment and at frequent intervals thereafter, when employees are exposed to hazardous operations, such as handling benzene, mercury, and chlorinated solvents. Recordkeeping of injuries and exposures to toxic materials also is important. Disaster planning with other plant personnel and research involving toxicological work on occupational diseases and epidemiology may be included in medical programs.

8.3. First Aid and Rescue. Immediate treatment is of primary importance in first aid. Thorough knowledge of first aid, as taught in courses by the American Red Cross or the U.S. Bureau of Mines, should be a primary part of chemical plant training programs. Rescue techniques also should be taught and practiced. OSHA requires that employees use the buddy system in which at least one fully equipped person remains outside the hazardous area, to watch the two persons in the hazard area and to initiate rescue if necessary (121).

9. Fire and Explosion Prevention and Protection

9.1. Fire and Explosion Prevention. Evaluation of potential fire and explosion hazards must take place early in the design of chemical plants. Prevention of such incidents involves the study of material characteristics, such as those in Table 1, and processing conditions to determine appropriate hazard avoidance methods. Engineering techniques are available for preventing fires and explosions. Containment of flammable and combustible materials and control of processes which could develop high pressures are also important aspects of fire and explosion prevention.

9.2. Fire and Explosion Protection. Extinguishment or control of fire is essential. Exposure of personnel to thermal-radiation hazards must be minimized and property protected. Extinguishing fire requires cooling below the flash point, removing the oxidant, or reducing the fuel concentration below the lower flammability limit. For combustible solids and high flash-point liquids, water can be used alone to extinguish fire. Water has an additional benefit as a result of its high specific heat and high latent heat of vaporization: it can be used to cool equipment, structures, and containers of hazardous materials, even where extinguishing is difficult, eg, fires involving low flash-point liquids and flammable gases. Water is the preferred fire-control medium. Designs for automatic sprinkler protection against specific hazards and general area coverage have been well developed and tested (50,70). Such systems may be composed of open sprinkler heads, ie, deluge systems, which are activated by temperature rise or flame detectors, or they may be closed-head systems that are activated by high temperature. One recent development is an on–off sprinkler head, which limits water damage.

The extinguishing capability of water can be improved, while much of the cooling benefits and low cost can be retained, by including additives, eg, foaming materials, surface-active agents to produce “wet” water, and chemicals, eg, carbon dioxide, to generate inert gases. Foams (qv) generally are formed by adding natural proteins or similar synthetic materials and aerating at nozzles to make a blanket, which floats on flammable materials. Because the foam excludes air and reduces volatilization, it can be used to cover spills and, thus reduce the potential for fire, as well as to extinguish existing fire. Ordinary foams are dissolved by polar solvents, eg, alcohols and ketones, and special alcohol-resistant foams have been developed.

Foam is especially valuable in fighting fires in large storage tanks. The foam usually is discharged remotely onto the surface of liquid from above, but some types of foam are suitable for subsurface injection to avoid explosion-caused disruption of the foam-supply piping and for protection of very large-diameter tanks. Sprinkler systems have been designed to spray foam from nozzles onto materials to be protected, as in warehouses. The effectiveness of water in extinguishing flammable-liquid fires also can be improved by decreasing the size of the droplets, which consequently volatilize rapidly in a fire to form an inert steam atmosphere. Fog also can be used to move or disperse flammable vapors in open areas and to reduce the danger of flash fire or explosion.

In some applications, water can be used in the form of vapor or steam to exclude, dilute, or drive air from enclosed areas. However, extinguishment of fire by means of oxidant reduction can be accomplished more effectively using inert gases, eg, nitrogen (qv), carbon dioxide, halogenated hydrocarbons, or helium-group gases (qv). Carbon dioxide (qv) is particularly useful because of its low cost and absence of residues. The effectiveness of some of these materials, particularly the halogenated hydrocarbons such as halons, is greater than could be expected if reduction in oxygen concentration were the only cause for fire extinguishment. For example, a CO_2 concentration of 40 vol% and oxygen concentration of 13 vol% is required to extinguish fire in most flammable liquids. An oxygen concentration of 13 vol% would be fatal to any humans in the protected area. In contrast, a concentration of only 4 vol% of Freon/Halon 1301, $CBrF_3$, resulting in an oxygen concentration of 20 vol%, provides similar effectiveness. However, as a result of the Montreal Protocol on Substances that Deplete the Ozone Layer (122), production of halons that contain bromine (which is particularly effective in combining with ozone) has been discontinued (123). Fire-extinguishing compounds that contain fluorine (which apparently does not react with ozone) and some chlorine (slightly reactive with ozone), such as DiChloroTriFluoroEthane (HCFC-123) are now available to replace the bromine-containing extinguishants (see CHLOROCARBONS AND CHLOROHYDROCARBONS TOXIC AROMATICS).

Most dry-chemical fire-extinguishing materials also function by inhibiting combustion rather than by cooling or by reducing oxygen concentration. The usual dry-chemical material is a bicarbonate, but some phosphates, eg, ammonium, provide a coating that makes the material suitable for use on fires involving solid combustibles, such as rubber tires, wood, and paper.

Portable fire extinguishers are classified according to applicability: Class A for solid combustibles; Class B for flammable liquids; Class C for electrical fires that require a nonconducting agent; and Class D for combustible metals that require a smothering action. Water frequently is used for Class A extinguishers; bicarbonates for Class B and Class BC; carbon dioxide or non-bromine halon for Class C; ammonium phosphate for Class ABC; and powdered salt, sodium chloride, for Class D.

Prevention of vapor–air or gas–air explosions is typically provided by (*1*) controlling the concentration of flammable materials below the lower flammable limit, (*2*) controlling the concentration of oxygen or other oxidant below the minimum oxidant limit (via inerting), or (*3*) ensuring that there are no ignition sources where flammable mixtures could occur (124). Prevention of runaway-reaction explosions is provided by (*1*) close control of operating conditions, (*2*) interlock-shutdown systems to stop reactant-material feeds, or (*3*) sufficient solvents or diluents to prevent attainment of runaway reaction temperatures (125).

Protection against explosions is typically provided by explosion venting, using panels or membranes that vent an incipient explosion before it can develop dangerous pressures (11,70). Other methods of explosion protection include suppression (injection of flame-inhibiting material) and containment (design to withstand explosion pressures). Protection from explosions can be provided by isolation, either by distance or barricades. Because of the destructive effects of explosions, improvement in explosion-prevention instrumentation, control systems, or overpressure protection should receive high priority. The National Fire Codes provide good guidance in designing processes and equipment to prevent and protect-against explosions.

Since explosions usually occur suddenly and without warning, prevention of explosion precursors (high temperatures, incorrect ratios of reactants, loss of cooling, inadequate overpressure protection, etc) needs to be addressed in process hazards analyses, as discussed later in this section.

9.3. Consequence Analysis. An analysis of the consequences of an undesired event enables the staff of a chemical-handling plant to take appropriate actions to prevent such events, and to establish priorities for such corrective and/or improvement actions. The consequences that are usually of interest are exposures to toxic materials (gases, vapors, aerosols, liquids, dusts, and solids), exposures to explosions (blast pressures and blast impulses), and exposures to fires (flash-fires and thermal radiation). There are several computer programs and methods that facilitate the analysis, and some of them are as follows (in an approximate decreasing degree of complexity and sophistication): SAFETI, SUPERCHEMS, PHAST, TRACE/SAFER, ALOHA/CAMEO, ARCHIE, and the USEPA Off-Site Consequence Analysis (OCA) Reference Tables (126). The differences in these methods involve (*1*) source-term definition (release rates, durations, and quantities); environmental factors (temperature, relative humidity, wind speed, wind directions, atmospheric stability, surface roughness, solar insolation, latitude, topography, population distributions, and time of day); results (risk contours, dispersion plots, and graphs); and database (lists of chemicals and their pertinent properties). Simplifying assumptions are used in the less-sophisticated programs, to limit the number of variables. The EPA OCA document and the relevant CCPS publication (127) provide good introductions to the calculations and methodologies that are involved in consequence analysis.

9.4. Disaster Planning. Plant managers should recognize the possibility of natural and industrial emergencies and should oversee formulation of a plan of action in case of disaster. The plan should be well documented and be made known to all personnel critical to its implementation. Practice fire and explosion drills should be carried out to make sure that all personnel, ie, employees, visitors, construction workers, contractors, and vendors are accounted for, and that the participants know what to do in a major emergency.

A checklist for total emergency planning has been described (128). In all emergency situations, the fire services, the safety staff, and the medical organization are of paramount importance for the conservation of life and property (129). Plans should be formulated to mobilize off-duty personnel and to bring in outside assistance when necessary. In highly industrial areas, it is usually practical to form a mutual-aid organization. To make such a system work smoothly, it is necessary to have periodic meetings to discuss problems, needs, and new developments. Drills designed to mobilize such assistance are also essential to their smooth functioning (130).

Plant security is an important aspect of disaster planning, as a preventive measure. Several publications (131–136) provide guidance on methods to deter, detect, delay, and respond to a security threat. Some of the important steps in a vulnerability assessment are: identify “target attractiveness”; define scenarios and consequences; evaluate existing security measures; prioritize vulnerabilities; and identify and implement appropriate countermeasures.

10. Control of Process Hazards

10.1. Process Hazards Analysis. Analysis of processes for unrecognized or inadequately controlled hazards (see Hazard Analysis and Risk Assessment) is required by OSHA (22). The principal methods of analysis, in an approximate ascending order of intensity, are checklist; what-if; failure modes and effects; hazard and operability (HAZOP) study; and fault-tree analysis (137). Other complementary methods include event trees, human error prediction, and cost/benefit analysis. The HAZOP method is one of the most popular methods because it can be used to identify hazards, pinpoint their causes and consequences, and disclose the need for protective systems. Fault-tree analysis is the method to be used if a quantitative evaluation of operational safety is needed to justify or prioritize the implementation of process improvements. Each method has advantages and disadvantages regarding scope, structure, intensity, results, and effort required.

10.2. Human Factors. Human failings have been found to be responsible for most catastrophic process incidents. Failings include (*1*) inadequate commitment of management to safety administration, policies, and programs, (*2*) inadequate commitment of employees to safety awareness, and (*3*) failing to observe safe practices. The OSHA standard (22) requires a formal evaluation of human factors, including training, communications, physiological and psychological stresses, process/human control interfaces, personal protective equipment, exit facilities, etc. Further, OSHA compliance auditors interview employees extensively concerning not only their knowledge of policies and procedures, but also their participation in the development of safety programs and related procedures and their participation in the analysis of processes and production operations for potential hazards.

10.3. Incident Investigation. Employers are obliged to report to the regional OSHA office the details of any incident that has caused a fatality or hospitalization of five or more personnel. A study of all incidents and injuries with the objective of determining the cause or causes can lead to correction of unsafe practices or conditions and prevent recurrence of the incident, or future occurrences of similar incidents. Sometimes relatively minor injuries, process interruptions, or other types of process incidents can be the key to disclosing an unsafe condition or an improper operation which has the potential for causing far worse consequences. Information needed in incident investigation comes from several sources, eg, examination of the site and of the equipment involved, and temperature, pressure, and flow charts and logbooks (138). Eyewitness accounts are necessary, but may be contradictory and unreliable; thus, caution in interpretation and verification are needed. Private consulting firms or experts from government agencies, including the U. S. Department of Energy [301-903-6061] can assist in obtaining the best interpretation of information involving an explosion or fire incident (138).

10.4. Center for Chemical Process Safety. In 1985, the American Institute of Chemical Engineers established the Center for Chemical Process Safety (CCPS) (New York). The objective of the CCPS was to eliminate catastrophic process incidents by (*1*) Advancing state-of-the-art process safety technologies and management practices; (*2*) Serving as a premier resource for information on process safety; (*3*) Fostering process safety in engineering and science education; and (*4*) Promoting process safety as a key industry value. One aspect of this goal was to compile information on the latest scientific and engineering practices, safety programs, and administrative procedures of members of the chemical industry, in the form of *Guidelines* publications, so that they could be shared with other (and particularly the smaller) members of the chemical and petrochemical industries.

The CCPS has now published a substantial library of the *Guidelines* books, covering many of the chemical-plant safety subjects discussed above, and in much greater detail. The library now consists of >35 volumes, with several volumes in the second edition.

Other publications include the proceedings of six international conferences and symposia, three training courses, and a computerized bibliography of *Guideline* references, all available from the Center for Chemical Process Safety (1-800-242-4363, and www.aiche.org/ccps).

10.5. Lees' Loss Prevention in the Process Industries. A publication that is a most valuable reference for safety professionals, and particularly those in the chemical or petrochemical field, is *Lees' Loss Prevention in the Process Industries* (139). The first edition, in 1980, consisted of two volumes; the second edition, in 1996, consisted of three volumes; and the third edition, published in 2005 after Loughborough University Professor Frank P. Lees' death in 2002, also consists of three volumes. These volumes contain many hundreds of pages that describe every conceivable aspect of chemical process safety, with methods for obtaining quantitative assessments of hazards and risks, the consequences of hazard occurrence, and the reliability and effectiveness of protective systems.

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Table 1. **Process Incidents Resulting in Casualties**

Description	Location	Date	Fatalities	Serious injuries
Ruptured bellows (vapor cloud explosion)	Flixborough, U.K.	June 1, 1974	28	89
Runaway reaction (toxic cloud)	Bhopal, India	Dec. 3, 1984	∼3000	∼200,000
Valve opened in error (vapor cloud explosion)	Pasadena, Tex.	Oct. 23, 1989	23	232
Dust explosions	Ky., N.C., Ill.	2003	14	80
Runaway reactions (explosions)	N.J., Pa.	1995, 1999	10	18

Table 2. **Properties of Chemicals**[a]

Chemical	Formula	Boiling point,°C	Odor threshold, ppm	Threshold limit values, ppm	IDLH[b] conc., ppm	Flash point, °C	Lower flamm. limit vol %	Autoignition temp., °C	NFPA instability[c]	Reportable spill quantity, kg
acetone	C_3H_6O	56	120	750	2500	−20	2.5	465	0	2270
acetylene	C_2H_2	−84	620	2500[d]	2500	[e]	2.5	305	3	[f]
acrylic acid	$C_3H_4O_2$	141	0.1	2	750	50	2.4	438	2	2270
ammonia	NH_3	−33	1.5	25	300	[e]	15	651	0	45[g]
benzene	C_6H_6	80	11	10[h]	500	−11	1.2	498	0	4.5
carbon disulfide	CS_2	46	0.25	10	500	−30	1.3	90	0	45
chlorine	Cl_2	−34	0.2	0.5	10		Not flammable		0	4.5[i]
diethyl ether	$C_4H_{10}O$	35	0.6	400	1900	−45	1.9	180	1	45
ethyl alcohol	C_2H_6O	78	30	1000	3300[j]	13	3.3	363	0	[f]
ethylene	C_2H_4	−104	1000	2700[d]	2700[j]	[e]	2.7	450	2	[f]
hydrogen	H_2	−253	no	4000[d]	4000[j]	[e]	4.0	500	0	[f]
hydrogen chloride	HCl	−85	12	5[k]	50		Not flammable		0	2270
hydrogen cyanide	HCN	26	2	10[l]	50	−18	5.6	538	2	4.5[m]
hydrogen sulfide	H_2S	−61	0.002	10	100	[e]	4.0	260	0	45[i]
methane	CH_4	−161	no	5000[d]	5000[j]	[e]	5.0	537	0	[f]
methyl alcohol	CH_4O	65	450	200	6000	11	6.0	464	0	2270

phosgene	$COCl_2$	8	0.7	0.1	2		Not flammable		1	4.5^n
propane	C_3H_8	−42	4500	2100^d	2100	^{e}	2.1	450	0	^{f}
styrene	C_8H_8	145	3	50^o	700	31	0.9	490	2	450
sulfur dioxide	SO_2	−10	1.5	2	100		Not flammable		0	^{m}
vinyl chloride	C_2H_3Cl	−14	15	5^p	5^h	−78	3.6	472	1	0.45

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[a] Refs. (10,13,30,51–56).

[b] Immediately Dangerous to Life and Health (IDLH). Not established for acrylic acid; value shown is the Emergency Response Planning Guideline-3 (ERPG-3) for exposure up to 1 h without life-threatening effects.

[c] National Fire Protection Association (NFPA). The NFPA instability range is from 0 (stable) to 4 (unstable).

[d] Simple asphyxiant; value shown is 10% of the lower flammable limit (LFL).

[e] Gaseous material.

[f] No reporting requirement.

[g] Material has an OSHA threshold of 10,000 lb (4500 kg).

[h] Suspected human carcinogen; exposures should be carefully limited to levels as low as reasonably achievable below the TLV.

[i] OSHA threshold of 1500 lb (680 kg).

[j] 10% of the lower flammable limit (LFL).

[k] Ceiling value; concentration that should not be exceeded; not appropriate to use a time-weighted average.

[l] Ceiling value and skin absorption; special measures to prevent significant cutaneous absorption may be required.

[m] OSHA threshold of 1000 lb (450 kg).

[n] OSHA threshold of 100 lb (45 kg).

[o] Skin absorption; special measures to prevent significant cutaneous absorption may be required.

[p] Confirmed human carcinogen; exposures should be carefully limited to levels as low as reasonably achievable below the TLV.