14

PRESSURE RELIEF SYSTEMS

14.1 INTRODUCTION

This chapter concentrates on the design of emergency relief devices and systems to minimize accidental releases of hazardous materials caused by equipment overpressure or vacuum. High integrity equipment and piping are the first layer of containment. Depressuring (controlled release) is another level of design to avoid large-scale releases. Pressure relief systems are the last resort; therefore, they should be designed for high reliability even though they will have to function infrequently. The design goal of all layers of containment is to minimize the actuation of relief devices.

In recent years, many companies have incorporated the principles of "depressuring" or "instrumented shutdown" of key equipment as a means to control a release and avoid the actuation of pressure relief devices. This minimizes the probability of failure of the device, because once used the device may no longer be dependable. Since maintenance of relief devices can be sporadic, this redundancy (instrumented shutdown or depressuring) provides yet another layer of safety. Regardless of the number of levels of containment and depressuring systems in place, overpressure protection must be provided.

This chapter deals with causes of overpressure, relief devices available, and problems encountered in sizing relief systems. Recent developments in the analysis of two-phase flow venting are discussed in Section 14.6. This chapter deals with relief systems where the effluent is handled by disposal to scrubbers and/or flares, by containment, or by release to the atmosphere. Disposal of effluents is covered in Chapter 15. Detonations and deflagrations are covered in Chapters 13 and 17.

Regulations, codes, standards and guidelines which apply to the design of pressure relief systems are listed in the References at the end of the chapter. Many aspects of design are governed by regulation; specification of relieving devices, relieving system design and discharge destination is often dictated by governmental agencies to limit toxic or hazardous releases to the atmosphere.

Industry practice is to conform to the applicable regulations, codes, and recommended practices. Often, these will provide different guidelines. A prudent approach would be to review all applicable codes, standards, etc., prior to choosing a design basis. In addition, the Center for Chemical Process Safety (CCPS), formed by the American Institute of Chemical Engineers

(AIChE), is developing guidelines and conducting research to further general knowledge in emergency relief system design. The Design Institute for Emergency Relief Systems (DIERS) was established by AIChE to address sizing relief devices for two-phase, vapor–liquid flashing flows. In addition, most engineering and manufacturing companies have developed internal engineering standards which address specific safety concerns.

In the following sections pressure safety valves and relief devices are addressed on the premise that the maximum allowable working pressure (MAWP) and design temperature of the equipment being protected are proper. Confirmation of this information would be done as a matter of course on a new design and will be completed on revamps or retrofits in order to comply with OSHA 29 CFR 1910.119 Process Safety Management of Highly Hazardous Chemicals (where applicable). The relief device design must be consistent with the system's temperature and pressure.

Storage tanks that operate at or near atmospheric pressure must receive a critical review of potential causes of overpressure, equivalent to the review for higher pressure vessels. NFPA 30 and API Standard 2000 provide guidance for design of this type of overpressure protection. In particular, NFPA 30 focuses on flammability issues, while API Standard 2000 focuses on both pressure and vacuum vent requirements. A common tank failure scenario is insufficient vent capacity (either pressure or vacuum) to allow for all operating cases plus rapid climatic changes. Strict adherence to API Standard 2000 is strongly recommended.

14.2 RELIEF DESIGN SCENARIOS

The designer of overpressure protection systems must consider all scenarios that constitute a hazard under the prevailing conditions and evaluate them in terms of the pressure generated and/or the rates at which the fluids must be relieved. The scenarios under consideration may cause a release from a single piece of equipment or from multiple equipment items. Overpressure may result from a single failure or multiple failures, and the probability of occurrence of multiple events leading to relief should be considered in the design.

The scenarios leading to overpressure are discussed in this chapter under several categories:

- fire
- blocked outlet
- operational failure
- equipment failure (hardware failure such as tube rupture or control system failure)

- process upset, such as runaway reactions or excessive exothermic reactions
- process causes, such as an imbalance of fluid flow rates
- utility failure

A detailed discussion of the causes of overpressure is given in API RP 521 and in the sections below.

14.2.1 Fire

The main result of fire exposure is heat input, causing thermal expansion or vaporization or thermally induced decomposition, resulting in pressure rise. An additional result of fire exposure is overheating a vessel wall to high temperature in the vapor space where the wall is not cooled by liquid. In this case, the vessel wall may fail due to high temperature even though the relief devise is operating. Guidelines for calculating heat input are found in API recommended practices, NFPA 30 (for bulk storage tanks), OSHA 1910.106, and corporate engineering standards. In determining heat input from fire exposure, NFPA allows credit for application of water to a tank; however, API does not.

Pressure vessels (including heat exchangers and air coolers) in a plant handling flammable fluids are subject to potential exposure to external fire. A vessel or group of vessels which could be exposed to a pool fire must be protected by a pressure relief device. Additional protection to reduce the device relief load can be provided by insulation, water spray/deluge, or remote-controlled depressuring device (control valve).

14.2.1.1 Determination of Fire Risk Area

Plant layout should consider spacing requirements such as those set forth by NFPA, API, Industrial Risk Insurers (IRI) or Factory Mutual (FM) and must include accessibility for firefighting (see Chapter 3, Plant Design). Several pieces of equipment located adjacent to each other that cannot be isolated by shutoff valves can be protected by a common relief valve, if interconnecting piping is large enough to handle the relief load. The designer has to determine which equipment items are affected in this fire risk area. With proper design, API RP 521 considers a fire risk area as a plot which can be limited to between 230 and 460 m^2 (2500 and 5000 ft^2). Other design criteria may apply if a risk area is located in a diked area which exceeds the API upper limits.

The surfaces of vessels or heat exchangers up to 9.1 m (30 feet) above grade or other fire supporting level shall be considered subject to fire exposure, in accordance with NFPA 30. It is usually assumed that all equipment is blocked in and contains the operating liquid at normal maximum liquid levels.

The surface area exposed to fire determines the surface area effective in generating or heating vapor; relief valve rate of discharge is affected by whether or not the area is wetted by liquid (hence, boiling). See API RP 520, Section 3 and Appendix D.

14.2.1.2 Determination of Relieving Capacities for Fire Contingency

Pressure relief capacity as described here is for thermally stable liquids such as saturated hydrocarbons and not for reactive or thermally unstable systems such as monomers. Methods for calculating the amount of vapor generated are given in API RP 520.

Gas Expansion in Vessels Exposed to Fire

Vessels that are in gas service and are exposed to external fire require a pressure relief device due to the thermal expansion of the gas. Depressuring a gas-filled vessel should not be considered as an alternative to providing a pressure safety valve for overpressure protection. The formulas for calculating the required orifice area of the relief valves are given in API RP 520 for both insulated and noninsulated vessels. It is important to note when taking credit for insulation that the insulation must have the capability of withstanding both fire and firewater impact (from fire hose). Upon exposure to fire, a pressure vessel not protected with water sprays, fire water, or insulation may overheat and fail within a few minutes.

Vapor Generation from Liquid-Containing Vessels Exposed to Fire

The amount of vapor generation from a vessel containing liquid and exposed to external fire depends on the thermophysical properties of the fluid inside the vessel, the relieving pressure and the heat input rate.

1. For a fluid that is below its critical temperature and pressure during relieving conditions, vaporization due to an external fire will create a volumetric expansion which may cause overpressure. The relieving rate is equal to the vaporization rate. Note that if cold temperature insulation is used on a vessel, the vessel is considered noninsulated (API RP 520), unless the installation would satisfy fire protection requirements as discussed in Chapter 16. The total heat absorbed is a function of the vessel dimensions, the liquid level and the insulation thickness, if any, of the vessel. The heat absorbed from fire impact upon the wetted surface area of the pressure vessel is calculated using the formula in API RP 520 or the chart in NFPA 30. Note that for special conditions, such as where no firefighting equipment or adequate drainage exists, specific equations apply; the designer should refer to API RP 520 for more detailed calculation procedures for these contingencies.

API Standard 2000 and NFPA 30 provide equations for calculating emergency relief venting for fire exposure for above ground tanks and pressure vessels.

2. For a fluid above critical temperature and pressure during relieving conditions, the relief valve orifice calculation becomes complicated. API RP 520 provides guidance and formulas for calculating orifice size and relief load calculations.
3. Two-phase flow can also occur in unique situations such as a bottom fire on a vessel containing a fluid exhibiting foaming characteristics such as latex (refer to the DIERS Project Manual for more information).

Fluids other than the normal process fluid (such as washing solvents) can sometimes be found in a vessel, and such eventualities should be considered when preparing the relief valve sizing calculations.

14.2.1.3 *Allowable Pressure Accumulation for Fire Contingency*

ASME Code Section VIII, Division 1, provides for allowable pressure rise for fire contingency. Under appropriate conditions, a maximum relieving pressure of 21% above maximum allowable working pressure (MAWP) is permitted. Again, specifics should be confirmed after a thorough code review.

14.2.2 *Operational Failure*

The following scenarios of various operational failures may result in overpressure conditions.

14.2.2.1 *Blocked Outlet*

Operation or maintenance errors (especially after a plant turnaround) can block the outlet of a liquid or vapor stream from a process equipment item resulting in an overpressure condition.

For the liquid blocked-outlet situation, the relieving load is typically the normal flow unless the source is a mechanical equipment item such as a compressor or pump. Examination of the characteristic curve of such equipment may reduce the relieving load at the specific relieving conditions, that is, set pressure plus overpressure. Alternatively, the system design pressure (setpoint) may be elevated above the maximum achievable operating pressure if economics will allow.

For the vapor blocked-outlet situation, the relieving load is the maximum vapor generation at the specific relieving conditions. This load may be reduced by taking credit for forward flow of vapor from the remaining vapor outlets if they exist (e.g., a partial condenser in a fractionator overhead system).

14.2.2.2 *Opening a Manual Valve*

Manual valves which are normally closed to separate process equipment and/or streams can be inadvertently opened, causing the release of a high pressure stream or resulting in vacuum conditions. Additional side effects of such a failure may include critical flows, flashing of liquid, runaway reactions, etc., and must be considered as a consequence for this operating deviation.

14.2.2.3 *Flashing of Liquid Feed to Downstream Vessel*

Control valves downstream of high pressure vessels containing liquid could fail open resulting in excessive flow of liquid generating a high vapor flow to the downstream vessel. Downstream vessels and equipment must be capable of handling the excessive vapors; otherwise, relief is necessary.

14.2.2.4 *Cooling Water Failure*

One of the most commonly encountered causes of overpressurization is cooling water failure. Two examples of the critical consequences of this event are the loss of condensing duty in fractionator overhead systems and the loss of cooling for compressor seals and lube oil systems. Different scenarios should be considered for this event depending on whether the cooling water failure affects a single equipment item (or process unit) or is plant-wide. Examples of plant-wide scenarios include cooling water pump failure, failure of any section of the main header or loss of fans on the cooling tower.

It is difficult to summarize the loads to be relieved from this failure. Most companies have unique approaches to determining the relief rates from towers, compressors, and the like. These approaches vary due to cooling considerations, instrumented shutdowns, etc. API RP 521 discusses many of these considerations.

14.2.2.5 *Power Failure*

Power failure will shut down all motor driven rotating equipment such as pumps, compressors, air coolers, and reactor agitators. As with cooling water failure, power failure can have a cascading negative affect on other equipment and systems in the plant. Different scenarios should be considered for this contingency depending upon whether the power interruption is local (to a single equipment item), to a unit substation, or plant-wide. Adequate backup features should be included in the plant's electrical design to reduce the probability of a major power interruption to an acceptable level.

14.2.2.6 *Instrument Air Failure*

The consequences of instrument air failure should be evaluated in conjunction with the failure mode of the control valve actuator. It should not be assumed that the correct air failure response will occur on these control valves (fail open, closed or in position). Some valves may stick in their last operating position and the choice of which valves are assumed to fail in their last operating position would be governed by maximizing the relieving load. If the failure position of the valve helped minimize the relieving rate, it should be assumed that the valve would not move. The relief valve size should be based on the failure of the most critical component of the air supply system. Following determination of the consequences of air failure, the designer should size relief devices based upon specific knowledge of the system including control valve flow characteristics and piping layout.

14.2.2.7 *Reflux or Recirculation Failure*

The loss of reflux or recirculation on fractionation towers is typically caused by power failure to the pumps, a pump trip, or when a control valve fails closed. The relieving rates should be analyzed based upon heat balances around the fractionator to account for the loss of this heat sink. Generally, it is assumed that overhead condensers are flooded and the gross overhead is a conservative estimate for the relief rate. However, the analysis should consider loss of fractionation effect on composition, reboiler temperature changes, etc, as discussed in API RP 521. In addition, one might consider calculating the effect of suppression of vaporization which occurs at the relief device maximum relieving pressure. This suppression will typically give lower estimates of the required flow.

14.2.2.8 *Thermal Expansion*

Equipment or pipelines which are full of liquid under no-flow conditions are subject to hydraulic expansion due to increase in temperature and, therefore, require overpressure protection. Sources of heat that cause this thermal expansion are solar radiation, heat tracing, heating coils, heat transfer from the atmosphere or other equipment. Another cause of overpressure is a heat exchanger blocked-in on the cold side while the flow continues on the hot side. Cryogenic systems are particularly vulnerable to such failures.

14.2.2.9 *Vacuum*

Equipment may inadvertently experience vacuum caused by the following contingencies:

- Instrument malfunction.
- Draining liquid from equipment without venting or gas repressuring.
- Shutting off purge steam without pressuring with noncondensable vapors, for example, air, nitrogen, or fuel gas.
- Extreme cold ambient temperature resulting in subatmospheric vapor pressure of certain materials.

- Loss of heat input to a process vessel handling low vapor pressure material while simultaneously maintaining cooling, condensing or loss of heat from vessel to ambient.
- Loss of heat to waste heat boilers with resulting steam condensation.
- Absorption process, for example, HCl vapors into water.
- Rapid climatic changes.
- Water addition to vessels that have been purged with steam.

Methods of protection against vacuum conditions caused by the above contingencies may include:

- Design equipment for full or partial vacuum conditions.
- Install vacuum relief devices (avoiding explosive mixtures if air is used).

14.2.2.10 Absorbent Medium Failure

In certain processes it is required that entrained gases be removed from liquids to avoid overpressure from accumulation of such gases and avoid upsets in downstream equipment. For example, a lean oil absorption system is often used for hydrocarbon services. In the production of CO-free hydrogen, carbon dioxide is removed before the hydrogen rich gas enters the methanator. In these cases loss of absorbent medium can cause overpressuring or excessive methanation reaction, and an evaluation of the system is required to determine if relief protection is warranted.

14.2.2.11 Loss of Motive Steam to Ejectors

This contingency is specific for ejectors used in vacuum services (e.g., vacuum towers in refineries). One scenario is the loss of motive steam which will, in effect, over pressure the towers. Relief valves are always provided on such towers and the relief load is generally considered as the sum of the process steam, overhead cracked gases and noncondensables.

14.2.3 Equipment Failure

This section addresses common equipment failures that may result in overpressure or vacuum relief requirements.

14.2.3.1 Heat Exchangers: Tube Rupture

The ASME Code states that "heat exchangers and other vessels be protected with a relieving device of sufficient capacity to avoid overpressure in case of internal failure." Characterization of the types of failure, determination of relieving capacity required, and selection and location of relief devices are left to the discretion of the designer. API RP 520 presents guidance in determining these requirements, including criteria for deciding when a full tube rupture is a likely contingency.

The relieving rate for tube rupture is commonly based on the assumption that one tube ruptures and provides two tube cross-sectional flow areas for material to flow from the high pressure side to the low pressure side. This material could be either vapor or liquid, with the phase determining the final relieving rate. Careful attention to two-phase flow and flashing fluid considerations is critical to the proper sizing of any relief device. For instance, high-pressure gas or flashing liquid on the tube side and low-pressure liquid on the low pressure side presents a very difficult relieving situation, which may require a rupture disk device to obtain the needed quick relieving response.

When calculating the flow out of the low-pressure side, credit can be taken for the fluid handling capacity of both the inlet and outlet lines unless either contains check valves or control valves which would tend to be closed by the effects of tube breakage. See API RP 521. Since pressure shock could occur on the low pressure side following tube failure, the proper placement and selection of the type of relief device [*rupture disk*] should be given due consideration.

The "two-thirds" rule is frequently used to establish the low pressure side design pressure as at least two-thirds of the high pressure side. The relief valve on the low pressure side does not have to be sized/checked for the ruptured tube case.

14.2.3.2 Heat Exchangers: Air Cooler Failures

There are two failures that commonly occur in air coolers, either fan failure or louver failure. A louver failure (closure) may be the result of a control failure, mechanical coupling breakage, or excessive vibration. This is considered a total loss of cooling/condensing and therefore the relieving rates are calculated using total loss of coolant as described in Section 14.2.2.4, Cooling Water Failure. This is a localized failure, however, and can sometimes be corrected quickly enough to avoid loss of production which might introduce other potential safety problems.

The loss of a fan is less detrimental due to continued natural convection effects. API RP 521 recommends that, in condensing service, partial credit between 20 and 30% of normal duty of the air cooler be taken. The relieving rate is then calculated using the remaining 70 to 80% of the duty. When practical, the designer should calculate the natural convective heat transfer rate for each case.

14.2.3.3 Automatic Control Valve

The design premise of the facility should include requirements for overpressure protection due to control valve failure. Two scenarios could be evaluated for this contingency:

- Failure of control valve in wide open position causing a high pressure fluid to enter a lower pressure system. This may result in partial flashing of fluid across the control valve causing two-phase flow.
- Failure of control valve in closed position (blocked inlet or outlet).

If a bypass valve has a larger valve coefficient, C_V, than the automatic control valve, consider flow through the bypass for relief load calculation.

14.2.4 Process Upset

14.2.4.1 Runaway Reaction

Runaway temperature and pressure in reactor vessels can occur as a result of several factors. Some of these are loss of cooling, feed or quench failure, excessive feed rates or temperatures, runaway polymerization, contaminants, catalyst problems, or instrument and control failures (e.g., agitation failure). The main concern here is the high rate of energy release and/or formation of gaseous products which may cause a rapid pressure rise in the reactor. The consequence of high vessel temperatures is a reduction of the allowable stress in the vessel. There are no general rules for determining the relief loads for this contingency. Design of adequate emergency relief requires a knowledge of heats of reaction, products of reaction, pressure-temperature relationships, and kinetics for both normal and upset conditions.

Before designing relief for overpressure, modifications in the process should be considered to see if the inherent safety can be improved (Chapter 2, Designing Inherently Safer Processes). These modifications might include:

- reduce amount, concentration or fill fraction of reactants, initiators or contaminants
- change operating temperature or pressure
- increase amount of solvent
- increase or modify emergency relief system
- redesign the process

After the inherent safety of the reaction is maximized, various protective methods can be incorporated into the design of a system such as:

- A higher margin in the design temperature or pressure of the equipment.
- Monitors and controls to mitigate runaway temperatures.
- High temperature shut downs or feed trip.
- Rapid vapor depressuring by remote controls.
- Addition of volatile fluids to absorb excess heat of reaction.
- Recycle of reacted product to dilute the feed.
- Addition of inhibitors to monomer systems.
- Addition of catalyst poison to kill the reaction.

API RP 520 and 521 do not address emergency relief for runaway reaction in batch reactors. The Design Institute of Emergency Relief Systems (DIERS) has developed procedures to obtain experimental data and to calculate the relief loads and vent sizes for runaway reactions; these procedures are covered in Section 14.6.

14.2.4.2 Process Causes

Imbalance of flow rates in and out of process equipment may cause overpressure as discussed in API RP 520, Section 3.

Pumps

Design pressure of equipment located downstream of a centrifugal pump is normally set at pump cutoff head combined with maximum suction pressure. However, if the downstream equipment has a low design pressure, or if the pump is a positive displacement type, a relief valve may be set at the design pressure of the equipment and sized to relieve pump capacity. The designer should evaluate the pump performance curve to determine the relief valve capacity at the relieving conditions.

Compressors

Design pressures for interstage receivers and recycle gas circuits and their associated relieving requirements depend upon the type of compressor used, the compressor performance curves, antisurge controls, settling-out pressure considerations and number of stages used. For detailed analysis of such systems, the designer should consult more comprehensive engineering standards and compressor vendors' literature.

Fired Heaters

Firebox: The design pressure of the firebox of a forced-draft furnace should be set to withstand the overpressure generated by the fans with the stack dampers fully closed. This is particularly important in furnaces that utilize the discharge flue gas from combustion in waste heat recovery systems.

Fired Steam Boilers: In accordance with ASME Boiler Code, Section 1, all fired boilers must be provided with relief valves to protect the boiler in case of blocked outlet.

Furnace Coils: Overpressure of process coils in furnaces can occur because of inadvertent closure of a block valve while the heater firing continues. This overpressure can cause tube failure due to overheating and consequent reduction in allowable stress. To protect the furnace tubes, a relief valve should be provided at the coil outlet upstream of the block valve.

Similarly, overpressure of process coils can be the result of closure of a valve at the inlet of the furnace. The coils will still be pressurized from downstream equipment. However, a relief valve in this case cannot provide the necessary protection because there is no forward fluid flow through the tubes, and overtemperature may occur below the normal operating pressure of the furnace tubes. The tubewall temperatures will increase until the tubes are overstressed even though the process pressure does not increase.

Several means for addressing this problem of a fired heater circuit, are:

- Low flow alarms and fuel cutout.
- Furnace feed control valves should be fail open.
- Limit stops or open bypass around hand-operated valves, if provided.

14.2.5 Loss of Process Utilities

The design problems created by a loss of utilities are discussed in Section 14.2.2.

14.3 PRESSURE RELIEF DEVICES

The most common method of overpressure protection is through the use of safety relief valves and/or rupture disks which discharge into either an open system, that is, to the atmosphere, to a containment vessel, or to a disposal system such as a flare or scrubber. Disposal of the effluents (vapor or liquid) is discussed in Chapter 15. The following sections provide brief descriptions of pressure relieving devices and guidelines for their use based upon their performance and service characteristics. After a relief valve is opened there is a possibility its performance is compromised and therefore it should be checked at the earliest convenient time.

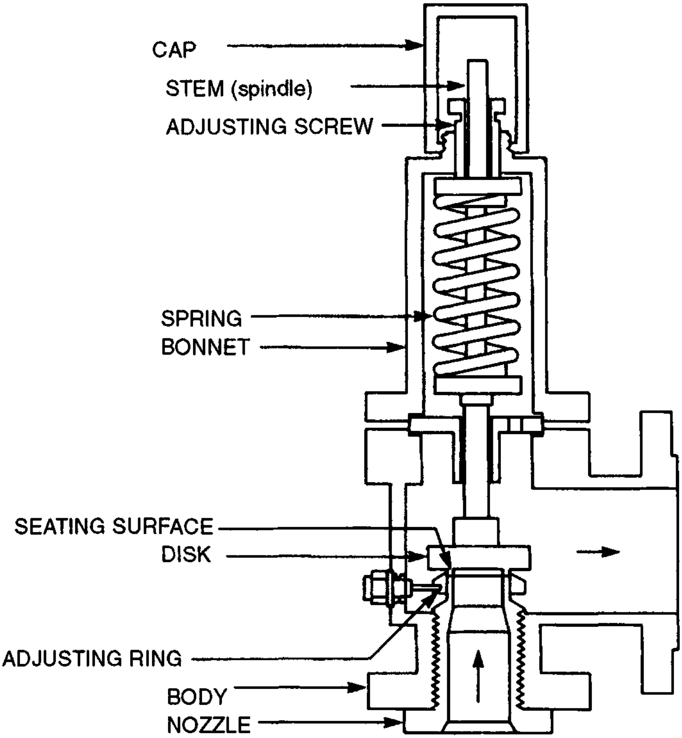

Figure 14-1 Typical conventional safety relief valve. (Source: API RP 520, part 1. Reprinted courtesy of the American Petroleum Institute.)

14.3.1 Safety Relief Valves

Conventional safety relief valves (Figure 14-1) are used in systems where built-up back pressures typically do not exceed 10% of the set pressure. The spring setting of the valve is reduced by the amount of superimposed backpressure expected. Higher built-up back pressures can result in a complete loss of continuous valve capacity. The designer must examine the effects of other relieving devices connected to a common header on the performance of each valve. Some mechanical considerations of conventional relief valves are presented in the ASME code; the manufacturer must be consulted for specific details.

Balanced safety relief valves may be used in systems where built-up and/or superimposed back pressure is high or variable. A balanced valve's capacity is not affected by back pressure until it rises to about 30% of set pressure. Most manufacturers limit back pressure on balanced valves to 45 to 50% of the set pressure. Care must be taken that back pressure developed does not exceed the mechanical limit of the bellows at higher set pressures. This consideration may limit the maximum back pressure permitted for a given service.

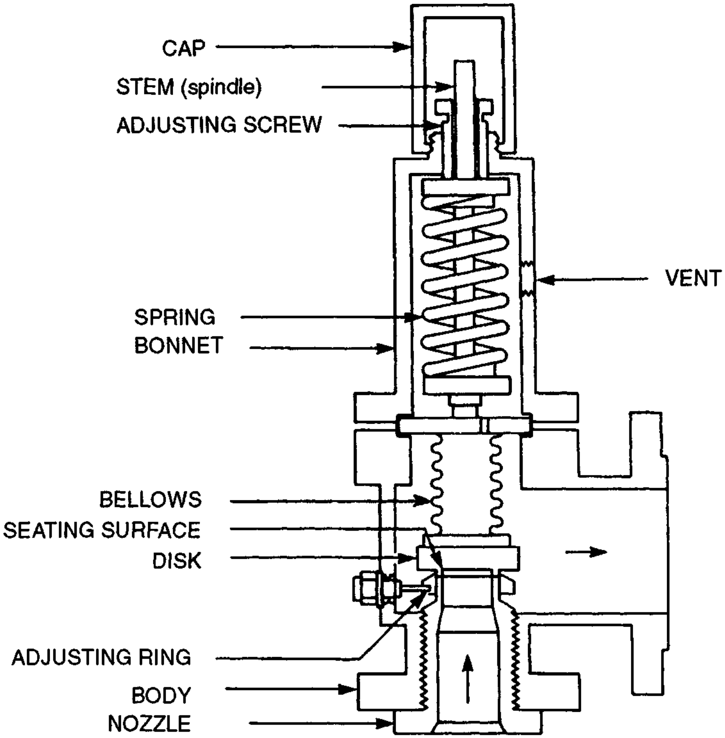

Figure 14-2 Typical bellows type balanced relief valve. For corrosion isolation, an unbalanced bellows safety relief valve is available. (Source: API RP 520, part 1. Reprinted courtesy of the American Petroleum Institute.)

There are two types of balanced relief valves: bellows and piston. Bellows type valves (Figure 14-2) are designed to equalize back pressure forces on both sides of the valve disk. The bellows is vented to either the atmosphere or a disposal system, provided its pressure is constant. These valves can be used in corrosive or fouling services; the bellows protects the spring from the process fluid. Bellows valves are more costly than conventional valves and require special maintenance and inspection to assure the integrity of the bellows.

Piston type valves (Figure 14-3) have the following characteristics:

- Top face of the piston has same area as the nozzle seat area.
- The piston guide is vented so that the back pressures on opposing faces of the disk are equal and cancel each other.
- Bonnets are vented to safe locations for hazardous materials.

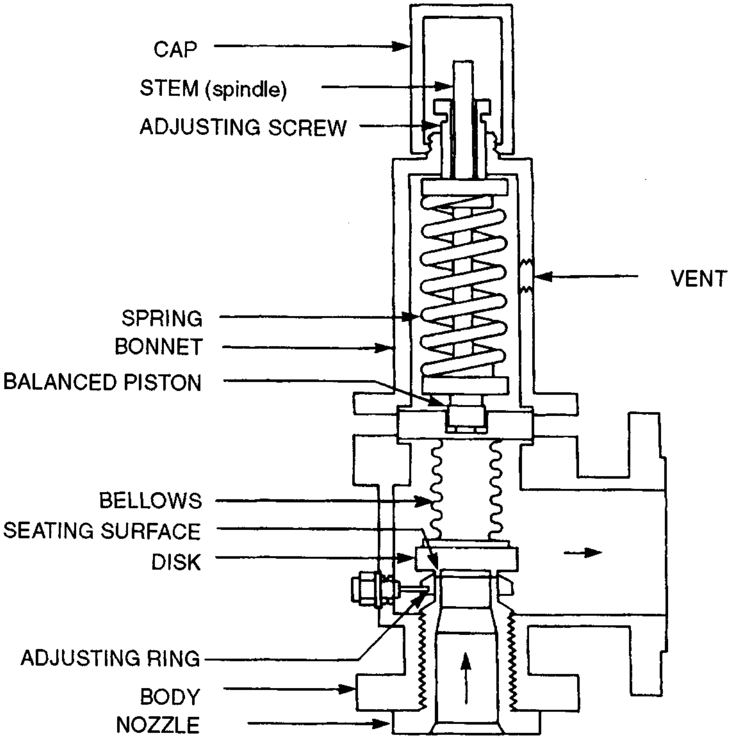

Figure 14-3 Typical piston type balanced relief valve. (Source: API RP 520, part 1. Reprinted courtesy of the American Petroleum Institute.)

14.3.2 Pilot Operated Relief Valves

In a pilot operated relief valve the major relieving device (the main valve) is combined with and controlled by a self-actuating pressure relief valve (the pilot control unit) (Figure 14-4). The pilot is a spring-loaded valve that senses the process pressure and opens the main valve by lowering the pressure on the top of an unbalanced piston, diaphragm, or bellows of the main valve. Conversely once the process pressure is lowered to the blowdown pressure, the pilot closes the main valve by permitting the pressure in the top of the main valve to increase.

Pilot operated relief valves are commonly used in clean, low pressure services. They are also used where a large relieving area at high set pressure is required. The set pressure of this type of valve can be close to the operating pressure and therefore accuracy of setting is important. In fact, pilot operated valves are frequently chosen when operating pressures are within 5% of set

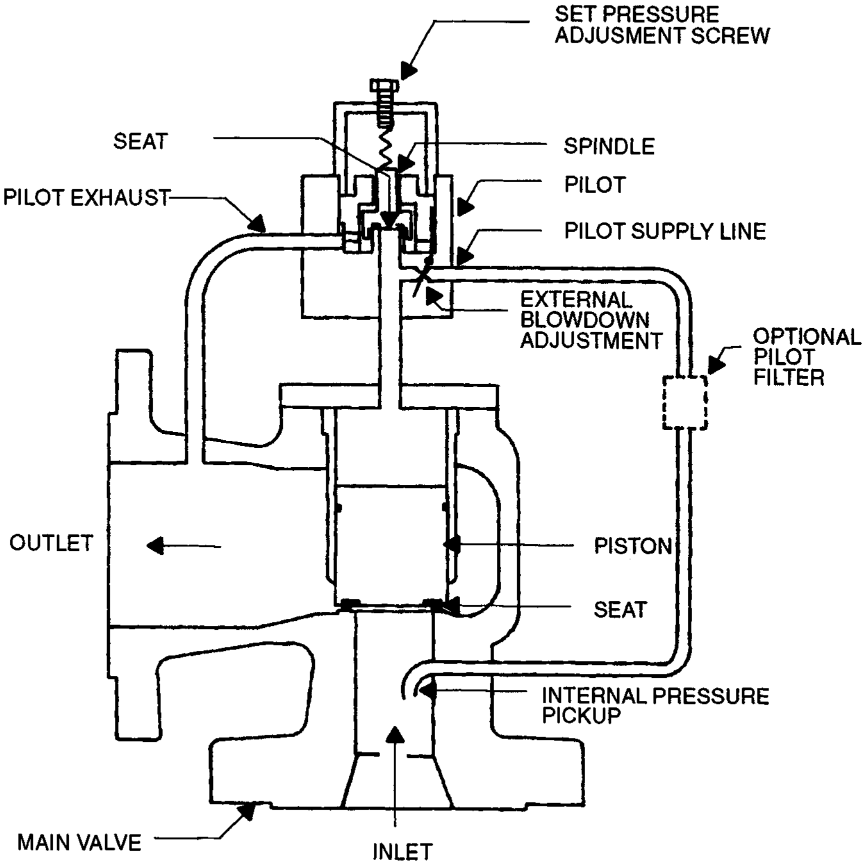

Figure 14-4 Typical pilot-operated relief valve. (Source: API RP 520, part 1. Reprinted courtesy of the American Petroleum Institute.)

pressures and a close tolerance valve is required. The main disadvantage of these valves is that they are normally temperature limited by the elastomer or plastic piston seal materials and limited to noncorrosive and nonfouling services. The advantages and disadvantages of pilot operated valves are summarized in Table 14-1.

14.3.3 Rupture Disks

A rupture disk is a device actuated by inlet static pressure and is designed to function by the bursting of a pressure retaining disk (Figure 14-5). A rupture disk assembly consists of a thin, circular membrane, made of metal, plastic, graphite, or a combination of materials, that is firmly clamped in a disk holder. It is designed to withstand pressure up to a specified level at which it will burst and release the pressure from the system being protected. It can be installed alone or in combination with other pressure relief devices. Rupture

Table 14-1 Advantages and Disadvantages of Pilot Operated Valves

Some advantages of pilot operated valves are:

- They are designed to remain tightly closed until their set point is reached. This means they are ideally suited for application where the operating pressure is higher than 90% of the valve set pressure.
- Chattering of the valve due to back pressure is not possible.
- Set pressure is not affected by back pressure.
- Valves can be used in vapor or liquid service with back pressure greater than 50% of set pressure (subject to vendor's verification).
- A valve's pilot and reseat pressure can be checked while the valve is in service.
- Blowdown can be specified as low as 2% of set pressure.
- A pilot operated relief valve can be specified to have modulating action, that is, to open only in proportion to the relief requirement. Thus, it reduces the upset obtained in the process unit and the product lost to the flare whenever a minor overpressure situation occurs. A modulating pilot operated valve has zero percent blowdown. It is designed to reclose at its set pressure.
- May cost less than direct spring valves above 3-inch size.

Some disadvantages of pilot operated valves are:

- The valves have more restrictive temperature limits than do spring-loaded valves.
- The technology is more complicated and so it takes more knowledge to specify a pilot operated valve and install it correctly.
- The valve needs design features generally not associated with a spring-loaded relief valve such as a filter in the sense line if the service is dirty and a back flow preventer if the valve discharges to a flare header system.
- These valves have more restrictive metallurgy selection.
- They may cost more than direct spring valves smaller than 3-inch size.

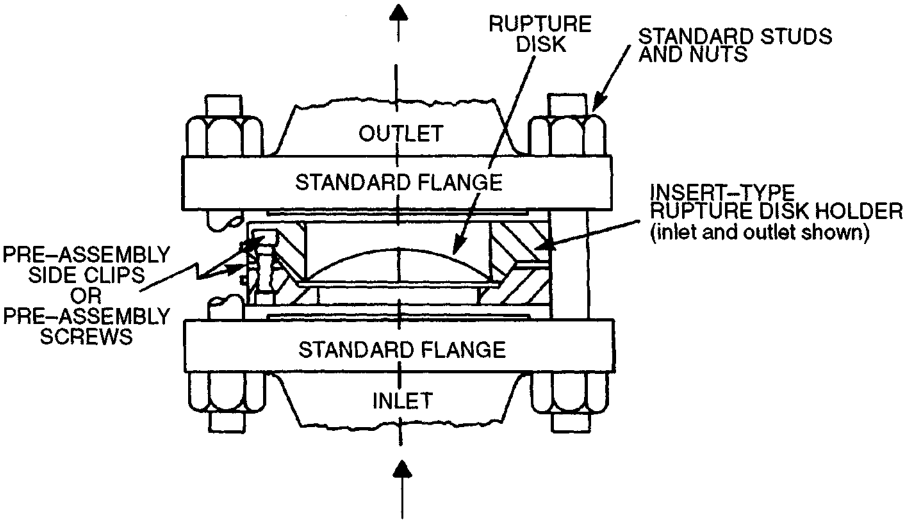

Figure 14-5 Typical rupture disk. (Source: API RP 520, part 1. Reprinted courtesy of the American Petroleum Institute.)

disks are available in several types and designs and can be used in pressure or full vacuum. Choice of types is based on safety and operating considerations and vendor alternatives should be closely evaluated.

The burst tolerance of rupture disk devices is typically 5% for set pressures over 40 psig, compared with tolerance of ±3% for pressure relief valves at set pressures over 70 psig; however, disks can be made to closer tolerances for special applications. In addition, manufacturing tolerances exist which can affect the stamped burst pressure on the rupture disk.

Rupture disks are sometimes used in preference to relief valves due to the larger relief capacity which can be obtained for a given disk size (larger orifice). Rupture disks do not reseat, however, and the process must be removed from service or the disk isolated to allow for disk replacement. Some advantages and disadvantages of rupture disks are given in Table 14-2. Rupture disks are also commonly used in series with a relief valve to prevent corrosive or hot fluid or particulates from contacting the relief valve or valve seat.

Special consideration must be given to rupture disk/relief valve assemblies to ensure proper operation. These include:

- Relief device capacity must be derated as required by ASME or by utilizing vendor test data.
- ASME Code requirement for monitoring pressure between the rupture disk and relief valve to ensure that the rupture disk may still burst should a pinhole leak exist in the disk.
- ASME Code requirement for bleed-off if disk is located downstream of the relief valve.

Table 14-2 Advantages and Disadvantages of Rupture Disks

The following are some advantages of rupture disks:

- They can be installed upstream or downstream of relief valves in highly toxic or corrosive services. Only rupture disks that have a nonfragmenting design may be used beneath a pressure relief valve.
- More effective than a relief valve in protection equipment from sudden explosions.
- Depending on materials of construction, they are more resistant to corrosion or plugging than other relief devices.
- They have applications in viscous and slurry services.
- In limited services they are more cost effective than relief valves.
- They rupture only when the designated pressure is reached and, therefore, do not simmer like a relief valve.

The following are some disadvantages of rupture disks:

- When a disk ruptures, the entire contents of the system it is protecting may be lost.
- It is difficult to detect if a disk is leaking unless other instruments like pressure indicators or burst disk indicators, detectors or alarms ar installed in the disk assembly.
- Old disks or those subject to high cycle fatigue may experience premature failure due to metal fatigue. To minimize this, rupture disk burst pressure should be set considerably above the full range of operating pressures. They may require replacement every year depending on plant operating and maintenance procedures.
- Rupture disks are subject to mishandling. Careful installation is of extreme importance. The disks are made of thin, fragile metals and any deformation during assembly may weaken them and result in premature rupture.
- Burst pressures are sensitive to temperature variations.
- Some types require greater operating margins.

- An excess flow check valve should be considered to allow for the pinhole leak case.

Reverse-buckling rupture disk assemblies with knife blades may exhibit a phenomenon called "rollover," where the disk rolls over onto the knife blades without bursting. Rollover can be caused by dull or corroded knife blades, mechanical damage to the rupture disk before or during examination, or improper use in a liquid service These assemblies should be inspected at routine intervals to make sure that the knife blades are still sharp and not corroded and that the rupture disk is intact and has not rolled over.

14.3.4 Liquid Seals

Liquid seals are U-tube hydraulic loops used in systems whose design pressure is slightly above atmospheric pressure. Seal depth and diameter are sized to pass the design relieving rate at the required design pressure. When designing a liquid seal, the following criteria should be considered:

- Seal loops should be filled with water, absorptive oils, or other suitable fluids.
- Continuous seal fluid must be provided to ensure adequate seal, especially after a blowout.
- Location of discharge for the seal fluid must be able to handle toxicity, flammability, etc., due to contamination by the relieving vapor.
- Winterizing must be provided where necessary.
- Safe disposal of vented process fluid needs to be provided.
- Seal depth should exceed the maximum normally expected system pressure by a suitable margin to allow for pressure surges.

A disadvantage to the use of a liquid seal is the inertia of the liquid. A liquid seal should not be used in situations of rapid pressure rise.

14.3.5 Pressure–Vacuum Relief Valves

For some applications, primarily atmospheric and low pressure storage tanks, pressure–vacuum relief valves (PVRVs) are used to provide pressure relief. These units combine both a pressure and a vacuum relief valve into one assembly that mounts on a single nozzle on top of the tank. These valves frequently operate under normal tank working conditions at low pressure differences (+2.5, –0.5 inches water gauge is common) but they must also be sized to handle the maximum possible pressure normal relief requirements for the tank. API RP 520 and API STD 2000 can be used as references for sizing. For emergency pressure relief situations an additional safety relief valve is placed on the tank.

14.3.6 Vacuum Relief Devices

Occasionally, a vessel may experience vacuum conditions due to excessive condensation or upset process conditions and, therefore, must be protected from collapse due to the vacuum. The designer in this case has an option to design the vessel for either full or partial vacuum, provide a vacuum relief device, or permit ingress of air, nitrogen, or fuel gas to the vessel to prevent a vacuum from developing. If vacuum relief is from a header, it must be assured that the header does not contain condensable vapors. Designing for full vacuum is the preferred approach whenever practicable. Glinos and Myers (1991) discuss the sizing of vacuum relief valves for atmospheric distillation columns. For information on specific vacuum relief devices, see vendor literature.

14.3.7 Miscellaneous Relief Devices

There are other types of relief devices available such as:

- Rupture pin or breaking pin devices.
- Spring-loaded nonreclosing pressure relief devices.
- Valves developed by certain manufacturers for use in specific services (e.g., for chlorine service).
- Rupture plugs (blowout plugs).
- Designated failure points (e.g., weak seams).

14.4 SIZING OF PRESSURE RELIEF SYSTEMS

A critical point in design is determining whether the relief system must be designed for single-phase or two-phase flow. Two-phase flow frequently occurs during a runaway reaction, but it may also need to be considered in a less complicated system such as a vessel with a gas sparger or bottom fire on a raised vessel. The following sections on sizing of relief valves apply to single-phase flow; for two-phase flow, see Section 14.6.

14.4.1 Sizing of Relief Valves

It is recommended that designers consider using personal computer programs to aid in valve sizing when a vendor has been chosen. Consult the ASME Code and API RP 520, along with vendor technical information.

14.4.1.1 Vapor Service

The ASME Code is the primary reference for pressure relief device sizing requirements. API RP 520 recommends formulas for calculating the discharge area of a relief valve for gas or vapor, for low pressure steam exhaust. Appendix E of API RP 520, Part 1, should be consulted for unusual situations in which deviations from ideal gas law behavior are significant.

14.4.1.2 Liquid Service

Liquid capacity certification is required for pressure relief valves designed for liquid service (ASME CODE, Section VIII, Division I). The procedure for obtaining capacity certification includes determining the coefficient of discharge for the design of liquid relief valves at 10% overpressure. Valves that require a capacity in accordance with the ASME Code may be sized using the equation given in API RP 520, Section 4.5.

Where liquid-full equipment can be blocked-in and continued heat input cannot be avoided, a pressure relief device shall be provided. The rate of expansion depends primarily on the rate of heat input and the liquid properties. Liquid expansion rates for the sizing of relief devices that protect heat exchangers, condensers, and coolers against thermal expansion of trapped liquids can be approximated using an equation from API RP 520, Appendix C.

14.4.1.3 Flashing Liquids

Simpson (1991) and Leung (1992) have presented methods for sizing safety devices for two-phase flow, including flashing flow. The Design Institute of Emergency Relief Systems (DIERS) has also developed methods for sizing relief systems for two-phase flow; this methodology is summarized in Section 14.6 of these Guidelines.

14.4.1.4 Relief Valve Inlet and Outlet Sizing

The inlet line of a relief valve must be designed using the criteria given in the codes and standards listed at the end of this chapter. No further discussion will be provided here other than to say that the proper operation of a relief device depends upon proper installation including line sizing. Consult the ASME Code for basic requirements for pipe sizing and limitations; consult API RP 520, Part II for additional information.

The outlet line size of a relief valve discharging to atmosphere is generally dictated by back pressure, velocity limitations and environmental considerations. Sizing of relief valves discharging into a closed system, for example, a flare, is impacted primarily by back pressure considerations. Design guidelines for sizing outlet lines are also given in the aforementioned design codes and standards.

14.4.2 Sizing of Rupture Disks

The sizing criteria for rupture disks are similar to those of relief valves. The ASME Code is the primary reference for flow through rupture disks. When rupture disks are used in conjunction with relief valves, a sizing factor must be used to derate the effective relief capacity of the disk/safety valve assembly. The designer must consult with the disk manufacturer or engineering standards to arrive at this factor. ASME (Section UG-127(a)(3)(b)(2), 1990 addendum) requires derating the relief valve capacity by a factor of 0.9 in the absence of an experimentally determined combination capacity factor.

14.4.2.1 Rupture Disk Used Alone

Equations for calculating the required discharge area for a rupture disk used independently are given in API RP 520, Part I, for gas or vapor service and for liquid service. The recommended coefficient of discharge (K_d) is 0.62, unless a code certified coefficient is available. Additional considerations may be applicable in accordance with the ASME Code.

14.4.2.2 Rupture Disk Installed Upstream of Relief Valve

API RP 520 discusses how to determine the combined relieving capacities of the valve and rupture disk, including application of a combination capacity factor.

- Because rupture disk leaks are possible, carefully monitor the pressure between the relief valve and disk, including venting.
- Use a nonfragmenting type rupture disk so valve operation will not be affected when the disk ruptures.

14.4.2.3 Rupture Disk Installed Downstream of Relief Valve

A rupture disk could be installed downstream of a relief valve to avoid back pressure or backflow from the system. An example would be to protect the relief valve from corrosive material. The following design criteria are recommended:

- The net area after rupture should be capable of passing the rated relief valve capacity without exceeding the allowable built-up backpressure at the relief valve outlet.
- The contents of the protected vessel must be free from gum buildup or clogging materials.
- Under <u>all</u> cases follow the ASME Code.
- Isolating block valves are required for maintenance. Provide a spare so that protection of the system is not interrupted during maintenance.

14.4.3 Sizing of Rupture Pins

Sizing is the responsibility of the manufacturer and is done using the ASME Section VIII capacity test method.

14.5 DESIGN OF RELIEF DEVICES: OTHER CONSIDERATIONS

14.5.1 Location

Normally, relief valves are installed at the top of vessels. Barring any code requirements, it is permissible to mount relief valves on the outlet piping from a vessel. In some towers handling corrosive or dirty fluids, relief valves are best installed below the packing or trays since there is a potential for column plugging. In other cases, it would be advisable to install relief valves at a point in the tower which provides the most advantageous temperature, phase, or density for relief, thereby avoiding possible disposal problems.

14.5.2 *Spares*

Under no circumstance should a system, where overpressure is possible, be operated without assured overpressure protection. This can be provided by sparing. Sparing of relief valves is now a more common installation approach (and the recommended approach) in order to allow on-line maintenance of the valve by switching. Use of spares should be accompanied by certain restrictions including:

- They are installed in parallel and isolated by full-port, three-way or transflow valves at the inlet and outlet. Full-port block valves can also be used to isolate relief valves installed in parallel.
- A bleed valve should be provided between the relief valve and the inlet block valve.
- Use of block valves is not a good solution unless key locks are used to assure a proper isolation sequence.
- After a valve relieves and the spare is being used, check the performance of the valve that relieved.

One relief valve can protect more than one piece of equipment connected by piping in the following cases.

- The relieving path between the equipment pieces and the relief device is free of any potential blockage or block valves.
- The pressure of the relieving path at the time of relief must assure that ASME code limits on equipment overpressure are not exceeded for any of the protected equipment.

14.5.3 *Accessibility*

Relief devices should be accessible for maintenance and inspection.

14.6 DIERS METHODS OF OVERPRESSURE PROTECTION FOR TWO-PHASE FLOWS

Emergency relief system (ERS) design is a multifaceted problem. Of particular significance is whether the relief system must be designed for single-phase (vapor *or* liquid) or two-phase (vapor *and* liquid) flow. The Design Institute for Emergency Relief Systems (DIERS) has developed methods to predict when two-phase flow might exist and the application of various sizing methods in ERS design (Fisher 1985, 1989). The *DIERS Project Manual* (DIERS 1992) is the best source of detailed information on these methods.

The most significant findings of the DIERS program are the ease with which two-phase vapor–liquid flow can occur during an emergency relief situation and the requirement for a much larger (by two to ten times) relief system.

Two-phase flow is dependent on the physical properties of the material being vented (surface tension, solids content), heat input rate to the vessel with resulting vapor formation (and bubble rise rate), and liquid level in the vessel. Two-phase flow frequently occurs during a runaway reaction, but it may also need to be considered in a less complicated system such as a vessel with a gas sparger or a unique fire case. Vapor–liquid mixtures can also form *in* the relief system as venting occurs (Huff 1992). In addition two-phase flow can occur intermittently during a release.

The DIERS methodology is important as a means of addressing situations such as two-phase flow not covered adequately by ASME and API methods. Because of uncertainties in application of these techniques to sizing relief systems, however, a prudent course for the designer is to use the most conservative calculation. The CCPS *Guidelines for Effective Handling of Emergency Relief Effluents* (in progress) will address calculation methods for selection of relief device size, prediction of flow, etc. (Huff 1992).

14.6.1 Vapor Disengagement Dynamics

Two-phase, vapor–liquid flow during a runaway reaction occurs as a result of vaporization and gas generation. Boiling takes place throughout the entire volume of liquid, rather than solely at the surface. Each bubble occupies volume and displaces the liquid surface upward. Individual bubbles are able to rise (slip) through the liquid (with a velocity that depends on buoyancy and surface tension) but are retarded by viscosity and the foamy character of the fluid. If a sufficient volume of bubbles become trapped, the liquid surface reaches the height of the relief device and two-phase flow occurs through the relief device.

The vapor and liquid motion inside a reactor or storage vessel during emergency relief venting is an extremely complex hydrodynamic problem. The question of vapor versus two-phase vapor–liquid relief depends primarily upon the prevailing disengagement regime, that is, bubbly and/or foamy behavior or churn-turbulent behavior. Vapor disengagement behavior is studied by developing a model of vessel flow, a model of vent flow, and an equation to couple the models in order to describe the discharge rate.

14.6.1.1 Vessel Flow Models

Vessel flow models estimate the liquid swell (degree of vapor–liquid disengagement) as a function of vapor throughput. The vapor may be generated uniformly throughout the liquid volume, formed preferentially near the top of the liquid due to hydrostatic head and recirculation effects, sparged at the bottom, or generated at the walls due to external heating. The vessel flow models define the relationship among these three parameters: the average void fraction in the swelled liquid, the vapor superficial velocity at the liquid surface, and the characteristic bubble rise velocity.

The vessel flow models used in the DIERS program are defined in Table 14-3 in order of increasing vapor–liquid disengagement (decreasing swell).

14.6.1.2 Vent Flow Models

Vent flow models estimate the vent mass flux and volumetric discharge rate as a function of the vessel pressure and the vent entrance quality. The key vent flow model parameters are the vessel stagnation pressure, the quality or vapor mass fraction entering the vent, the vent mass flux, the vent cross-sectional area, and critical pressure ratio or vent exit pressure.

Table 14-3 Vessel Flow Models

Model	Characteristics
Homogeneous Vessel Model	Assumes zero vapor–liquid disengagement in the vessel, i.e., the vapor bubble rise velocity relative to the liquid is zero. With this model, the vapor mass fraction or quality entering the vent line will be the same as the average vapor mass fraction in the vessel. This model may approximate conditions when the vessel contents are extremely viscous or foamy or when the venting time is too short for appreciable bubble rise.
Bubbly Vessel Model	Assumes uniform vapor generation throughout the liquid with limited vapor–liquid disengagement in the vessel. The liquid phase is continuous with discrete bubbles.
Churn-Turbulent Vessel Model	Assumes uniform vapor generation throughout the liquid with considerable vapor–liquid disengagement. The liquid phase is continuous with larger regions of coalesced vapor than in the Bubbly Vessel Model.
Non-Boiling Height Vessel Model	This is a churn-turbulent model with top biased vapor generation. The Churn-Turbulent Vessel Model is applicable only to a top portion of the fluid. Below this portion, boiling does not occur and, thus, there is no liquid swell. This nonboiling portion or nonboiling height is estimated from a balance between hydrostatic head effects and recirculation effects.
Complete Vapor–Liquid Disengagement Vessel Model	Assumes that (1) all the vapor is formed at or near the liquid surface or (2) that the slip velocity of the vapor relative to the liquid is large enough so that the swelled liquid does not reach the vent. Use of the this model will always result in the vent entrance quality of unity or all vapor venting; while use of any of the partial vapor–liquid disengagement models could result in either all vapor or two-phase venting.

The various vent flow models reflect differences in assumptions as to: which phase is continuous, whether flow is turbulent or laminar, frictional effects, relative velocities between the phases, whether the flow path is isentropic or isenthalpic, and the degree of approach to vapor–liquid equilibrium both along the vent and at the choking plane. Descriptions of the models and the actual model equations are given in Chapter II of the DIERS Project Manual. The purpose of all the models is to allow calculation of the vent mass flux as a function of the vessel stagnation pressure and the vent entrance quality.

14.6.1.3 Coupling Equation

The coupling equation is a vapor material balance written at the vent entrance. This equation couples vessel and vent flow models providing an integrated system model for calculating the volumetric discharge rate from the vessel into the vent. The coupling equation and DIERS vessel flow model are applicable to top-vented, vertical, right circular cylindrical vessels when it has been established that two-phase flow will occur and that some vapor–liquid disengagement will take place. Refer to the DIERS Project Manual for more details.

14.6.2 Characterization of Runaway Reaction Behavior

Direct experimental sizing of emergency relief devices is limited by equipment used in the experiment. Graphical, analytical and direct scaling methods are also limited to certain types of reactions:

- *Volatile/Tempered Reaction*—The reactants, products and/or solvents must be volatile. Heat of vaporization cooling during vapor or two-phase flow venting is sufficient to control the change of temperature with time at the set pressure of the ERS device during the entire course of the reaction.
- *Hybrid/Tempered Reaction*—Noncondensable gases are produced as a result of a decomposition reaction. The reactants, products and/or solvent must be volatile. Heat of vaporization cooling during vapor or two-phase flow venting is sufficient to control the change of temperature with time at the set pressure of the ERS device during the entire course of the reaction. Note: The ERS device is able to control the temperature and pressure at the set pressure.
- *Hybrid/Nontempered Reaction*—Noncondensable gases are produced as a result of a decomposition reaction. The reactants, product and/or solvent, if volatile, are present in insufficient quantity or have insufficient heat of vaporization during vapor or two-phase flow venting to temper

the reaction throughout its entire course. Note: The ERS device is not able to control the temperature and pressure at the set pressure.

- *Gassy/Nontempered Reaction*—Noncondensable gases are produced as a result of a decomposition reaction. The reactants, products and/or solvent are not volatile or have an extremely low volatility. The heat of vaporization during vapor or two-phase flow venting is insufficient to temper the reaction at any point.

14.6.3 Two-Phase Flow Viscosity Characterization

Viscosity characterization was found to be an important ERS design consideration. DIERS conducted a limited program to measure the two-phase vapor–liquid flashing mass flux for certain high viscosity fluids through nozzles, long constant diameter vent lines and long vent lines with internal restrictions. Mass flux reductions of an order-of-magnitude were measured for laminar (viscous) compared to turbulent (nonviscous) flow in a constant diameter vent line. Internal restrictions in long vent lines resulted in a vapor, rather than a liquid, continuous flow regime. Mass flux reductions for laminar compared to turbulent flow were not as great for this situation. Refer to the DIERS Project Manual for details.

14.6.4 Obtaining Experimental Data for Emergency Relief System Design

A careful experimental program using representative samples is required to obtain data needed to design an ERS. The present state of experimental development should be considered when selecting an apparatus to acquire these data. Methods for obtaining and using experimental data for ERS design are summarized below.

14.6.4.1 Accelerating Rate Calorimeter

The Accelerating Rate Calorimeter® (ARC) has found widespread application for thermal stability (exotherm onset) and runaway reaction studies. Methods to fit kinetics from the data have been reported. The standard ARC sample container cannot be sampled during a runaway reaction. Fractional adiabatic temperature rise is used to infer the consumption of reactant (i.e., reactant concentration). The sample to be tested must therefore contain only one rate-determining reactant if kinetics fit from ARC data are to be valid.

14.6.4.2 DIERS Bench-Scale Apparatus

DIERS sponsored development of a bench-scale apparatus and a low thermal inertia test cell which can be used to provide thermal stability and runaway reaction kinetic data. The low thermal inertia essentially overcomes a limitation of other commercial devices, namely understating the magnitude of the self-heat rate and the adiabatic temperature rise. For the first time runaway reactions in the laboratory can approximate the severity of those in industrial vessels. This behavior is extremely useful for the validation of a computerized runaway reaction model which typically includes kinetics, stoichiometry, heats of reaction, physical properties and vapor–liquid equilibrium constants assembled from various sources.

This apparatus can also be used to:

- Differentiate among materials which exhibit homogeneous versus non-foamy behavior during emergency relief by measurement of the final void fraction in a test cell.
- Determine the effect of viscosity on homogeneous-equilibrium flashing flow.
- Measure parameters required for graphical or analytical methods for emergency relief device design.
- Size emergency relief devices directly by using top- or bottom-vented experiments.

The DIERS Project Manual, Chapter VI, provides recommendations on testing for the bench-scale apparatus for the cases listed below:

1. Thermal Stability Testing/Data Adjustment
2. Onset/Disengagement Behavior Testing
3. Flow Rate Calculation/Viscosity Characterization
4. ERS Design: Fauske Analytical Methods/FAI Nomograph
5. ERS Design: Leung Analytical Methods
6. ERS Design: Area–Charge Scaling Method (Top Vent Test/Top ERS Device)
7. ERS Design: Area–Charge Scaling/Scaling Equation Method (Bottom Vent Test/Top or Bottom ERS Device)
8. Methodology for Fire Exposure

General experimental and safety recommendations are also provided.

14.6.4.3 Reactive System Screening Tool (RSST)

Following completion of the DIERS program, Fauske and Associates, Inc. developed the Reactive System Screening Tool® (RSST) (Creed and Fauske 1990; FAI 1989). This adiabatic calorimeter can be used for characterization of and vent sizing for tempered, hybrid, and gassy reactive systems.

14.6.4.4 Kinetic Model

If a kinetic model is developed using experimental data to determine the reaction mechanism and its associated rate constants, this model can be coded into the Systems Analysis for Integrated Relief Evaluation (SAFIRE) program

(DIERS 1986) and used to determine the relieving requirements during an uncontrolled reaction.

14.6.5 How the Test Methodology Fits into the ERS Design

The first task in ERS design is to define and test the worst credible incident scenario. The test conditions should specify:

- The amount, concentration and fill fraction of reactants, solvents and potential contaminants.
- The temperature, pressure and degree of agitation of the process.

Small-scale screening tests are often necessary to give an indication of the approximate onset of an exotherm and the severity of a runaway reaction and to define or redefine the worst credible incident scenario.

The DIERS methodology is important as a means of addressing situations such as two-phase flow not covered adequately by ASME and API methods. Because of uncertainties in application of these techniques to sizing relief systems, however, a prudent course for the designer is to use the most conservative calculation.

14.6.6 SAFIRE Computer Program for Emergency Relief Sizing

The results of the large-scale test program and the complexity of analyzing a runaway reaction accompanied by the venting of flashing fluids required a computer model capable of handling this complex problem. The Systems Analysis for Integrated Relief Evaluation (SAFIRE) program began as a tool developed by Fauske & Associates, Inc. (FAI) to assist in interpreting and extending the results of the large scale test series. To allow wider use of the program, the SAFIRE model can incorporate user-defined coding for non-idealities in vapor–liquid equilibria and complex reaction chemistry.

The original FAI model was modified to handle general multicomponent flash and reaction routines and the problem of dealing with severe non-idealities in vapor–liquid equilibria and complex reaction chemistry, which vary greatly from problem to problem.

The SAFIRE code is organized primarily as a "rating" code. It can be used to evaluate the pressure/temperature/time history for various emergency scenarios with a specified relief system. The code also has a limited design capability, which can be used for simple geometries to determine the vent size which will limit the maximum pressure to a specified value. A summary of input data requirements is shown on Table 14-4.

SAFIRE was deliberately set up with a wide variety of user-controlled options; this means SAFIRE is *not* a suitable tool for unsophisticated users. An improper specification of a flow model, for example, may lead to gross

Table 14-4 Summary of SAFIRE Emergency Relief System Input Data Requirements

Control Parameters	Vessel Description	Physical Properties	Initial Conditions	External Heat	Inlet Streams	Reaction Information	Vent Geometry
• Simulation type (heat-up, vent, etc.) • Integration control mModel: Euler or Runge–Kutta • Start time • End time • Step size (variable or constant) • Print contro • Fluid behavior in vessel • Type of flow in vessel	• Vent Location • Vessel Shape • Volume • Diameter • Height • Limit pressure • etc.	• Molecular weight • Critical temperature (function of temperature) • Vapor pressure • Liquid density • Liquid heat capacity • Gas heat capacity • Latent heat • Surface tension • Liquid viscosity • Gas viscosity • Vapor–liquid equilibria	• Temperature • Pressure • Amount of material • Composition	To include vessel: • Wall thickness • Density • Heat capacity • Thermal conductivity • Heat transfer coefficient	• Start time • End time • Temperature • Flow rate • Composition • All vapor or all liquid	• Stoichiometry (reaction equation) • Rate (kinetics, Arrhenius coefficients) • Order • Heat of reaction	Search for Size? • Nozzle diameter, discharge coefficient • Long pipe number of sections, length, diameter, entrance losses

undersizing of the vent system with catastrophic consequences. This same complexity, however, makes the code very versatile.

The code can model many aspects of emergency relief situations such as:

- Complex runaway reactions with or without gas generation
- External heat loads (e.g., fire)
- Venting of gases (compressible or incompressible) or liquids (flashing or nonflashing) or mixtures of liquid and gas
- Vapor–liquid disengagement in the vessel being vented
- Nonidealities in vapor–liquid equilibria and in gas compressibility
- Various vessel and vent line geometric combinations

The user can model these aspects by appropriately setting input switches, and by defining the reaction kinetic and activity coefficient relationship in user added subroutines.

14.6.7 DIERS Methods for Sizing Pressure Relief Systems

This section is intended to provide guidance to the various calculation methods developed by DIERS to safely size a relief system for two-phase flow venting due to a runaway reaction in a vessel. These methods can be used to identify potential hazards in an existing system or design grass-root systems for new plants.

In evaluating the adequacy of relief systems for an existing plant, the first task for the design engineer is to determine if two-phase flow potentially exists in the subject system. DIERS developed a procedure to differentiate among materials which exhibit homogeneous (foamy) versus nonfoamy two-phase, vapor–liquid flow onset (start)/disengagement (stop) behavior during runaway reaction emergency relief. This procedure is outlined in detail in the DIERS Project Manual.

Once the data are collected, hand calculations can be performed to arrive at the necessary relieving loads and relief device sizes. Alternatively, and more accurately, SAFIRE should be used to perform such calculations. However, the designer must ensure that the proper characterization of the vessel flow and vent models with proper process data are entered into the program. If in doubt about which flow models to use, the designer is advised to perform the calculations for the various vessel flow models and select the most conservative results to design the relief system.

14.6.8 DIERS Fire Case Methodology

DIERS has contributed to the analysis of the relief requirements for a vessel exposed to an external fire case in two significant categories: (1) vessels containing a material that can self-heat and (2) liquid-filled vessels.

14.6.8.1 Materials with an Exothermic Reaction Potential (Self-Heating) Exposed to an External Fire

If a material has a potential for self-heating, additional heat input obtained during an external fire will aggravate the problems. Heat input from the fire will raise the bulk liquid temperature to a point where the rate of self-heating becomes excessive. Thus, the temperature of a reaction mixture is raised by the fire without consuming reactant. Also, the corresponding time interval required to reach an uncontrolled reaction is shortened and may provide insufficient time for an operator to restore those safety systems which were disrupted by the fire, such as the cooling system, a quench system, an inhibitor injection system, or a blowdown system. However, once the reaction becomes uncontrolled, heat from the fire contributes little to the overall heat balance of the reactor.

The DIERS methodology recommends conducting experiments to determine the effect of heat gain due to fire exposure. ERS sizing methods that depend upon tempering the uncontrolled reaction by boiling a solvent may not be valid if the solvent boils off during the fire case.

14.6.8.2 Liquid-Filled Vessels Exposed to an External Fire

During the initial phase of an external fire, the liquid contents in a vessel will expand as the liquid is heated and, if the vessel is almost full, only flashing liquid will be vented. The expansion continues as bubbles are formed at the vessel wall. There may not be sufficient vapor space to accommodate this swell and to provide vapor disengagement above the liquid interface. At this stage, a mixture of liquid and vapor will flow through the relief device, but once the liquid inventory is sufficiently depleted, the relieving rate will become all vapor. The maximum relief area requirement occurs during the initial stage when both liquid and vapor are flowing through the relief device.

14.7 EMERGENCY DEPRESSURING

The most common emergency facilities incorporated into plant safety designs are:

- Emergency Depressuring System
- Emergency Shutdown System
- Emergency Isolation System

Emergency shutdown and isolation systems are discussed under process control (Chapter 9, Process Control). These emergency shutdowns of equipment and heat sources are extensively employed to limit relief loads (Zheman and Early 1992).

There are several situations where emergency depressuring can be effective in reducing the risk of failure of:

- Reactors where potentially uncontrollable runaway reactions exist.
- Equipment where upset temperatures can lead to equipment failure at or below design pressures.
- Equipment exposed to fire where there is a loss of process fluids normally used to control temperature rises.
- Process units operating at pressures above 1000 psig.

Vapors from emergency depressuring can be routed to a flare system, to special vapor blowdown facilities, or to the atmosphere. Flare systems are discussed in Chapter 15, Effluent Disposal Systems, and will be addressed in detail in the forthcoming *Guidelines for Handling of Emergency Relief Effluents* (CCPS, in progress). Vapor blowdown facilities are provided for high pressure systems to prevent equipment in these systems from excessive stresses that can lead to failure in emergency situations. The design premise is to reduce the pressure in the subject equipment from its operating pressure to 50% of its design pressure (API RP 521). Control valves in depressuring service must be designed to fail in a way to minimize the overall hazards arising from total utilities failure. Auto-refrigeration effects must be considered when high pressure systems are depressured into lower pressure systems.

14.8 REFERENCES

14.8.1 Regulations, Codes of Practice, and Industry Standards

The editions that were in effect when these *Guidelines* were written are indicated below. Because standards and codes are subject to revision, users are encouraged to apply only the most recent edition.

API RP 520. *Sizing, Selection, and Installation of Pressure-Relieving Devices in Refineries. Part I, Sizing and Selection, 5th ed., July 1990, and Part II, Installation, 3rd ed., November 1988*. American Petroleum Institute, Washington, D.C.

API RP 521. 1990. *Guide for Pressure-Relieving and Depressuring Systems*, 3rd ed. American Petroleum Institute, Washington, D.C.

API STD 526. 1984. *Flanged Steel Safety Relief Valves*. American Petroleum Institute, Washington, D.C.

API STD 527. 1991. *Commercial Seat Tightness of Safety Relief Valves with Metal-to-Metal Seats*. Washington, D.C.

API STD 2000. 1992. *Venting Atmospheric and Low-Pressure Storage Tanks Nonrefrigerated and Refrigerated*. American Petroleum Institute, Washington, D.C.

API RPD 2001. 1984. *Fire Protection in Refineries*. American Petroleum Institute, Washington, D.C.

ASME. 1992. *Boiler and Pressure Vessel Code, Section I, Power Boilers, and Section VIII, Pressure Vessels.* American Society of Mechanical Engineers, New York.

ASME B31.1. 1992. *Power Piping.* American Society of Mechanical Engineers, New York. ANSI approved.

ASME B31.3. 1990. *Chemical Plant and Petroleum Refinery Piping.* American Society of Mechanical Engineers, New York. ANSI approved.

ASME. 1988. *Performance Test Code PTC-25, Safety and Relief Valves.* American Society of Mechanical Engineers, New York. ANSI approved.

29 CFR Part 1910 119. Process Safety Management of Highly Hazardous Chemicals, Explosives and Blasting Agents. *Federal Register*, February 24, 1992.

NFPA 30. 1990. *Flammable and Combustible Liquids Code.* National Fire Protection Association, Quincy, Massachusetts.

NFPA 69. 1986. *Explosion Prevention Systems.* National Fire Protection Association, Quincy, Massachusetts.

NFPA 70. 1993. *National Electrical Code.* National Fire Protection Association, Quincy, Massachusetts.

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- Complete prestartup training and assure that all documentation and spare parts are onsite prior to startup.
- Develop a systematic review and evaluation scheme that will validate the integrity of the BPCS and SIS through its life cycle.

9.4 ALARM SYSTEMS PHILOSOPHY

Development of the alarm system includes determining what parameters should be alarmed, how they should be alarmed, and how they should address operator response. Guidance is provided in publications from the Instrument Society of America, the Institute of Electrical and Electronic Engineers, the American Institute of Chemical Engineers, and the Institute of Chemical Engineers.

The need for stand-alone dedicated alarm systems, even where modern PES controls are implemented, continues for two primary reasons. First, with modern distributed control systems there is a tendency to overalarm. This overalarming tendency compromises the reliability and safety of an alarm system. Unless an alarm condition exists only rarely, it is almost certain to be disconnected or ignored. Dedicated annunciators help to ease operator comprehension of process unit status, particularly in a critical upset situation. Consequently, a dedicated, stand-alone annunciator has the ability to draw attention to specific alarm information and provides an important advantage over a corresponding cathode ray tube (CRT) alarm display. Priority alarm or time sequencing of alarms in PES time history is also useful to show the sequence of process variations.

The second primary factor contributing to the survival of stand-alone alarm systems is the desire to provide redundancy for critical alarm functions. Even if displayed on a CRT console, a separate annunciator display offers added security in the event of a CRT workstation failure.

9.5 SAFETY SYSTEM MAINTENANCE TESTING

Reliability and availability goals of safety systems should be taken into consideration during the design phase of the safety system when redundancy and failure modes are addressed. However, no safety system can be presumed to perform its intended function under abnormal conditions every time. In a normally operating continuous process, the safety components remain in one position over an extended period of time and may become fixed. It is therefore mandatory to conduct regularly scheduled testing to exercise these components periodically and thus ensure operation.

Safety system components typically are thought of as the initiating device (sensors), the interlock circuit and the final control device. However, a testing bypass device to facilitate periodic on-line testing of the safety components should also be considered an integral part of any safety system design for continuous processes. Testing bypass devices may not be necessary for safety system components in batch processes where the periodic testing can be carried out between the batches. Bypass switches can be provided in various combinations based on the safety system design and operational testing philosophy.

Testing bypass switches can be provided around process sensor inputs for on-line testing and maintenance purposes. It is prudent in such cases to provide redundant sensors, so that some system availability can be maintained while testing one of the sensors. In a microprocessor based system it is possible to bypass the inputs in the software program to allow the sensor testing. However, caution is recommended since software changes are not always readily visible to operating personnel and can be inadvertently left active thus corrupting the program logic. Switches can be provided as individual bypass switches per sensor input, as common bypass switches for multiple sensor inputs (of 2 out of 3 logic), or per unit.

It is imperative that administrative controls regarding bypass testing be clear and thorough so that bypassing occurs only when appropriate; all appropriate personnel are aware of the bypass status; and all systems are properly activated following testing and maintenance. In general, systems which are not user-friendly, or interfere with the work can be expected to be defeated. It is incumbent on the designer to set up simple reliable systems which will allow all normal operations, including startup and shutdown to occur safely.

Interlock logic can be tested by providing a bypass around the output relays or modules while simulating input action. Microprocessor based interlock logic, consisting of input, output, memory, processor and communication modules, are generally self diagnostic, at least in part, to identify major system faults.

Typically, the operation of the final control device cannot be fully tested as this will interrupt the process. However, some routine testing of the final control element can usually be carried out. If a physical process bypass or redundant equipment in parallel is provided, full testing is possible. In the case of the solenoid operated pneumatic device, the operation of the solenoid can be easily tested by providing a bypass around the pneumatic signal going to the final control device. In the case of the motor operated device, the operation of the power interrupt relay in the power supply circuit for the final control device is tested by providing a bypass switch in parallel to the power interrupt relay. If caution is exercised, it is also possible to partially move the final shutdown valve with solenoid and relay.

Testing of the entire safety system should be carried out routinely and by qualified personnel. A well defined test procedure should be developed which requires that proper records be maintained for auditing purposes and to identify problem areas so that corrective maintenance action can be taken.

9.6 IMPLEMENTING THE PROCESS CONTROL SYSTEM

As mentioned earlier, development of the PES requires a team approach, using chemical and safety engineering participation, as well as electronic and instrumentation expertise and operation and maintenance experience.

9.6.1 Process Control Design Team

While organizations vary in their makeup and titles, the following are considered typical positions for this discussion. The personnel listed would be supported by consultants, as required, to provide the required knowhow.

- Process Engineer—thoroughly understands the chemistry, unit operations, and the equipment used to carry out the operations. Responsible for flow sheet data, operating limits, design conditions for process equipment, etc.
- Instrument Engineer—thoroughly familiar with state-of-the-art measurement equipment, control systems, final control elements and their application to chemical process systems. Capable of designing control and interlock strategy.
- Process Hazards Engineer—familiar with the various qualitative and quantitative hazards analysis methods, as well as corporate policy for hazards management.
- Operations Representative—familiar with plant operating and safety practices and policies. Preferably the person who will be responsible for operating the process under design.
- Maintenance Representative—familiar with maintenance practices, equipment that plant personnel are familiar with, methods of testing and checkout of system components after they are commissioned. Preferably the person who will be responsible for maintaining the process equipment under design.
- Materials Engineer—familiar with corrosion problems of the process materials and selection of suitable materials for measurement and final control equipment.
- Process dynamics consultant—capable of performing dynamic analysis of the process and control system. Verifies adequate hold up volumes for stable control, confirms control strategy design.

9.6.2 General Process Information

Several process related considerations may need to be resolved between the process engineer and the instrument engineer, such as:

- Material balance
- Energy balance
- Mitigation of hazardous events
- Product quality
- Energy consumption

The following is a partial list of information the instrument engineer requires from the process engineer in order to provide a good process control system:

- Flow sheet data (max/min flows, temperature, pressure, etc.) for all streams containing instruments. Note that all these streams are frequently not included on flow diagrams.
- Required turndown (minimum operating flows). Many incidents have occurred due to undetected flows below flowmeter low range points that appear to the control system as zero flow rate.
- Stream conditions under abnormal operations. Will the flowing stream remain conductive at all times? Will there be significant changes in viscosity, freezing points, or condensation points? What unusual thermal expansion properties may occur? What methods are planned to thaw frozen lines and equipment. Sensors and final control elements must be suitable for the extreme conditions.
- What are the limits of acceptable quality and what measurements indicate that this quality is being maintained? Where a complex analyzer is used to assure an acceptable product quality, every effort must be made to back this up with more common measurements of process conditions such as a relationship between temperature and pressure. The process engineer can provide good guidance in this area.
- What are the limits of safe operation (temperatures, pressures, flow ratios, etc.)? What independent, diverse measurements are available to sense an approach to these unsafe conditions?

Note that it is assumed at this stage of design all efforts to provide an inherently safe process system as discussed in Chapter 2 have been expended.

The process engineer must provide valve sizing data such as the pressure drop available to each control valve at maximum and minimum flow rates. The process engineer must understand that all excess flow as the result of safety factors (not included in pressure drop calculations and pump specifications) must be absorbed by the control valve.

9.6.3 Process Hazard Identification and System Specification

Process hazards considerations to be resolved by the process engineer, instrument engineer, process hazards engineer, operations representative and maintenance representative are as follows:

- Identify all potential hazardous events.
- Evaluate the level of risk for each hazardous event (consequences/frequency) see Figure 9-4.
- Is a SIS required?
- What is the integrity level required for the acceptable mitigation of each hazardous event?
- Does the SIS coupled with other noninstrument independent safety layers meet corporate risk management guidelines?
- At the initial meeting on this subject, establish timing and personnel to be involved in later hazard review activities; see Figure 9-5 for an example scenario.
- Note that process hazards assessment activities are applicable, regardless of the level of technology. These activities are not the result of using PES's although the complex methods of these systems must be considered.

9.6.4 Process Control Dynamics

Control dynamics considerations to be resolved by the process engineer, instrument engineer, and process dynamics consultant are:

- In continuous processes, are hold up volumes adequate for stable control?
- Are measurement dead times small enough for good control (sensing element location, equipment arrangement, equipment type, etc.)?
- Is control strategy sound?
- Is cycle time of programmable systems adequate for fast control loops?
- Are required operator actions sufficiently complex that a training simulator may be required?
- Does the control strategy provide a complete energy and material balance, such that the operator does not have to change a number of controller set points when changing throughput (production rate).

9.6.5 Materials of Construction

Materials of construction of piping and equipment are clearly defined early on in the design effort. The components of sensors and final control elements, however, are frequently not available in these same materials. The materials engineer provides guidance in determining which of the available materials

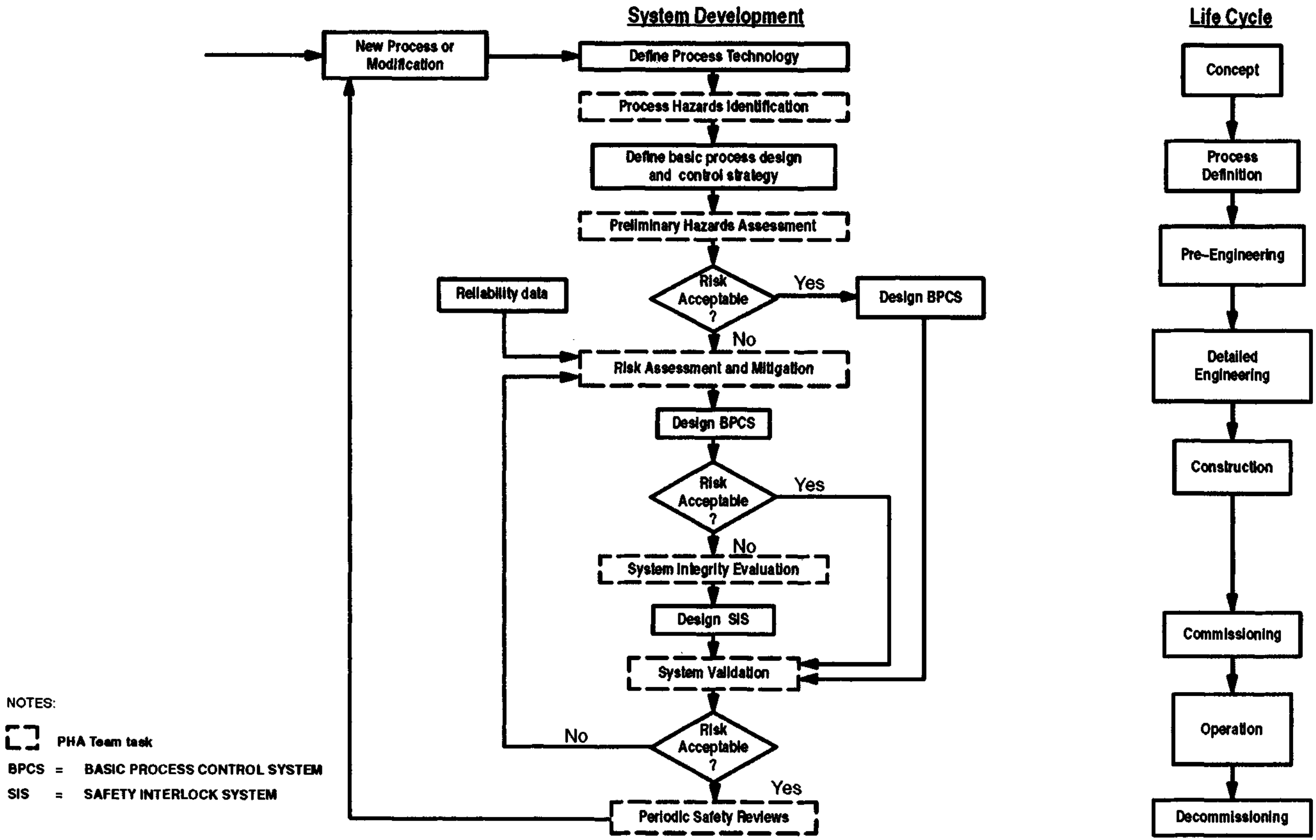
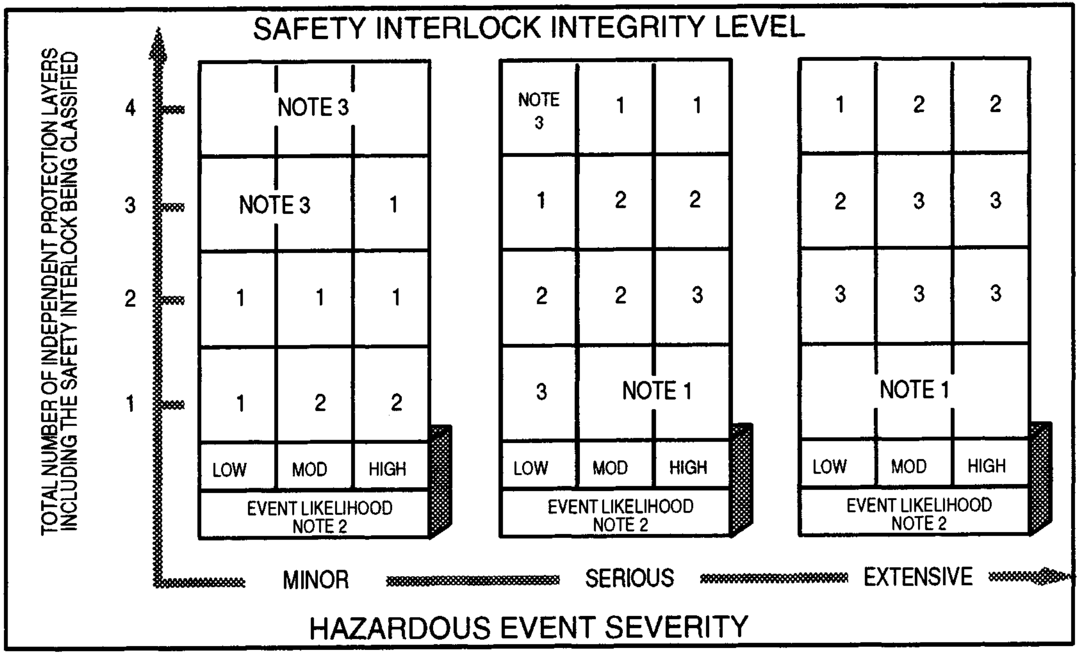


Figure 9-4 Process hazard analysis activities during process life cycle (Drake and Thurston 1992).



MINOR

	LOW	MOD	HIGH
4	NOTE 3		
3	NOTE 3		1
2	1	1	1
1	1	2	2

SERIOUS

	LOW	MOD	HIGH
4	NOTE 3	1	1
3	1	2	2
2	2	2	3
1	3	NOTE 1	

EXTENSIVE

	LOW	MOD	HIGH
4	1	2	2
3	2	3	3
2	3	3	3
1	NOTE 1		

NOTES:

1. One Level 3 Safety Interlock does not provide sufficient risk reduction at this risk level. Additional IPL's are required.
2. Event Likelihood – Likelihood that the hazardous event occurs without the SIS IPL in service.
3. SIS IPL is probably not needed.

IPL = Independent Protective Layer
SIS = Safety Interlock System

Figure 9-5 Linkage of process risk to SIS integrity classifications (Drake and Thurston 1992).

are suitable. Materials of construction requirements are to be resolved by the process engineer, instrument engineer, and the materials engineer.

The process engineer must provide guidance as to unusual conditions such as clean-out materials or temperatures of clean-out fluids that may influence materials selection. The process engineer can also provide the reasons for certain material requirements. For example, 304L and 316L stainless steels are frequently specified for piping to minimize problems associated with field welding. Instrument components are frequently not available in these materials, but since the instruments are not welded in the field standard 304 and 316 stainless steel, which are commonly available, may be adequate. The materials engineers can provide answers in these areas.

9.6.6 Operational Requirements

Operational requirements to be resolved by the process engineer, instrument engineer, and operations representatives include:

- Location of central control room—it should not be located near hazardous process equipment or storage facilities for hazardous materials.
- Local versus remote start-up, operation and shutdown of each piece of equipment. Assure adequate readout/adjust facilities where required. Encourage remote operation where safety is not compromised.
- Standard control/monitoring strategy for motors.
- Automatic versus operator-assisted start-up/shutdown.
- Procedure for bringing the process system to a safe state on the loss of control room equipment (CRT/keyboards of the PES).
- Review control strategies and other operating requirements in detail to assure thorough understanding by operations personnel.

9.6.7 Maintenance Requirements

Maintenance requirements to be resolved by the process engineer, instrument engineer operations representative and maintenance representative are:

- Is the system design and installation compatible with plant maintenance procedures?
- Does the design include adequate features for testing the SIS?
- Is the equipment being specified compatible with existing equipment that plant personnel are familiar with?
- Is there an adequate maintenance training program for new types of equipment?
- Are detailed procedures in place for making changes to the BPCS and SIS?
- Are detailed procedures in place for bypassing safety as well as sequential interlocks?

- Are detailed test procedures in place for verifying the proper operation of the BPCS and SIS prior to initial operation and following maintenance shutdowns?

9.6.8 Miscellaneous Considerations

Many other considerations go into the development, design, checkout, operation and maintenance of a process control system.

9.6.8.1 Basic Process Control System (BPCS)

Some miscellaneous considerations for development of the BPCS are:

- Use high quality, mature equipment. The frequency of occurrence of hazardous events is related to the probability of failure on demand of the SIS and the frequency of demands put on the SIS. Since failures or malfunctions of the BPCS frequently put demands on the SIS, only first quality components should be employed along with the utmost care in design, installation, checkout, and maintenance.

  Much has been written on the importance of SISs, however, their fundamental purpose (the ability to reduce the frequency of hazardous events) is significantly affected by the performance of the BPCS. Use only high quality material equipment.
- Minimize the variety of system components in order to minimize training and spare parts costs over the life of the facility. The use of more expensive components that have a broader area of application frequently results in the lowest life cycle cost.
- Maximize the use of override (constraint) controls. These will permit an operation to function at a lower throughput versus an interlock shutdown. The use of Programmable Electronic Systems (PES) has minimized the cost of this type of control feature.
- Compare safety-related analyzer readings to simple measurements where possible. Where on-line analyzers are used in control loops, try to use the combination of simple measurements (temperature, pressure, flow ratio) as a check on the reading of the on-line analyzer. If simple measurements indicate the analyzer reading may be in error, it probably is.
- Make comparisons between controller (proportional–integral–derivative, PID) output signals and measured variables. Deviations from normal provide prompt indications of problems with the measurement or the final control element.
- Provide control strategy to assure that the process does not operate below the limit of flowmeters. Where set points cannot be limited above flowmeter minimums, configure slight negative limits on flow set points and zero limits on flow readings to assure full down scale integration of the controller output on zero set point conditions.

- Verify shutdown conditions. Use verification of known shutdown conditions as a permissive for each restart (flowmeters and differential pressures equal zero, valves with limit switches verified in their proper shutdown position, etc.) These design features reduce the mean time to detection of failures.
- The facility should not be considered "started up" until all control functions perform properly in the automatic mode without routine adjustments by the operators. Performance of the system should be monitored by logging transfers to manual control, set point adjustments, etc.
- It must be kept in mind that in recent years advances in control systems (DCS, PLC, computers) have significantly outpaced those in sensors, final elements, and process equipment. The power of these systems should be utilized where applicable to monitor, compare, and make routine calculations that will assist in determining errors and malfunctions in the field instruments and process equipment.
- Where experience or judgement indicates certain measurements will be difficult with frequent false readings, multiple sensors should be provided with appropriate control strategy (2 out of 3 voting).
- Where PESs are used, avoid unnecessary upgrades of software or firmware. Most of these "upgrades" initially contain new problems and defects. Where upgrades are necessary, allow adequate time for the software to mature before implementing. Do not upgrade BPCS and SIS at the same time. The BPCS upgrade should be done before the SIS upgrade.
- System design, installation, and checkout must be carefully monitored for errors or omissions that lead to subtle, internally undetectable errors in measuring instruments such as the following:
  —Improper slope (pockets) in impulse lines.
  —Impulse lines not maintained full or empty (depending on design) during all possible process and ambient conditions.
  —Lack of, or failure of, freeze protection.
  —Loss of purge.
- Check and recheck for faults that result in subtle errors in measurements.

9.6.8.2 *Safety Interlock System (SIS)*

The considerations that were listed above for the BPCS which also apply to the SIS, are:

- Use high quality, mature equipment.
- Minimize equipment variety.
- Compare safety related analyzer readings with simple measurements where possible.
- Verify shutdown conditions.

- Use multiple components where needed for adequate attainment (2 out of 3 voting).
- Avoid unnecessary upgrades of software or firmware. Do not upgrade BPCS and SIS at the same time; the SIS upgrade should follow BPCS upgrade.
- Check and recheck for faults that result in subtle errors in measurements.

For the SIS, some additional considerations are discussed below.

Each independent protection layer in the SIS (independent sensor, control function, and final control element) should provide a minimum of a 100 fold improvement in the probability of failure on demand. That is, one layer will have one failure for each 100 demands, two independent layers protecting against the same hazardous event will have one failure for each 10,000 demands. Probability for one layer is 10^{-2} or 0.01; for two layers, the probability is 10^{-4} or 0.0001. Expressed as availability, one layer = 0.9; two independent layers = 0.9999.

A thorough checkout of the SIS cannot be overemphasized. It is critical that the final check be made with the system connected together in its final configuration and location. Partial tests, such as a factory acceptance test of a PES, do not assure proper operation of the SIS. These partial tests establish responsibility for SIS component failures, but a collection of partial tests do not assure proper system operation.

SIS operation should always be automatic. In other words, proper operation does not depend on the action of any person when an abnormal condition is sensed. Systems that rely on an operator taking a prescribed action in response to an alarm are not independent protection layers in the context of SIS design. Some operator actions may be considered a protection layer in the context of overall mitigation of an event, but they should not be considered with the SIS.

The SIS must be designed to meet the integrity level established by the Process Hazards Assessment Team for the hazardous events requiring mitigation. Examples of SIS structures for 3 integrity levels are shown in Figure 9-6. The following features should be employed when applying these examples:

- For integrity level 1, a single logic solver is shown. This may be a simple relay or a PES. If a PES is used, the processor should be redundant since it serves a large number of I/O points.
- For integrity level 2, system redundancy of sensors, logic solvers, and final elements is applied based on experience and judgement. PES logic solvers should have redundant processors.
- For integrity level 3, redundant sensors, logic solvers, and final elements are required. Sensor and final elements should be diverse, where diversity does not compromise performance. If logic solvers are PES, they should have redundant processors and the PESs should be diverse.

A controversial subject that receives much discussion is the sharing of components between the SIS and the BPCS. It is strongly recommended that logic solvers for the SIS and BPCS be independent (no BPCS functions performed in the SIS logic solver, and no SIS functions performed in the BPCS logic solver). Although *Safe Automation Guidelines* (CCPS 1993) recommends that the SIS and BPCS be physically and functionally separate, there may be some disadvantages that must be considered.

The sharing of sensors and final elements offers advantages and disadvantages. For example, a failure of a sensor may put a demand on the SIS (if an upscale measurement is hazardous, a failure of the sensor downscale will cause the BPCS to put a demand on the SIS). This can be offset by using both the upscale value and an unreasonably low reading to cause a shutdown trip.

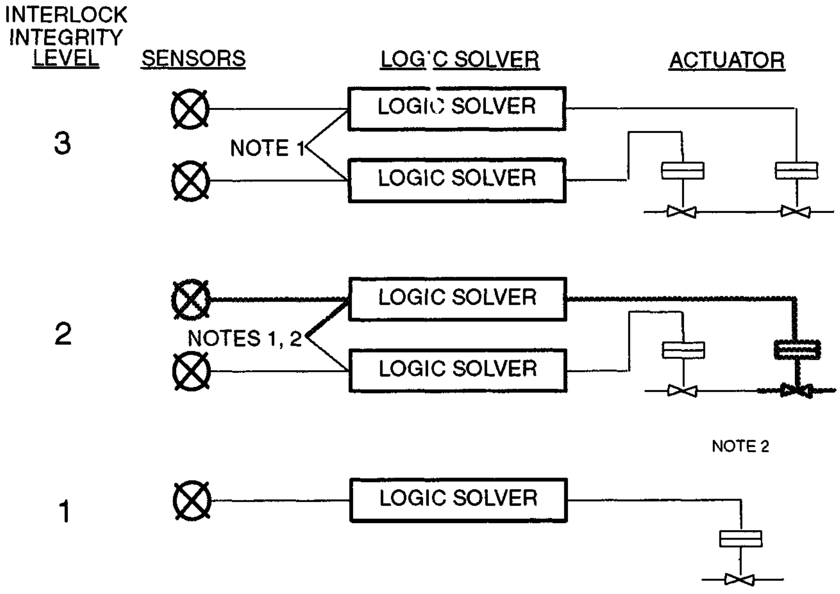
An advantage of sharing sensors and final elements is the significant reduction in the mean time to detect a failure of these components, since the failure will immediately show up in improper performance in the BPCS control loop. It is recommended that sensors and final elements be shared under any of the following conditions:

- In addition to the SIS layer of integrity level 1 or 2 (see Figure 9-6) where only a single sensor or final element is used, there exist an independent physical protection layer such as a relief valve or dike (see Figure 9-2).
- Where two sensors or final elements are employed as in integrity level 3 (see Figure 9-6). In this case one of the two sensors or final elements may be shared.

Note that as in any design approach, this "sharing" must be deemed appropriate by the Process Hazards Assessment Team. For example, if a final element is to be shared, the Team must concur that adequate shutoff will be achieved using the BPCS final element.

During the design development, equipment specification, selection and installation, the concept of the interlock "loop" or "chain" must continually be kept in mind. This "chain" is depicted schematically in Figure 9-7. Its purpose is to show that the ability of the chain of components to lift the weight is limited by the weakest link in the chain. Figure 9-8 illustrates the folly of paying excessive attention to specific links in the chain. In recent years much attention has been paid to the PES portion of the chain due to the complexity of possible failure modes, etc. This attention has led many designers to employ very high levels of security in the PES equipment with little attention being paid to field devices, wiring practices, etc.

A common potential for hazardous events that is frequently either overlooked, or given inadequate attention in process system design is backflow of one stream into another under abnormal operating conditions or equipment malfunction. This type of malfunction can result in more serious events than those initiated by process malfunctions, especially where the backflow occurs



INTERLOCK LEVEL	AVAILABILITY RANGE
3	0.999 to 0.9999
2	about 0.999
1	about 0.99

NOTES:

1. Redundant sensor values are available to each logic solver for diagostic purposes.
2. Sensor, logic solver, and/or final element may be redundant as availability needs dictate.

Figure 9-6 Examples of SIS structures (Drake and Thurstone 1992).

into utility systems, such as cooling water, inert gas, or instrument air. Dependence on check valves must be carefully analyzed by the Process Hazards Analysis Team for adequacy. Generally some form of instrumented protection is employed in addition to check valves when backflow can result in serious events. Some common approaches are flowmeters, where flow is continuous from one system to another, or differential pressure measurement operating single automatic valves, or double block and bleed valve assemblies.

9.6.9 Practical Considerations

In the main, chemical process BPCSs and SISs are designed to actuate a trip action when deenergized. In other words, the circuits are normally energized, and loss of power, broken wires, or unmade connections will cause a system shutdown or prevent start-up. Certain rare applications may require energize-

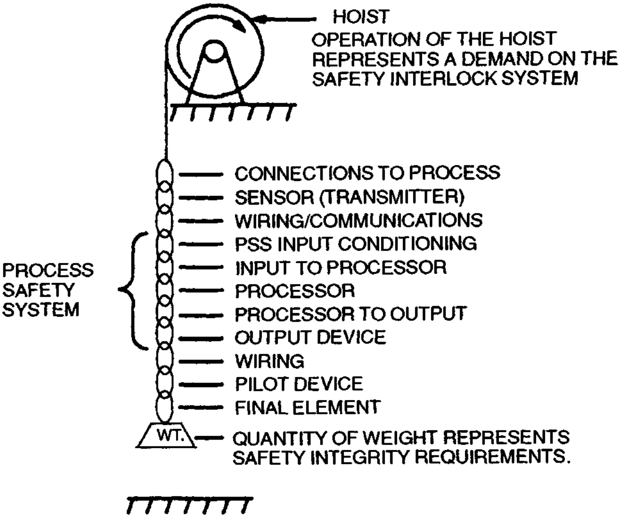


Figure 9-7 Schematic chain of elements (links) that must perform for successful interlock action (lift weight on demand) (Greshofsky 1992).

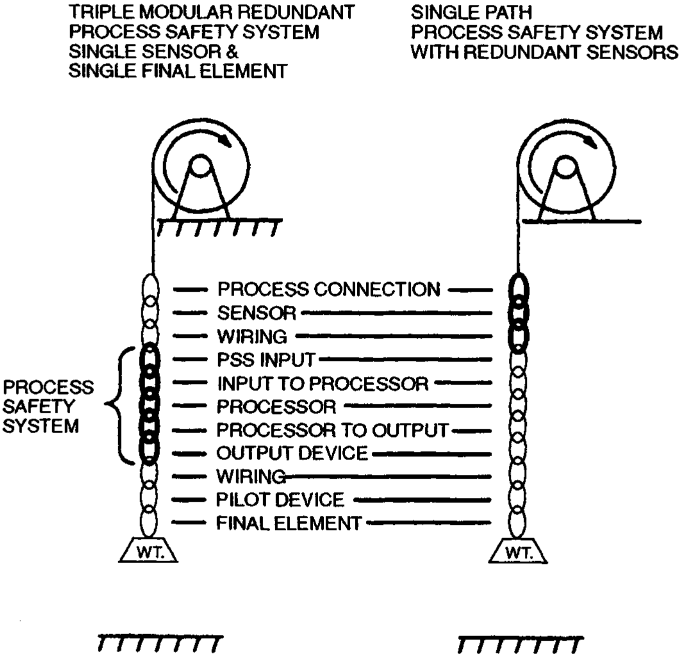


Figure 9-8. Two examples of inconsistent interlock chains (Greshofsky 1992).

to-trip systems (where the final element is energized to drive it to a safe state). Energize-to-trip systems require extensive analysis and special design features such as circuit monitoring for continuity, very high reliability power supplies, and rigid procedures to be followed on loss of power and/or circuit continuity.

Another common potential for a hazardous event is the chemical reactor. Some considerations are offered to address potentially hazardous situations:

For runaway reactions due to

(*a*) *misloading the reactor (too much material, wrong material, too little solvent), consider:*

1. Diversity and redundancy in instrumentation.
2. Small feed tanks or pre-mix tanks.
3. Minimizing manual additions.
4. Preventing operators from inserting out of range values as set points.
5. Bubble tight shutoff of valves. Use block valves, not control valves, for shutoff.
6. User-friendly control panels to indicate reactor sequence.

(*b*) *insufficient cooling (loss of coolant, loss of heat transfer), consider:*

1. Heat balance using temperature and flowrate of coolant.
2. Closed loop jacket systems; they maintain better heat transfer, but have some control lag.
3. Computer simulation of reaction and cooling loop before operation.
4. Direct injection of coolant in case circulation loop fails (i.e., pump failure).
5. Monitor cooling media control valves for maximum open condition.
6. Use constraint control. That is, if any critical process variable exceeds certain values, take action.

(*c*) *loss of agitation, consider:*

1. Monitoring agitation with sensor located below shaft coupling that joins motor to agitator.
2. Interlocking reactant shutoff valves with agitator.
3. Backing up agitator drive systems for critical agitation requirements (i.e., polymerizations).
4. Developing emergency procedures for agitator failure (i.e., what action should be taken if failure occurs).

For loss of containment due to

(*a*) *equipment or piping leaks, consider:*

1. Testing reactor with pressure or vacuum prior to start up.
2. Using ambient air monitors for hazardous or flammable materials.
3. Using "air-to-open" reactor bottom valve with air bleed off when closed.
4. Determining the effect of coolant leak into the reactor or reactants into coolant.

(*b*) *overpressurization, consider:*

1. Monitor relief devices (burst disk indicators, temperature, pressure).
2. Shutdown sequence well designed and regularly tested.
3. Relief system designed and maintained to prevent plugging.
4. Vent relief to safe location.
5. Proper supports and restraints for relief system piping.

For reaction(s) occurring outside the reactor due to ***backflow of reactants, consider*****:**

1. Backflow prevention equipment or instruments.
2. Regulation (or limit) of pressure levels in feed lines and reactor.

9.6.10 Example of BPCS/SIS Design to Achieve Class 3 Integrity

Description of Process—Reactants A and B are mixed in proper proportions. Refer to Figure 9-9. High temperature downstream of mixer indicates a hazardous condition which can result in injury to personnel and/or significant environmental impact. Shutting off Reactant B mitigates the hazard.

Assumptions—Process Hazards Assessment Team indicates an integrity level 3 system is required to meet corporate policy for the mitigation of the potential hazardous event. The Team has determined that the modulating control valve in stream B is an adequate final element for the SIS.

System Design Features

- The SIS consists of redundant sensors, logic solvers, and final elements.
- Valve closed switches verify proper operation of final elements on trip by the SIS.
- Sensors are monitored and continuously compared in the BPCS.
- SIS relay operation is monitored in the BPCS.
- Malfunctions sensed by the BPCS (flow ratio deviations) shuts off stream "B" via soft switch driving 4–20 mA output signal to zero.
- Either SIS output closes both valves in stream "B."
- Following BPCS or SIS trip, system must be manually reset by operator (logic not shown in Figure 9-9).
- Temperatures may be used in the BPCS to provide override action to avert a SIS trip.
- SIS logic solvers are diverse (PES versus relay). If two PESs are used for the SIS logic solvers, they must be obtained from different manufacturers or a different vintage if from the same manufacturer.

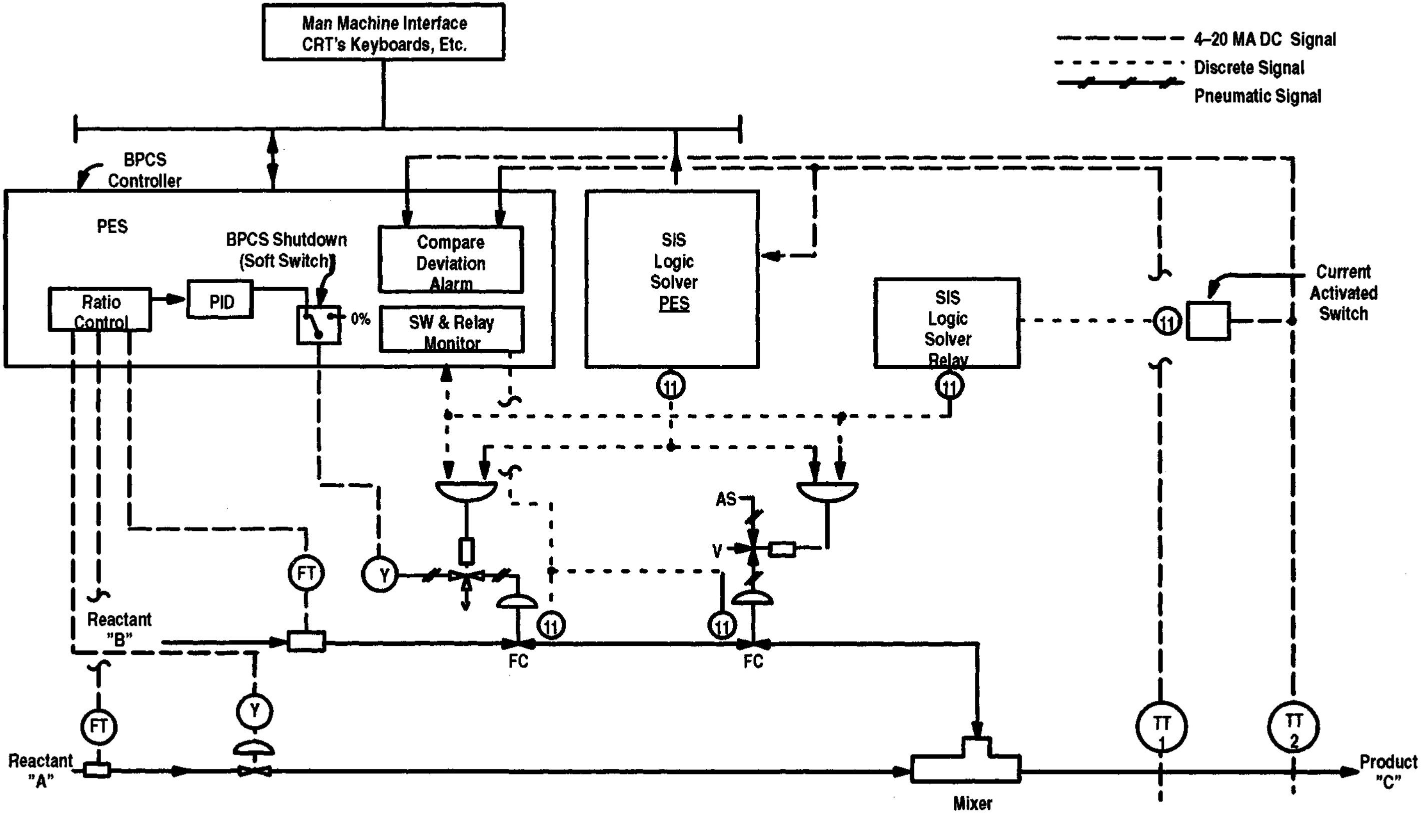


Figure 9-9 Example of integrity level 3 SIS function. (See text for description.) (Greshofsky (1992.)

- The PES logic solver and the BPCS controller may be the same type of hardware; however, no BPCS functions are performed in the SIS logic solver, and no SIS functions are performed in the BPCS controller.
- System is de-energized to trip. Valves in stream "B" close on electrical power failure, air failure, or open circuits to solenoid valves.

9.7 SUMMARY

For detailed guidance on improving safety in both the basic process control system and the safety interlock system, consult *Guidelines for Safe Automation of Chemical Processes* (CCPS 1993). The primary emphasis is on programmable electronic systems, but the principles may be applied to all types of control system hardware. The HSE (1987) report on programmable electronic systems includes several detailed checklists for use in design of computer-based systems. Appendices 9A and 9B (adapted from CCPS 1992b) beginning on the facing page illustrate the types of checklists that many design groups have developed.

Some important aspects of control and instrument systems, from a safety viewpoint, are:

1. Allocation of supervisory roles between operator and automatic control systems must be analyzed.
2. Each design should be checked in detail for the need of an elaborate instrumentation system based on potential hazards and operating difficulties. Before deciding to provide an elaborate system to combat the hazards, determine whether the hazards can be reduced by changing the basic process design.
3. The control and instrumentation design philosophy should be clearly defined early in the design process. The philosophy includes process characteristics and disturbances, the plant operational constraints, the scope of control systems, the role of plant operations, and the administration of fault conditions.
4. The design philosophy should also cover monitoring instrumentation, display, hard-wired alarms, protective systems, interlocks, trips, emergency isolation and use of manual/analog computer control.
5. Measurements should be taken from the correct location and of the variable of direct interest.
6. If a measurement variable is used to initiate an interlock or trip action, redundant measurements should be used for normal control and for a trip or alarm.
8. The fail-safe design of equipment such as control and solenoid valves (in case of failure of signal, instrument air or electricity) should be based on overall process consequences. This methodology, however, should not discourage design approaches that tend to minimize false trips provided no aspect of safety is compromised.

9. Proper performance and reliability specifications for critical instruments should be defined and assessed quantitatively if possible. Reliability estimates should include the practices that the operators adopt in their use of instrumentation.
10. The control system should also take into account startup and shutdown conditions when large process deviations are often encountered.

APPENDIX 9-A SAFETY CONSIDERATIONS FOR MONITORING AND CONTROL

These issues may need to be considered in design of computer-based systems:

Key Process Interlocks

- Ensure agitator is operating before reactant is added to prevent overpressurization
- Ensure a minimum temperature is achieved before the next chemical is added to prevent a buildup of reactants and delayed exothermic reaction
- Ensure dryer fans are operating to remove residual flammable vapors generated in process

Shutdowns

- High temperature or high pressure alarm, stop flow, activate cooling on coils, etc., to bring about safe shutdown
- Vibration switches on cooling tower fans
- High temperature shutdown on oil lubricated air compressors (more than 100 psig) to prevent fires or explosions
- Chemical short-stop addition system to immediately stop reaction
- Vibration monitors, alarms, and shutdowns on high speed machinery
- Mushroom buttons, pull cords, pressure sensitive pads, proximity switches on machinery to provide emergency manual shutdown

Monitoring

- Manual temperature or pressure gauges to indicate condition of batch during power outage
- Alternate power source (battery or generator) for sensitive equipment during power outage
- Alternate power source (battery or generator) for critical instruments during power outage
- Redundant instrumentation on very critical parameters: temperature, pH, pressure, oxygen content
- Alignment (cold settings) of machinery.
- Method to log key settings (pressure switches, timers, expansion joints, etc.) after start-up

Analyzers
- Oxygen analyzers to ensure inert stream to flare or furnace
- Oxygen (percent) analyzer to monitor nitrogen generating station for quality of inerting gas
- Oxygen analyzer to ensure adequate oxygen to prevent polymerization or formation of by-product
- Flammable gas analyzer to trigger alarms for spills in process areas or sewers or to activate ventilation system
- Calibration of the units with the known concentrations of the gas(es) being monitored

Computers and Programmable Controllers
- Alternate power source to prevent memory loss during power outage
- "Key" control to prevent unauthorized program changes
- Approval hierarchy and procedure for process (program) changes
- Safe storage of back-up programs
- Documentation procedure to monitor portion of computer program bypassed during trouble-shooting
- Display and trend recording of key safety related variables
- Emergency conversion from computer to normal instrument control mode

Sight Glasses
- Pressure type glasses require periodic adjustment to minimize weepage
- "Push-to-activate" light behind sight glass

Electrical Equipment in Hazardous Areas
- Pressurized system may require a low-pressure, time-delayed alarm
- Provision for continuous air flow or low pressure alarm on control cabinets in classified areas
- Sealing of conduit lines from hazardous to nonhazardous areas to prevent transmission of flammable vapors through conduit to ignition sources

Back-up Systems
- Emergency blower to maintain positive flow to flare
- Self-contained nitrogen or air systems to open dump valves during emergency
- Inert gas to provide mixing (sparging) on power loss

Occupational Safety Issues
- Interlocked gates to prevent accessibility to rotary and double cone dryers in caged areas
- Access hatches on centrifuges interlocked to power or motion
- Interlocked covers and openings on hazardous machinery such as blenders, mills, conveyors. (Adapted from: CCPS 1992b, Appendix 8F)

APPENDIX 9-B INSTRUMENTATION AND CONTROL CHECKLIST

1. What hazards will develop if all types of motive power used in instrumentation should fail nearly simultaneously?
2. In the event that all instruments fail simultaneously, is the collective operation fail-safe?
3. What provision is made for process safety when (a) an instrument, critical to process safety as well as in process control, is taken out of service for maintenance? (b) an instrument goes through a dead time period for standardization or when, for some other reason, the instrument reading is not available?
4. What has been done to minimize response time lag in instruments directly or indirectly significant to process safety? Is every significant instrument or control device backed up by an independent instrument or control operating in an entirely different manner? In critical processes, are these first two methods of control backed up by a third ultimate safety shutdown?
5. Has the process safety function of instrumentation been considered integrally with the process control function throughout plant design?
6. How are highly exothermic reactions protected by dual, independent instrumentation, including alarms and interlocks?
7. What is being done to verify that instrument packages are properly installed? Grounded?
8. What are the effects of extremes of atmospheric humidity and temperature on instrumentation?
9. What gauges, meters, recorders cannot be read easily? What modifications are being made to cope with or solve this problem?
10. Is the system completely free of sight glasses or direct reading liquid level gauges or other devices which, if broken, could allow escape of the materials in the system?
11. What procedures have been established to test and prove instrument functions?
12. What periodic testing to check performance and potential malfunction is scheduled?

(Adapted from *Plant Guidelines,* CCPS 1992b, Appendix 13D; a similar list appears as ISA-SP84, Draft 10)

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9.8.1 Regulations, Codes of Practice and Industry Standards

The editions that were in effect when these *Guidelines* were written are indicated below. Because standards and codes are subject to revision, users are encouraged to apply only the most recent edition.

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8

THERMAL INSULATION

Protection against external fire with thermal insulation can make the difference between a sustainable loss and a catastrophe. However, corrosion under wet thermal insulation can often be a route to a serious accident. Many cryogenic processing units have experienced process piping failures from external corrosion, particularly where the piping was in intermittent use. In 1989, a major chemical company replaced a Type 300 series steel column at a multimillion dollar cost, because of corrosion under wet thermal insulation (Pollack and Steely, 1990). These are but two examples of a phenomenon that is receiving increasing attention from safety review teams.

Insulation may be applied to a surface to perform one or more functions such as temperature control (heat conservation or freeze protection), personnel protection, condensation prevention, or sound attenuation. The major process safety issues related to thermal insulation are:

- fire exposure protection of equipment and piping
- corrosion under wet insulation
- spontaneous ignition of insulation wet with flammable or combustible liquids

This chapter will discuss how these process safety considerations are affected by the properties of insulation, such as thermal performance, moisture absorption, and fire resistance.

8.1 PROPERTIES OF THERMAL INSULATION

8.1.1 Thermal Performance

Insulation is used to prevent heat loss or gain for process control and it is often necessary for the protected process system to function properly. For example, if a process fluid condenses or freezes or vaporizes in a line, a hazardous condition may exist, such as overpressurization, loss of process control or runaway reaction. For calculating heat transfer rates and determining simple heat loss or gain, guidelines are published (ASTM, Standard C680). Computer programs are available to aid the engineer in selecting the optimum thickness based on a predetermined set of parameters such as energy costs, local usage rates and capital costs. Insulation is also applied to protect workers from injury; however, personnel protection is outside the scope of these *Guidelines.*

8.1.2 Absorption of Liquids

Absorption of moisture or process liquids can lead to a hazardous condition, such as lowered thermal performance, corrosion under wet insulation or a fire if the absorbed liquid is flammable. Corrosion problems created by moisture absorption are so significant that they are discussed separately in Section 8.3.

Thermal performance is impaired when the insulation material is wet. Moisture can enter insulation material through a break in the weather barrier, by a leak in steam trace tubing, or by a process leak in the insulated system. When the air spaces in insulation become filled with water or other liquid, the insulation's conductivity approaches that of the liquid. For example, the conductivity of water at 70°F is 4.1 Btu in/ft^2 hr compared to 0.17 for air. This makes the transmission of heat across each space approximately 24 times greater when saturated with water as when dry (Malloy 1969).

While some insulation materials can regain thermal performance after being dried out, in others, such as calcium silicate, the moisture may never be completely driven away. Some insulation materials, such as some expanded perlites, may be treated with water repellents. If the liquid absorbed is a chemical product, it can create more problems than loss of thermal performance. Some chemicals can react with the resins or binders in the insulation to cause degradation. Combustibles and some flammable liquids, such as organic heat transfer fluids and other oils, may be absorbed in porous insulation and self-heat to the point of self-ignition (Britton 1991, Britton and Clem 1991). Test methods have been developed that can be used to determine the minimum spontaneous ignition temperature of liquid/insulation combinations involving isothermal heating of liquid-soaked cubes of insulation.

Systems that are heat traced with a heat transfer fluid require additional precautions to prevent the fluid from leaking into the insulation. Generally, oversize insulation covers both piping and tracer. Since the tracing lines are hidden by the insulation, leaks may go undetected.

Increased weight of wet insulation systems should be addressed in design of support structures, pipe racks, etc., since some insulation materials can absorb more than twice their dry weight in fluid.

8.1.3 Fire Safety

Fire safety is related to three major properties of insulation:

- combustibility of the insulation itself
- combustibility of absorbed liquids
- integrity during fire

For maximum safety, insulation should be noncombustible, nonabsorptive, and nonmelting. Insulation materials that increase the facility's combustibility should be avoided. Avoid using plastic foam insulation materials of the polyisocyanurate type. Some plastic foam insulation materials that emit toxic gases when subjected to fire are prohibited in some locations. Insulation materials are tested according to ASTM E-84 for flame spread and smoke development. Insulation systems can be tested according to ASTM E-119 to determine their resistance to a slowly developing fire. The conditions specified in ASTM E-119 may not truly reflect fire exposure from burning highly flammable/combustible liquids, such as hydrocarbons. Other methods to test fire resistance have been developed (Britton and Clem 1991).

Absorption of flammable material creates a fire hazard even when the insulation itself is noncombustible. Spontaneous insulation fires may occur when a combustible liquid leaks into porous insulation and reaches a temperature where runaway self-heating occurs (Britton 1991). The insulation provides a large contact surface for reaction and a lower heat loss environment, where the temperature will rise until autoignition occurs, usually only smoldering. However, sudden influx of air during efforts to remove the smoldering insulation is often the cause of a fire. Green and Dressel (1989) give an excellent introduction to the problem of heat transfer fluid fires. An option is to install nonabsorbing insulation, such as cellular glass for a short distance on both sides of locations (such as flanges) where leaks are likely to occur. Other options are to provide means to carry away leakage, or to eliminate the source of the leakage.

The abilities to withstand high temperature exposure, combustion and smoke development are desirable qualities in an insulation system. Fire resistant insulation material will not only be fire safe; it will also provide fire protection for the insulated component. In this role, the insulation minimizes the heat transfer to the protected surface and minimizes the potential for failure of the equipment and subsequent release of fuel or hazardous materials. Fire resistance is an alternative to the use of other protective systems such as sprinklers or physical barriers to protect critical systems in the plant.

As used in this chapter, fire protection and fire endurance refer to the ability of the insulation system to protect equipment from an external fire. Fire resistance refers to the ability of the material to resist transfer of heat from a fire to the other side. Resistance is defined by fire resistance ratings (consult NFPA 15 and NFPA 251). Insulation used for fire protection is also covered in Chapter 16, Fire Protection.

The fire envelope refers to the area where flame impinges on equipment or structures. API RP 520 and 521 define the "fire exposed area." In addition to "fireproofing" the structure in these areas, it is considered appropriate to use fire resistive insulation systems on critical components in these areas, even though they may not contain flammable liquids. Fire protective insulation of electrical and instrumentation cabling can be important, since loss of power or control signals can result in disablement of emergency response equipment and controls.

Fire resistant thermal insulation may be used to protect vessels, critical equipment, and piping that is subject to exposure to external fire. The insulation serves to:

- Lower the rate of heat input and boiling of liquid inside piping and equipment. For nonreactive systems, this allows the use of a smaller pressure relief device and reduces the quantity of any hazardous effluent that might have to be handled and disposed of, and it allows additional time to evacuate the contents.
- Insulate heat-sensitive and/or reactive chemicals from excessive temperature rise.
- Protect the structural integrity of vessels and piping by limiting the maximum temperature of the outer wall, for example, the vessel wall in the vapor space, or the outer wall of a double-walled insulated vessel.

8.1.4 Fabrication

Some insulation materials perform well thermally, but are difficult to fabricate; they do not form well to the substrate or to adjoining insulation sections, or shrink after application and leave gaps in the system. These gaps cause "hot spots" on the jacketing surface or cold spots on hot process temperature systems. Poor insulation fit-up and the resulting problems can be reduced if the chosen insulation material is fabricated to standard dimensions and is tested for linear shrinkage and dimensional stability at the conditions for which it is being specified. In addition, allowances should be made for the differential expansion between the pipe and the insulation.

Determination of linear shrinkage and dimensional stability for high temperature insulation may be conducted using methods given in ASTM C356. Other ASTM guidelines address fabrication tolerances both in the manufacturers' shops and at the job site (ASTM C585) and various types and shapes of insulation covers. If the insulation is being fabricated at the job site, a quality assurance program is critical.

8.1.5 Durability

If the insulation does not hold up well in service, the thermal performance and ultimately the safety of the whole system can be affected. Insulation that is crushed or torn may allow a heat flow path or expose the equipment or piping surface to outside elements such as fire, moisture or corrosive atmospheres. For example, if insulation is damaged on a high temperature line where cabling or instrument tubing runs in close proximity, the tubing could become overheated and fail.

Insulation is frequently damaged by foot traffic. It is strongly recommended that means of access such as catwalks or manlifts be provided wherever possible to allow maintenance of equipment without damaging the insulation.

Excessive vibration affects both the insulation and the substrate. The substrate may also be subjected to wear by some insulation materials. Fiber-type insulation containing short fibers is prone to degradation from excessive vibration. In cellular glass and foam type insulation, wear is controlled by the application of an antiabrasive compound or a layer of fibrous insulation to the inside surface of the foam insulation before it is applied to the substrate. Antiabrasive coatings are available in solvent/resin types (good for low to moderate temperatures) and water-base types for use in higher temperatures.

8.2 SELECTION OF INSULATION SYSTEM MATERIALS

For optimum thermal performance, the selection of material is the key factor. However, the choice is not as simple as selecting the material with the lowest thermal conductivity. After materials engineers and piping designers have made preliminary choices of materials, the process engineer/safety engineer should look at safety issues of the system as a whole.

Thermal insulation, usually as blocks or batts, provides for thermal efficiency as well as fire protection. Cementitious materials, usually applied wet and activated by fire exposure can be used for fire protection when thermal efficiency in normal operations is not important. Wright and Fryer (1981) present a good summary of fire protection materials options.

Insulation systems (including jacket, banding, and supports) commonly installed on piping and equipment for reactive chemical service for the purpose of fire protection should incorporate the following features:

- A noncombustible inorganic insulation material such as calcium silicate or cellular glass
- Double layer construction with all joints staggered
- High melting point jacketing
- Well-secured jacketing, typically by stainless steel bands.

High melting point jacketing may be stainless steel or other lower cost jacketing materials developed as alternates. One such material is a sheet steel product with a coating of corrosion-resistant aluminum-zinc alloy applied by a continuous hot dipping process.

ASTM C795 identifies requirements for insulation materials acceptable for use over austenitic stainless steel including corrosion testing and chemical analysis.

Insulation containing sodium silicate in high concentrations (relative to chloride ion) may be used to inhibit corrosion.

8.3 CORROSION UNDER WET THERMAL INSULATION

Corrosion under wet thermal insulation is recognized as a major problem. Corrosion is often the initiating event for loss of containment, fire, or explosion. Because the corrosion is hidden, it is usually not discovered until it's too late. Ironically, both the causes and methods of prevention are relatively simple and have been known for years. Selection of thermal insulation has become routine but potential for deficiencies in fabrication and installation still occurs. For example, a serious problem occurred on a multistoried column subjected to monthly testing of the firewater high pressure spray. The metal weather-jacketing system was not designed to be impenetrable to the upward spray of the system (Pollack and Steely 1990).

8.3.1 Contributing Factors

Materials of construction for piping and equipment are usually selected based on the internal environment, that is, the process fluids they will contain. Selection of insulation also must consider the external environment, that is, vapors or fluids, such as rainfall, process fluids and corrosive gases, that may be absorbed by the insulation. The combination of physical and chemical factors in the environment will accelerate corrosion.

8.3.1.1 Service Temperature

The primary temperature range for corrosion is probably 60 to 82°C (140 to 180°F). At higher temperatures, the corrosion rate is higher even though water is driven off faster. High temperatures can cause localized, very aggressive corrosion at points of evaporation. Corrosion occurs even at lower temperatures; Therefore, it needs to be considered at all service temperatures.

8.3.1.2 Intermittent and Cyclic Service (Temperature Transition)

In high temperature systems when the water is driven from the insulation, salts collect and may result in very aggressive corrosion when the location is rewetted. In low temperature systems, thawing locations exist that typically stay wet, creating localized corrosion. Both thawing and vaporizing transition zones exist on vessel and pipe nozzles, clips, and skirts. Even on the body of a single piece of equipment, the temperature may range from below to above freezing, creating a temperature transition zone.

Corrosion problems are intensified by the cyclical nature of process operations. Service cycles cause temperature cycles and temperature transition zones. Many insulated items spend time in a down cycle, for maintenance or for other reasons. When the equipment cycles down, insulation that typically conserves heat can absorb moisture that corrodes the steel until the unit is again hot and drives the water off.

Sometimes the process itself is cyclic, with frequent variations, and consequently the corrosion potential is greater. Since no insulation system can be considered completely waterproof, the surface beneath the insulation can be intermittently wet and dry. At localized points of water intrusion or evaporation, the system is subject to severe, localized attack, due to concentration of salt upon evaporation.

8.3.1.3 *Equipment Design*

In the past, equipment design typically assumed that vapor barriers would remain intact; they do not. New designs can include vapor barrier improvements to keep water out, and methods such as drains and vents to let moisture escape. Attachment of nozzles, clips, and insulation must be designed to control moisture into and out of the insulation.

Certain designs contribute to especially corrosive situations. The location of vents and drains, along with faulty sealing methods, allow water entry (and often retention). Size reductions in towers create water trap potentials. Corrosion is likely to occur where fluids or salts could accumulate (Figure 8-1) such as:

- Attachments to piping and process equipment (e.g., support brackets).
- Piping and instrumentation connections, especially vertical segments.
- Unsealed or damaged jacketing (or removed for inspection)
- Low points, especially if jacketing is damaged above the low point.
- Bottom of absorbent insulation.
- Dead legs.
- On vertical equipment where support stiffener rings protrude outside insulation.

System designs must include proximity studies to assure insulation does not interfere with adjacent pipe, equipment, or structures.

8.3.1.4 *Materials of Construction of Piping and Equipment*

Selection of materials, based on process considerations, has become fairly routine, as discussed in Chapter 5, Materials Selection. Materials known to be susceptible to corrosion are usually treated with appropriate coatings or insulation. However, the process engineer must critically analyze, and communicate to the materials engineer, any ambient conditions that might cause external corrosion. These ambient conditions include atmospheric conditions in the plant as well as the insulation material itself.

Austenitic stainless steels are susceptible to stress corrosion cracking (SCC) (see Chapter 5, Material Selection, for more on SCC). This problem is most

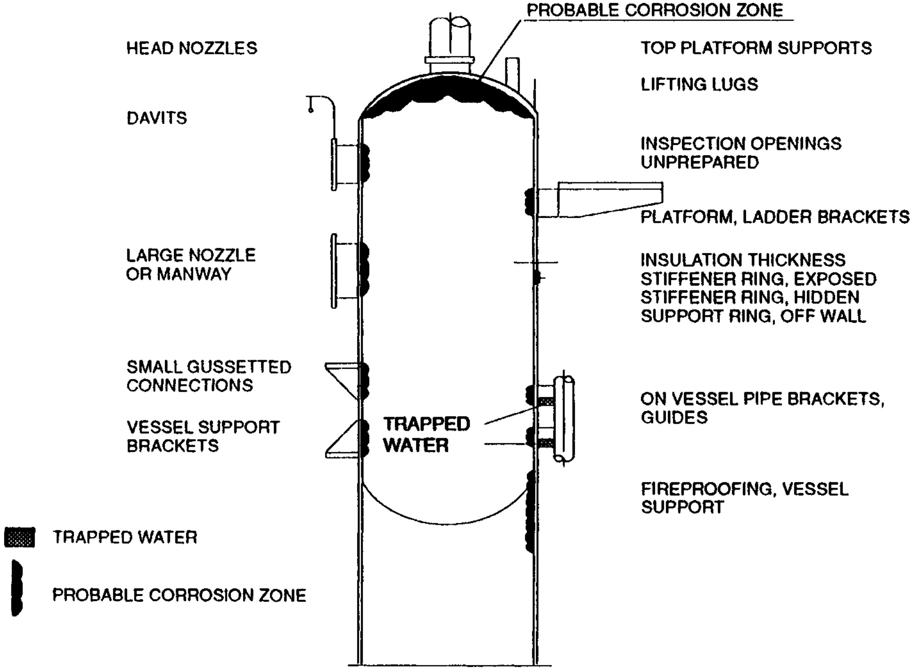

Figure 8-1 Areas where corrosion under insulation is likely to occur.

prominent in process plants located in coastal areas and those producing chloride-containing chemicals. Some commonly used insulation materials contain a small amount of leachable chloride ion that might contribute to this type of corrosion if water is allowed to enter the insulation system. What is more important, chloride ions can enter the insulation system either from rain, water washdown of equipment, fire protection deluge water, or from chloride absorbed from the plant atmosphere. Abrasion-resistant coatings used on cellular glass insulation, labels, and paints are other potential sources of chloride ion that can induce SCC under insulation, as are polyvinyl chloride or other plastics containing chlorides.

SCC is more likely to occur if the temperature of the stainless steel is between about 60 and 121°C (140 to 250°F). Cycling temperature conditions appear to increase the potential for SCC, because water ingress and retention of the chlorides are more likely under these conditions.

8.3.1.5 Climate

Proximity to airborne salt is the primary problem; plants on the sea coast are more prone to problems. The facility itself may provide a source of moisture and contaminants (such as cooling tower fallout areas). Olefins plants with subambient conditions can result in condensation dripping which creates an unfavorable climate, especially when airborne salts can be washed from adjacent equipment into insulation.

8.3.1.6 Material Stress Conditions

Residual stresses from fabrication are typically relieved by some sort of thermal stress relief. However, certain fabrication techniques leave steel in as-fabricated conditions. The cold bending of pipe for noncorrosive service (as defined by process material contained) reduces initial fabrication costs significantly for smaller (8 inch and under) diameter pipe, but leaves residual stresses that can cause galvanic attack of the outer diameter of the stressed part. Stainless steels typically have sufficient residual stresses from fabrication so that chlorides will cause severe cracking above 60°C (140°F).

8.3.2 Prevention of Corrosion

The primary methods of preventing corrosion under wet insulation are preventing the entry of water into the system and protecting the surface of the piping or equipment. Since no insulation system can be presumed to be entirely waterproof, protective coatings are extremely important in preventing corrosion. Methods to reduce corrosion under insulation are also listed in Table 8-1. Additional methods of corrosion prevention are discussed in Chapter 5, Material Selection.

Table 8-1 Design Practices to Reduce Corrosion Under Insulation

- Incorporate the following corrosion prevention design measures. Avoid primary reliance on mastic seals and caulking as a weather barrier, both of which tend to dry with age and exposure to elevated temperatures. Weather-proofing jacketing should be designed such that natural runoff will occur. Nozzles, manways, ladder and lifting lug clips, platform angle iron mounts, bleeder valves, fittings, valves, etc., should be designed for all connections to be outside the insulation.
- Use insulating materials which contain low concentrations of chlorides or other contaminants that might induce SCC of stainless steel piping and equipment.
- Inspection ports which are designed for water-tight construction are available to allow for corrosion inspection of the substrate.
- To minimize galvanic corrosion, avoid direct contact between dissimilar metals by coating the parts with insulating coatings or petrolatum tape.
- Most insulating materials contain, or can absorb moisture in storage and installation. If a tight, impermeable weather barrier is installed over such insulation, and then placed in hot service, the moisture should be allowed to evaporate through release vents.

8.3.2.1 Preventing Entry of Water

Installing and maintaining flashing and caulking at structural or piping penetrations of the insulation is used to prevent water ingress. The condition of the insulation sealant can determine whether corrosion occurs under the insulation. Hydroscopic insulation must be carefully maintained at joints. Although keeping water out is effective in preventing corrosion, it is very difficult to do consistently (ASTM 880).

8.3.2.2 Protective Coatings

Corrosion problems are most prevalent on insulated steel surfaces operating in the temperature range of 60 to 121°C (140 to 250°F). For this service, the immersion grade epoxy-phenolics and amine-cured coal tar epoxies are frequently used, depending on the operating temperature. Proper preparation of the surface is critical in determining how well the protective coating works. Surface preparation and protective coatings should be used on all stainless steel piping and equipment used in critical systems.

For protecting insulated surfaces from 130 to 540°C (270 to 1,000°F), a NACE Publication (1989) describes coating systems and tapes that are chemically resistant to humid environments containing chlorides and sulfides. Although corrosion may be reduced at very low temperatures, it can be appreciable at intermediate temperatures in the range of –45 to 2°C (–50 to 35°F). For these temperatures, NACE provides recommendations for suitable coating materials as well as surface preparation and application methods required for reliable performance.

Piping systems that run very hot are often not painted; intermittent service then leads to very high corrosion potential. Field construction welds are often made where the pipe was prepainted; these locations are often omitted when the rest of the system is painted, but corrosion attack at these locations can often be severe.

8.3.3 Inspection Programs

Inspection programs to detect corrosion are an important feature of maintenance of insulation materials and the equipment. Dressel et al. (1991) describe nondestructive testing methods to look for corrosion. Design of the process system should facilitate inspection. Unfortunately, removal of insulation to inspect for corrosion may allow moisture to enter the system. To avoid repeated repair, removable and replaceable insulation should be used on items like valves, which require frequent (more than 6 times per year) maintenance (Britton and Clem 1991). The objective is to maintain the integrity of the insulation system to prevent entry of moisture.

Personnel exposure to hazardous components of insulation is a complex issue and beyond the scope of these *Guidelines*. OSHA and EPA regulations should be consulted.

8.4 REFERENCES

8.4.1 Regulations, Code of Practice, and Industry Standards

The editions that were in effect when these *Guidelines* were written are indicated below. Because standards and codes are subject to revision, users are encouraged to apply only the most recent edition.

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6

PIPING SYSTEMS

On a Saturday afternoon in 1974 a vapor cloud explosion occurred in the reactor section of the caprolactam plant at the Flixborough Works (U.K.). Inside the plant, 28 people were killed and another 36 were injured. Injuries and damage were widespread outside the Works. "The cause of the Flixborough disaster was a modification to a 28 inch pipe connection between two reactors.... The modification involved the installation of a temporary 20 inch pipe with bellows at each end. The design of the pipe system was defective in that it did not take into account the bending moments on the pipe due to the pressure in it. The bellows were not installed in accordance with the manufacturer's instructions. The pipework assembly was not adequately supported. The relevant British Standards, notably BS 3351 and 3974, were not followed" (Lees 1980). Further details and additional references are given in Appendix 1 of Lees' book. The Flixborough disaster was by far the most serious accident that had occurred for many years in the U.K. and was instrumental in the development of hazard analysis and loss prevention techniques.

6.1 INTRODUCTION

The foundation for safe piping design is provided by the codes and standards that are available throughout the industrial community. Engineers select applicable codes and standards as the minimum requirements for the design of a safe chemical facility. There are many sound and accepted industrial standards and codes throughout the world, but this chapter will focus on those used in the United States.

"Loss of containment from a pressure system generally occurs not from pressure vessels but from pipework and associated fittings. It is important, therefore, to pay at least as much attention to the pipework as to the vessels" (Lees 1980). The purpose of this chapter is to provide information on safe engineering practices in the areas of detailed piping and valve specifications, piping flexibility analysis, piping supports, special piping materials of construction and maintenance in accordance with the proper ASME B31 code. The chapter will focus on process lines carrying hazardous materials.

Codes of practice and standards address the solutions to common problems, but establish only minimum design, fabrication, testing, and examination requirements for average service. Many circumstances relating to service, operation, materials and fabrication, inspection or unusual design deserve special consideration if the resulting piping systems are to operate safely and be reasonably free from frequent maintenance. Standards and codes of practice related to the safe design of piping are the following codes issued by American Society of Mechanical Engineers (ASME); those also approved by American National Standards Institute (ANSI) are indicated with an asterisk:

B31.1*	Power Piping
B31.2	Fuel Gas Piping
B31.3*	Chemical Plant and Petroleum Refinery Piping
B31.4*	Liquid Transportation Systems for Hydrocarbons, Liquid Petroleum Gas, Anhydrous Ammonia, and Alcohols
B31.5*	Refrigeration Piping
B31.8*	Gas Transmission and Distribution Piping Systems
B31.9*	Building Service Piping
B31.11*	Slurry Transportation Piping Systems

These various sections provide different margins of safety for pressure piping systems, based on service considerations and industry experience.

Of all the ASME B31 series piping codes, only ASME B31.3 clearly defines special requirements for toxic fluid services. The code defines Category M Fluid Service as that which has the potential for serious harm to personnel. A single exposure to a very small quantity of a toxic fluid, caused by leakage, can produce irreversible harm to persons by inhalation or bodily contact, even when prompt restorative measures are taken. The owner of a chemical facility must designate which, if any, chemicals are designated Category M. B31.3 Code provides the designer with a basic set of requirements that will, when properly applied, aid the designer in achieving a design suitable for the intended purpose. Additional requirements may be necessary to complete the engineering design and ensure a safe, reliable system. The impact of designating the fluid service as Category M should be factored into the cost estimate, as many of the requirements are more stringent than those for general fluid service.

6.2 DETAILED SPECIFICATION

Early in the design stages of any project, the process engineer transmits information to the piping specifications personnel. Much of this is standard process data, but it is critical as a starting point for preparing the project piping specifications (Nayyar 1992). Such information includes:

- Process fluids/materials (influences materials of construction, gaskets, joint design, sealing materials, etc.)

- Ranges of temperatures and pressures (influences line flange class, pipe wall thickness, materials of construction, gaskets, sealing material, piping flexibility, etc.)
- Flow conditions or criteria such as two-phase flow, high pressure drop valves (for noise and vibration considerations), corrosive or erosive fluid properties, or high velocity situations
- Special valving needs (such as plug or vee-ball, and VOC emission control valves)

In addition to transmitting the above information, the experienced process engineer should also review the process flow diagram with the piping and material specialist in order to address as many considerations as possible prior to development of the detailed design. The piping material specialist can then specify piping details within the piping specifications through detailed commodity codes. This allows such things as special gaskets, seal or trim materials, special pipe bends or branch connections to be automatically purchased in bulk from a bill of material. Thus, detailed analysis of each single piping element is addressed without requiring potentially inexperienced engineers to identify all potential equipment or material limitations. Appendices 6A and 6B are examples of piping design checklists.

Normally the materials specialist or process design engineer is responsible for specifying materials of construction for the piping system. The process engineer must supply the materials specialist with all anticipated design process conditions, including any "upset" conditions.

6.2.1 ASME B31.3 Code Restrictions

There are code restrictions on selection of materials (Chapter V). Examples of code restrictions from ASME B31.3, para. 323.4.2, are:

- Ductile iron shall not be used for pressure-containing parts at temperatures below –20°F (–29°C) or above 650°F (343°C). Austenitic ductile iron is used for low temperatures.
- A 571 stainless steel shall not be used below –320°F (–196°C).
- Cast iron shall not be used above ground within process unit boundaries in hydrocarbon or other flammable fluid service at temperatures above 300°F (149°C) nor at gauge pressure above 150 psi (1030 kPa). In other locations the pressure limit shall be 400 psi (2760 kPa).
- Malleable iron shall not be used in any fluid service at temperatures below –20°F (–29°C) or above 650°F (343°C) and shall not be used in flammable fluid service at temperatures above 300°F (149°C) nor at gauge pressures above 400 psi (2760 kPa).
- High silicon iron (14.5% Si) shall not be used in flammable fluid service.
- Lead and tin and their alloys shall not be used in flammable fluid services.

6.2.2 Categorizing Process Services

Fluid parameters and other parameters which could affect the safety and operation of the piping system include:

- Flowing medium chemistry, pressure, temperature, velocity, viscosity, density, specific gravity, system contaminants, catalysts, hydrotest water
- Type of flow, e.g., turbulent, laminar, flashing, cavitating or two-phase
- Pipe orientation, e.g., horizontal, vertical, or inclined
- Valve stem, handwheel, and operator orientation
- Anticipated localized conditions, such as overpressurization due to inadvertent line isolation and unrelieved thermal expansion

As noted for many other performance requirements, all system operating conditions and combinations of conditions, such as normal, startup, shutdown, standby, abnormal/upset, emergency, and test must be taken into account. Some systems may have several different modes of operation, and could be exposed to different conditions, depending upon system configuration and the phase of plant operation. Operating transients, such as pressure surges or thermal stresses, may be created during startup, shutdown or reconfiguration. The potential for overpressurization may occur during isolation of a portion of the system as noted above. Unique configuration or setups may be used during system flushing and performance testing and should be considered.

Fluid transients occur when systems are started or stopped, flow is increased or decreased, components malfunction, or thermal conditions change. For example, relief valves, check valves, and fast-acting flow control and isolation valves can produce pipeline forces and moments that should be considered in piping system design. Of concern are dynamic fluid effects such as pressure transients, flashing and cavitation, column separation, and thermal shock initiated from operation of either the valve or the system. Many fluid transients can be eliminated or minimized by system design and/or operating procedures.

Particulates may cause excessive seat leakage and permanent damage to the valve seat or disc. Contaminants may cause piping corrosion or erosion.

6.2.3 Problems Associated with Special Materials

6.2.3.1 Thermoplastic Pipe

Special materials, such as thermoplastics, should be limited in use to situations where temperature and pressure extremes are not encountered. The use of nonmetallic piping requires consideration of:

Temperature

- Do not locate in areas of high or low temperature extremes
- Techniques for applying adhesive and joint makeup are affected by temperature
- For flammable fluid designs (fiber-reinforced plastic) FRP *pipe,* but not fittings, may be approved.

Pressure

- Prevent pressure surges
- Provide vacuum and overpressure relief
- Do not use for above ground compressed air

Other considerations

- Isolate from vibrating equipment
- Protect from sunlight (ultraviolet radiation effect)
- Only a limited number of standards have been developed for design and/or examination
- Piping constructed of nonmetallic materials may require more support; this requires input to and from other design groups
- Use of filament-wound reinforced thermosetting resins (i.e., FRP) requires the compatibility of the resin with process chemicals to ensure that neither the resin nor the process chemicals are degraded
- Installation may also require special preparation and handling to prevent damage
- Special joints, connectors and adhesives may be required

Mruk (1992) discusses the design, application, and installation of thermoplastic piping. Secondary containment is also available in fiberglass and thermoplastic systems (McCallion 1990).

6.2.3.2 *Plastic-Lined pipe*

Use of plastic-lined pipe requires consideration of these issues:

- Vacuum
- Installation/joining techniques
- Fire protection
- nondestructive examination (NDE) such as visual, liquid penetrant, and leak testing

Two potential problems with plastic-lined pipe that could lead to fires and explosions are: (1) they may leak badly at flanges and permeation vents, and (2) flange gaskets may not survive a fire (Bacchetti 1992). However, an available connection system for plastic-lined pipe may solve these potential hazards. It is a "high-integrity flange" which confines and directs the permeation vent. It also has a fire-safe metal seated backup to the flange gasket.

6.2.4 Double-Walled Piping

Double-walled piping is used to provide secondary containment for selected hazardous materials (McCallion 1990). Methods to detect leakage (and alarm devices) are installed between the two walls. Monitoring requirements are established by the EPA. The use of double-walled piping requires consideration of the following issues:

- Electrical grounding or continuity
- Support of the internal pipe to prevent sag
- Testing of the system
- Possible distortion due to differential thermal expansion

A handbook on double-walled containment piping has been written by Ziu (in progress) which provides details on design, fabrication, monitoring, and installation.

6.2.5 Above-ground versus Below-ground Piping

The choice of whether process piping runs should be above or below ground depends upon the impact or effect of leakage and the potential for catastrophic loss of containment. For instance, pipeline carrying a flammable fluid would be run underground to minimize potential vehicular impact. Double-walled piping is being used more frequently for belowground pipelines. Conversely, fluids for which leakage can represent environmental hazards are often run above ground where leakage can be readily detected.

6.2.6 Cathodic Protection—Effects of Grounding

Cathodic protection is discussed in Chapter 5. Care should be taken in designing cathodic protection since the desired effect can be defeated by improper grounding. This would be analogous to an electrical short circuit.

6.2.7 Jacketed or Heated Piping

Jacketed or heated piping is a design choice when the process fluid must be heated to prevent solidification and when close temperature control of the process fluid is required. Safety concerns include excessive thermal input when process flow stops, contamination of process fluid by heat transfer fluid, and problems of fatigue or stress introduced by thermal cycling or differential expansion.

Jacketed piping can be fabricated with full or partial jackets. Full jackets are used when maximum heat transfer is desired. Partial jackets should be used when there is the possibility that product contamination or danger of hazardous conditions could occur if the product in the main piping and the heating medium in the jacket were mixed, or where temperature control is not critical and localized hot spots would not be detrimental.

6.2.8 Velocity Criteria

Process and utilities piping are usually sized on the basis of economic criteria (optimum velocity and pressure drop). However, quite often, velocity limitations have to be imposed in order to avoid hazards which could occur because of the following conditions:

- corrosion
- erosion
- vibration
- noise
- water hammer
- static electricity

There is very little information in the open technical literature on velocity limitations. Most of the criteria used in industry are "rules of thumb" which have evolved from operating experience. The discussion below is based on design criteria obtained from a number of engineering contractors and chemical manufacturing companies (Grossel 1993).

6.2.8.1Corrosion, Erosion, and Vibration

Liquids. It has been found from experience that a number of liquid streams, both alkaline and acidic, can cause corrosion and erosion when flowing above certain velocities in carbon steel and even stainless steel pipe. Recommended velocities are given below for a number of commonly encountered streams.

Service	Definition	Maximum velocity (ft/sec)
Caustic	Solutions involving NaOH, KOH and water mixtures of these and hydrocarbons in which the caustic is more than 5% of	4
Concentrated H_2SO_4	Water solutions of 80% to 100% concentration by weight and mixtures in which the acid is 5% or more of the mixture by volume	4
Phenolic water	Solutions of 1% or more by volume	3
Aqueous amine solutions	MEA, DEA (CO_2 rich	10

Usually, liquid velocities are limited to 10 ft/sec in plastic- or rubber-lined piping to avoid excessive erosion.

In most liquid systems, erosion is not a problem for velocities under 20 ft/sec in metal piping. If a liquid contains small amounts of solids as contaminants (the liquid is not really a slurry) which may possibly cause erosion, fairly low velocities are recommended, i.e., less than 5 ft/sec.

Vapors and Gases. Erosion problems are not usually a concern with pure vapors or gases. Some companies, however, limit the vapor velocity in accordance with the following formula:

$$V = \frac{100}{\sqrt{\rho G}}$$

where V is velocity in ft/sec and ρ_G is gas or vapor density in lb/ft^3

Wet vapors, however, can sometimes cause erosion problems. For example, the following velocities are recommended by some engineering contractors:

Service	Maximum Velocity (ft/sec)
Wet phenolic vapors	60
Wet vacuum exhaust	450

Vapor–Liquid Mixtures

Two-phase (vapor–liquid) systems are often subject to erosion, especially in those process lines operating at high velocity flows in the annular or mist regimes. At least four correlations have been used by engineering contractors, which are as follows:

1. $\frac{\rho_{av} V_m}{9272} \leq 4$ for 6" and larger lines

   $\frac{\rho_{av} V_m}{9272} \leq 3.5$ for 4" pipes

   $\frac{\rho_{av} V_m}{9272} \leq 3.0$ for 3" pipes

2. $\rho_{av} V_m^3 \leq 45{,}000$ for all pipe sizes

3. $V_m \sqrt{\rho_{av}} \leq 100$ for all pipe sizes

where ρ_{av} is the weight average mixture density in lb/ft^3, and V_m is the mixture velocity in ft/sec

4. $V_m \leq \frac{160}{\sqrt{\rho_h}}$ for all pipe sizes

where $\rho_h = \rho_L\lambda + \rho_G(1 - \lambda)$, homogeneous mixture density, lb/ft^3

$$\lambda = \frac{Q_L}{Q_L + Q_G}; \qquad Q \text{ is volumetric flow rate in ft}^3/\text{sec}$$

6.2.8.2 Noise

Excessive piping noise will be avoided if velocities are kept below the following limits:

1. Liquids: $V \leq 30$ ft/sec
2. Gases and Vapors: $V \leq \frac{100}{\sqrt{\rho}}$

where V is velocity in ft/sec and ρ is vapor or vapor–liquid mixture density in lb/ft^3

6.2.8.3 Static Electricity

Certain hydrocarbons and organic chemicals can accumulate static electricity charges during their flow in piping which can then discharge at the terminus equipment, resulting in fires and explosions. Walmsley (1992) presents recommended velocities for hydrocarbon liquids flowing in piping which will minimize or eliminate these static electricity hazards.

6.2.9 Insulation

Corrosion under insulation and prevention (or detection) of leaks of flammable fluids are major safety issues. These topics are discussed in Chapter 8.

6.3 SPECIFYING VALVES TO INCREASE PROCESS SAFETY

The Code requirements for valves include ANSI B16.34, B16.5 and MSS Standards.

6.3.1 General Design Features

- The key to safe valve selection and installation lies in the generic specifications written for the plant, with specific requirements created only for well-defined purposes. The factors that need to be addressed in creating these specifications are discussed below.
- The service that the valve will perform (on/off, throttling, back-flow prevention, etc.), including the pressure drop and the amount of permissible leakage though the valve, will determine the type of valve (gate, ball, diaphragm, etc.) that can be used.

- The need to visually determine the operating position (open/closed) of the valve may also be a factor. Visual determination is evident on rising stem gate valves and quarter turn valves (butterfly, plug, and ball). Other types of valves may require indicator attachments to allow for visual identification.
- The process fluid conditions the valve must accommodate [chemicals, material phases (including solids), temperature, pressure, and flow rate] will determine the pressure and temperature class, end connection type, and the materials of construction for the valve body, internals, seat, trim, and seals/gaskets. Consideration of corrosion/erosion and temperature stress will be part of the determination.

These specifications may be altered by fire safety requirements where the valve must remain operational during a fire. These requirements may upgrade the material of construction or alter the type of valve used. For certain types of fire situations, specialized valves can be specified that have metal internals that expand at high temperatures to prevent material flow between the valve body and the internals. "Fire-safe" valves have the following design aspects: the component does not feed fuel to a fire through leaks to the atmosphere; the component is capable of stopping line flow (that is, fuel will not bypass the component); and the component will remain operable. These characteristics vary widely from manufacturer to manufacturer and there are several standards which can be applied. A useful table comparing several "fire-safe" test specifications was provided in a recent article by Hendrick (1990).

Regulatory limits on vapor leakage from valves will determine the stem packing requirements. For materials with little or no vapor pressure the standard compressible rope packings can be used. Vapor leakage may be addressed by providing a stuffing box and stem, or flexible graphite packing. Backseating the valves will relieve the load on the packing.

For materials that have appreciable vapor pressures, particularly for materials regulated under the EPA New Source Performance Standards (NSPS) fugitive emissions regulations, the newer low emissions packings developed by many of the valve manufacturers can be used to greatly reduce the level of emissions from the valve. Additionally, substituting one type of valve for the current one may also reduce emissions; nonrising stem gate valves (i.e., plug and ball types) leak less than rising stem (i.e., gate) valves. Substitution of one type for another must be carefully reviewed (i.e., nonrising stem valves have the valve stem subject to the fluid continually and internal threads can accumulate process residues (fines) which would hamper operation).

For those instances where no leakage can be tolerated for valve operations, bellows valves, diaphragm valves, and lantern (dual) seal valves can be specified. Diaphragm valves use a flexible membrane to control flow in the valve, bellows valves put an internal flexible bellows assembly attached to the valve body and the stem to seal off leakage, and lantern seal valves use dual stem packing with a lantern gland between them where a pressurized barrier fluid can be introduced. All three of these solutions have potential safety or environmental problems. The diaphragm valve's membrane can wear and eventually rupture allowing process materials into the valve body. The same holds true of bellows valves. The lantern seal valve requires that the seal fluid be compatible with the process as well as not creating a vapor leakage problem of its own. For any of these valve types it may be necessary to install monitoring equipment to detect leakage from the process side of the valve into the valve internals. For lantern seal valves it may be necessary to install a collection and treatment system to control the lantern fluid.

Generally, bellows seals prevent contamination of process fluids and prevent leaks. They are available to ANSI Class 600 through 1500; they have limited corrosion resistance, limited life cycle, and are difficult to clean for maintenance in case of a pinhole leak. Dual seal design allows for disposal of leaked material, allows for purge with inert gas or a specific fluid, allows testing, and has a longer cycle life equivalent to conventional single packing. Hydroformed bellows require a taller valve height which must be allowed for in layout.

Options that must be considered when specifying stem seals/packing include:

- Live loading (Belleville washers)
- Gasket material: consult manufacturer for suggested applications in acid, caustic, severe process hazards because material may soften or harden. Spiral wound graphite-filled gaskets are used for steam, hydrocarbon and general process conditions.
- Gasket style (laminated sheets, ring joint, spiral wound, metallic, envelope, etc.)

If secondary containment can't be provided for the entire piping system, consider containment of the flanges. A monitoring or leak detection system can be added. The leaks can be collected by a flange shield and routed to a collection device.

Check valves are used to prevent reverse flow, such as flow into a plant from storage vessels, reverse flow through a pump, and reverse flow from a reactor. "Reverse flow of one reactant from a reactor into the feed pipe of another reactant is likely in many cases to result in an explosion" (Lees 1980). Several incidents are described by Kletz (1976). Check valves are selected with consideration of service. Options include ball, piston, spring-loaded wafer, swing, tilting disc and intrinsically damped. Check valves are notorious for their poor reliability; the failure rate is very high. Hazardous services (where backflow can create a hazardous situation) should not depend totally on a check valve. Some positive backflow prevention device would then be required, such as instrumented backflow prevention.

The location of a valve should be selected to lessen the potential for two-phase flow. For example, a valve which has a high pressure drop on entry to a vessel which would result in two-phase flow should be located at the vessel inlet nozzle if possible to minimize vibration and avoid mechanical damage to the systems.

6.3.2 Maintenance and Operation

Maintenance issues include:

- Location for ease of access
- Provision for occasional lubrication and working to prevent "freeze up" and inspection or testing for leaks
- Accurate assembly of valves to interfacing hardware. This includes such issues as alignment, bolt load, tightening patterns, thread engagement, lubrication, distortion due to overtightening, etc.

6.3.3 Failure Modes

Valves may fail in-place, fail open, or fail closed. How they fail is really a process control issue; the failure of valves is discussed in Chapter 2. Manual valves generally "fail-in-place." An exception would be stem pullout from a gate valve where the gate may drop to a "closed" position (depending on physical orientation).

6.3.4 Emergency Isolation Valves

Emergency isolation valves are used to prevent the loss of large quantities of flammable or toxic materials. Large quantities of material are likely to be lost at pumps, drain points, and hose connections. Determination of whether to install an emergency isolation valve should consider inventory, the condition of the material, and the possibility of isolating the inventory by other means (Lees 1980). Loss of air, hydraulic, or electric power should not result in loss of operation of a valve. Fusible-link valves are often used to actuate valve closure in a fire condition.

6.4 JOINTS AND FLANGES

Welded joints will limit the number of points susceptible to leakage but these also pose problems when maintenance is required. Proper tightening of flange joints and selection of bolts and gaskets will lead to minimal leakage at flange joints.

6.4.1 Options for Joints and Flanges

Various types of joining methods are used:

- Welded fittings—the preferred method where fugitive emission control is a primary issue
- Quick connect—these should not be used in hazardous service
- Screwed or threaded—these are used primarily for instrumentation and maintenance and also for nonhazardous fluids. ASME B31.3 Code restricts size range based on fluid service.
- Bolted, flanged connections—For these connections, the raised face is typical; a ring type joint provides a better seal; and a ring type with smooth finish allows the least leakage.

In order to keep the joint tight and keep leakage to a minimum, the following issues may need to be considered:

- Specification of surface finish (e.g., smoother finish for hazardous or toxic materials; stock finish for general process)
- Choice of bolting materials
- Welding technique: weldneck flanges provide better alignment
- Imbedment and relaxation losses are inherent to a bolted, gasketed assembly, but can be compensated for
- Choice of gasket material and design. The trend is to the use of metallic spiral wound gaskets. However, these require proper installation or they can leak badly. Russell (1974) discusses problems with spiral-wound gaskets and installation requirements for safe operation.
- Installation procedure and inspection for leak tightness

6.4.2 Quick Connectors and Flexible Connectors (Hoses)

Ease of use by one person (no tools or only limited tools required) makes quick connectors convenient. However, the potential for leaks means they must be specified properly and used with care. Special ends may be used on hoses to avoid misconnections (see Chapter 4). Dry disconnect hose couplings are available and should be used for hazardous fluids.

Flexible connectors are quite often used in batch processing where hard piping may be too complex; they reduce the importance of alignment. However, they may tend to fail quickly due to wear, susceptibility to chemical attack, or fatigue of the hose material unless properly specified. Only metal flexible hoses should be used for hazardous fluids.

6.5 SUPPORT AND FLEXIBILITY

The term "pipe support" is used generically to encompass a whole range of integral and nonintegral pipe attachments, variable and constant spring hangers, sliding supports, rod hangers, shock suppressors, vibration dampeners, anchors, pipe support frames, etc. The purpose of pipe supports is to transmit the loads acting on piping systems to building structures or other structures.

6.5.1 Standard Design Issue: Types of Loads

Process piping may be subjected to the following load categories:

- *Dead loads* consisting of the weight of piping components, insulation, and normal contents
- *Thermal loads* due to:
  - —Free expansion or contraction of the piping system prevented by restraint or anchors
  - —Difference in expansion characteristics of the piping material
  - —Support, anchor and terminal movements resulting from the flexibility and/or thermal expansion of equipment, supports or anchors
- *Occasional loads* represented by one or more of the following:
  - —Impact forces caused by internal or external conditions such as changes in flow rate, hydraulic shock, liquid or solid slugging and flushing
  - —Wind-induced forces on exposed piping systems
  - —Earthquake-induced forces
  - —Vibration resulting from impact, pressure pulsation and resonance in compressors
  - —Forces due to let-down or discharge of fluids
  - —Recoil forces from explosion relief
- *Hydrostatic test loads*—loads imposed on a piping system as a result of hydrostatic testing.

ASME Code B31.3 stipulates that the piping layout and design of supports should be directed toward preventing the following:

- Leakage at joints
- Excessive piping sag in piping requiring drainage slope
- Unintentional disengagement of piping from its supports
- Excessive stresses in the supporting (or restraining) elements
- Resonance with imposed or fluid-induced vibrations
- Excessive interference with thermal expansion and contraction in piping which is otherwise adequately flexible
- Excessive forces and moments on connected equipment
- Piping stresses in excess of those permitted by the Code

A pipe or structure which is subjected to a temperature change will change its physical dimensions if it is free to do so. If the piping and/or structure is restrained from free dimensional change, it will be placed in a state of stress and will exert forces and moments on the restraints. Since most piping is connected to equipment at either end and held in position by supports (restraints) the basic problem in piping flexibility analysis is to determine the effect of the forces and moments. The conventional and preferred method of providing flexibility is to add sufficient piping to a configuration so that the forces to deflect the piping are reduced.

The loadings due to temperature change act simultaneously with the loading to maintain the pressure boundary and span the distance between supports. The piping codes use simplified formulas to determine the magnitude and effect of the loading. Actual exact stress values are not calculated for all operating conditions. Piping code design is based on both theory and testing. Many complex technical issues are simplified through the use of conservative limits. The variables and tolerances on the manufacturing and assembly of piping, components and equipment are addressed by safety factors. Different types of stresses have different degrees of significance. The significance is addressed by different allowables. The most important factors for the process engineer therefore must be the communication of the most severe service conditions that the piping and equipment will experience. These service conditions will control the material used and therefore the allowable stress values. The ASME B31.3 Code contains requirements and applications for thermal expansion data.

The codes use a concept called allowable stress range. The service life of a piping system is affected more by the range of stress variation than the magnitude of stress at a given time. Since piping systems usually are composed of components of different physical sizes, the smaller or thinner components become focal points for concern. These components may be thought of as the weakest links in the system. The codes logically direct attention to the most common susceptible areas. Standard industry practices provide guidance to the piping stress analyst to ensure adequate review of piping systems.

The designer must also consider the requirements for flexibility in special conditions:

- Steam purging, which may differ from standard operating conditions
- Hydrotesting
- Startup, when temperature may be higher than the operating temperature
- Startup, when attached equipment is cold
- Shutdown
- Cyclic conditions

- Process excursions
- Steam tracing
- Reactive force (recoil) of discharge on vessels
- Reactive forces of relief devices

The basic underlying concerns for some types of equipment are briefly described below:

- Centrifugal pumps, steam turbines, centrifugal compressors—excessive pipe loads cause equipment casing to distort. This creates misalignment between equipment and the driver and results in an early failure of the bearings.
- Fired heaters—restrictions imposed on the nozzle loads, particularly rotations, are dictated by consideration of clearances between the tubes and the refractory lining of the heater.
- Shell-and-Tube type heat exchangers—high pipe loads may cause excessive stresses in the exchanger shell.
- Flange leakage—certain flanges in hazardous areas may need to be analyzed for possible leakage. It should be realized that sometimes the bending moment required to cause the flange to "open up" is very small.

6.5.2 Expansion Joints

Flexibility may be provided by including in the piping system mechanical devices specifically designed to absorb expansion-induced piping movements through deformation of their components. It should be noted that the expansion joints should only be considered as the last resort, when all attempts to attain adequate piping flexibility through layout modifications have failed. In such cases, close monitoring of the conditions of the joints must be performed. The concerns that exist with regard to expansion joints are:

- Expansion joints tend to develop cracks when used to absorb large lateral deflections.
- They require additional anchors and guides in controlling thermal movements.
- Expansion joints should not be used in streams with high levels of particulates, although liner sleeves can mitigate this problem.

Examples of situations where expansion joints may be warranted are:

- Where adequate piping flexibility cannot be achieved due to the space limitations
- Where the pipe length has to be limited to minimize the pressure drop to satisfy process requirements

- Where reactions on the connected equipment are excessive and cannot be reduced by conventional means (pipe loops). This is commonly encountered when using equipment with fragile nozzles, such as graphite heat exchangers.
- Where mechanical vibrations need to be isolated
- Where design considerations outweigh the disadvantages of the expansion joints (low pressure, large diameter piping systems frequently fall into this category)

6.5.2.1 Classification, Selection and Application of Expansion Joints

There are several types of expansion joints used in the chemical industry. The selection of a particular type is dictated by the piping geometry and the amount and type of movement that the joint must accommodate. In order to select the appropriate expansion joint, the piping system must first be reviewed for the tentative location of the anchors. By means of anchors the piping system is segmented into simple, individually expanding configurations. The number of anchors is dictated by the complexity of the system, amount the thermal movement that a single expansion joint can absorb, the location of the branch connections and connected equipment, the availability of structural members, etc. It is usually advisable to simplify the system so that single and double expansion joints in straight axial movement can be used. In order to minimize the number of the expansion joints, the distance between anchors should be selected so as to utilize expansion joints with the maximum number of convolutions. In order for an expansion joint to adequately perform its intended function, the piping system, in addition to being anchored and supported, should be properly aligned by using piping guides. In systems containing expansion joints, pipe guides perform two functions: (*a*) to direct piping movements into the expansion joint, and (*b*) to prevent buckling of the line.

There are two principal types of expansion joints: packed type expansion joints and bellows type expansion joints. Since the packed type joints have not been extensively used for thermal expansion, only bellows type expansion joints will be discussed in this section. For a detailed discussion of the classification of expansion joints, see publications from the Expansion Joint Manufacturers Association, Inc. (EJMA).

In the process industry, most expansion joints utilize metal bellows. Bellows appear in a variety of shapes. The bellows convolutions (the smallest flexible unit of a bellows) are formed by thin sheet metal, usually stainless steel or Incoloy alloys. Special care should be exercised in the selection of material for metallic bellows due to the thinness of the metal subjected to high stresses and strains and possible corrosion attack. Use of a more corrosion resistant, stronger, or exotic material than specified pipe materials are required. Expansion joints made of Teflon are often used in highly corrosive environments.

Expansion joints are designed to sustain a permanent deformation at the rated movement. But if the number of movement cycles of the joint exceeds that for which the joint is designed, the bellows will fatigue. Conversely, an unrealistically high number of movement cycles used in the joint design may result in a joint so long that it is subject to squirm failure. Both are constrained by EJMA design requirements.

Liners or interval sleeves should be specified for expansion joints under the following conditions (Pathway):

- When pressure drop must be held to a minimum and smooth flow is desired
- When flow velocities are high and flow-induced vibration could prove harmful to the bellows.
- When turbulent flow is generated upstream of the expansion joint. Note: heavy gauge liners may be required.
- When there is a possibility of erosion, such as in lines carrying catalyst or other abrasive materials.
- When there is reverse flow. *Note:* in most cases heavy gauge sleeves should be used and weep holes provided in the liner.
- When extremely high temperatures are present. Liners produce an air barrier which will decrease the operating temperature of the bellows. *Note:* the bellows should not be externally insulated.

Purge connections are used in conjunction with internal liners to prevent packing or collection of solids in the area between the liner and the bellows. Purge connections are also used to introduce cooling media, usually air or steam, between the bellows and the liner in high temperature service.

For toxic chemicals the use of a multi-ply (double-wall) expansion joint is recommended. A check hole is provided in the outer wall and connected to a closed toroidal chamber, to which a pressure monitoring instrument is attached; the instrument will alarm if a leak occurs in the inner wall of the bellows.

Because expansion joints are highly engineered items, applications and specification should be developed by a qualified piping engineer/designer familiar with expansion joint system design. The selection and application of an expansion joint in a piping system must be done as a "system approach." The expansion joint shall be properly located, with the pipe support system (i.e., anchors, guides, stops, hangers, and supports) as an integral part of this "system approach." When an expansion joint is required for a piping system to accommodate thermal expansion, vibration, differential settlement or equipment loading reduction, the pressure thrust resulting from the introduction of the expansion joint will be the most critical problem encountered. Often the axial force is so large that proper pipe restraints cannot be feasibly designed. Thus the expansion joint cannot be used for axial movements, and its use is limited.

6.5.2.2 Causes of Expansion Joint Failure

A properly designed, manufactured, installed and maintained expansion joint may be expected to give many years of satisfactory service. Failures, however, have occurred. Experience indicates that the typical causes of expansion joint failure can broadly be attributed to the following:

- Damage to the expansion joint during shipping and handling
- Damage due to improper installation and insufficient protection during and after installation
- Improper anchoring, guiding and supporting of the piping system
- Anchor failure in service
- Excessive bellows deflection (greater than design values)
- Mechanical or flow-induced vibrations caused high cycle fatigue
- Bellows corrosion and erosion
- System overpressure
- Packing of particulate matter in the bellows convolutions obstructing proper movement of the bellows
- Pressure transients (including damage during pressure testing prior to startup)

6.6 VIBRATION

The significance of vibration is that stresses developed in components due to vibration displacements can result in failure of the component. In addition, these vibrations can be transmitted to other equipment and structures. Vibration of piping and components can be classified as either steady state or transient. Transient vibration can be caused by water hammer, earthquake, slug flow, or relief valve thrust forces. Steady state vibration can be caused by pressure pulsations from mechanical equipment subject to pulsating flow, such as reciprocating compressors and pumps, valve chattering, or turbulent flow conditions.

Stress analysis is the calculation of the stress in a component and the comparison to a safe limiting value. The limiting value will be related to time or frequency and is dependent upon the properties of the material. One of the more significant methods of indicating a property of a material is the design fatigue endurance curve. Simplified, the endurance curve indicates failure limits (stress values) based on cycles. Higher cycles require lower stress values; in other words, high stress values result in reduced cyclic life.

The ASME B31 Code does not require that the endurance curve be used to qualify piping components experiencing vibration. The Code requires that the design eliminate excessive and harmful effects of vibration. The Code indicates a reduction in allowable stress range (thermal flexibility) based on high cyclic usage. High cyclic usage (700,000 to 2 million cycles) limits stresses to 30% of normal allowable. The code formula continues to reduce the allowables as the cycles increase. The intent is to limit the number of expansion stress cycles during the lifetime of the plant. Since a vibrating line may easily experience 1 million cycles per day the designer must apply good engineering judgment.

Fortunately, vibration is addressed in the ASME Boiler and Pressure Vessel Code Section III, Division I, the Nuclear Class I Components section. The unfortunate part is that this section is not as simplified as the ASME B31.3 Code. ANSI STD OM, Part 3, *Requirements for Preoperational and Initial Start-Up Vibration Testing of Nuclear Power Plant Piping Systems,* presents formulas to assess vibration. The piping design engineer might consider the following caveats: "Double the calculated displacement stress, and if it is less than 80% of the design fatigue value, it is acceptable" or "If the velocity is greater than 0.5 inch/second, call for further analysis."

In order to consider the effect of vibration, displacement and frequency need to be identified. A measured displacement of a component in a piping system can be used as one of many inputs in a calculation to determine stress levels. However, vibration is a complex issue and not wholly calculable.

Water hammer displacements and seismic displacements are not usually thought of as high cyclic conditions. In these conditions the allowable stresses would be much higher than the value permitted for steady state vibration.

The process engineer has little control over vibration stress levels, but sizing a line that has two-phase flow so that it is in slug flow regime will definitely cause hundreds of hours of discussion, analysis and concern. Steady state vibration will most often be caused by pulsating flow from reciprocating equipment. API Std 618 gives guidance as to the type of analysis required. This is usually an acoustical analog study combined with mechanical frequency analysis. The goal of these two methods is to avoid resonance.

Resonance can often be avoided by proper placement of both fixed and elastic supports. Pulsation dampeners or surge tanks are other options to reduce pulsation. Reduction of piping system stresses may be achieved by removing geometric discontinuities (e.g., hanger lugs, insulation supports, and small pipe connections (Casiglia 1992). Where changes in section are required, changes in contour should be gradual and smooth.

6.7 SPECIAL CASES

Some chemicals or situations require unique piping systems. Special attention is devoted to minimizing leaks (especially at piping connections and valves) and avoiding ignition. Pipe stress is not generally affected by specific chemicals. Temperature and pressure requirements of specific chemicals, however, may influence choice of materials of construction. This determination is usually made by a metallurgist (see Chapter 5 for more information).

6.7.1 Oxygen and Oxygen-enriched Atmospheres

Oxygen and gas mixtures containing large amounts of oxygen (oxygen-enriched atmospheres) react chemically with organic materials which can result in fires and explosions. Therefore, it is essential that piping for transporting these gases be very carefully cleaned to remove any traces of oils, greases, or other hydrocarbon materials before the gases are admitted to the piping. Procedures for cleaning of components and systems to be used in oxygen or oxygen-enriched gas service are described in CGA Publication G-4.1 (CGA 1985).

General precautions for safe handling of gaseous oxygen are contained in CGA Publication G-4.4 (CGA 1980) and ASTM G-88. For liquid oxygen, a thorough discussion of safety concerns and required design practices is presented in CGA Publication P-12 (CGA 1987).

The main hazard of oxygen-enriched atmospheres is enhancement of flammability. Combustible materials of all kinds, including people's clothing, but even steel equipment, undergo combustion much more easily in oxygen-enriched air (Lees 1980). Of particular importance is the greatly increased intensity of burning and rate of flame spread. Because of the inherent fire and explosion hazard, careful design is required for all components, such as mechanical and electrical systems (NFPA 53M). Special consideration should be given to:

- Materials of construction
- Electrical wiring and equipment
- Prevention of ignition

6.7.2 Chlorine

Piping for chlorine must be ultra clean and lightning protection should be provided. Choice of material for the piping section depends on whether the chlorine is wet or dry. Small concentrations of water result in a marked increase in corrosion; therefore, the line is designed to facilitate keeping the chlorine dry (Lees 1980). Chlorine lines are addressed in two Chlorine Institute publications: *Piping Systems for Dry Chlorine* and *Chlorine Pipelines*.

Liquid chlorine has a very high coefficient of thermal expansion and therefore requires protection against hydrostatic rupture. See Chlorine Institute publications for recommended maximum pressure and temperature and criteria for pressure relief (pressure relief devices or expansion tank). It is very important to provide control of line breaks; therefore, automatic shutoff valves and / or excess flow valves should be installed.

6.7.3 Phosgene and Other Toxic Chemicals

Piping design practices discussed here for the safe handling of phosgene should be applied to other toxic chemicals. Phosgene should be handled in double-walled piping with the annular volume monitored to detect a leak in the inner pipe. Some users vent the annular pipe volume into a solution of Congo Red for phosgene detection (Bianchi and Alspach 1984). As many pipe joints as possible should be welded and the number of flanged joints should be kept to a minimum. All butt welds should be fully radiographed. Screwed joints and socket welds should not be used.

The pipework system should be kept simple with the minimum number of valves. If lines cannot be self-draining, the valves should be positioned to prevent locking in of liquid phosgene to avoid overpressurization caused by thermal expansion. All process valves in service in phosgene mixtures greater than 5% should be either flanged or weld jointed to the pipework and the valve body should be made from forged steel with a globe or wedge sealing action. Also, the stem should be fitted with a bellows seal with a packed gland backup. Before the decision is made to weld valves into pipelines, consideration should be given to maintenance problems and to problems associated with the welding together of dissimilar metals.

All piping should be carefully supported to prevent the fatigue failure due to vibration and rubbing. Special attention may have to be given to pipes connected to rotating machinery, compressors, pumps, etc., to reduce induced vibration. More details on phosgene piping can be found in ICI Code of Practice No. 3, Phosgene (1973).

6.7.4 Hydrogen

Hydrogen piping inside buildings should be designed to have as few flanged joints as feasible to minimize the potential for hydrogen leaks and possible subsequent deflagrations. The piping should preferably be of welded construction, including valves with socket weld ends. High integrity valves which minimize leakage, such as bellows seal valves, should be used. A good source of information on piping systems for gaseous hydrogen has been prepared by the Linde Division of Union Carbide Corporation (1987).

6.7.5 *Acetylene*

Acetylene is a flammable and explosively unstable material. It undergoes explosive decomposition at any pressure and temperature and even without the presence of oxygen. Acetylene decomposition may be initiated by shock, temperature, or reactive substances. The explosion hazard with pure acetylene is most severe in pipelines, where a deflagration may transition to detonation (see Chapter 13).

Choice of materials of construction is particularly important. Under certain conditions acetylene forms readily explosive acetylide compounds when in contact with copper, silver, and mercury. For this reason, acetylene and the use of these metals, or their salts, compounds, and high-concentration alloys is to be avoided. Only steel, wrought-iron, or stainless steel pipe should be used for acetylene piping systems. Joints in piping must be welded or made with threaded or flanged fittings (heavier wall thickness pipe should be used when threaded piping is used). Cast-iron fittings should not be used.

Brass containing less than 65% copper in the alloy, and certain nickel alloys, may be suitable for use in acetylene service under normal conditions; however, generally acceptable alloys can be rendered unsatisfactory when conditions involve contact with highly caustic salts or solutions, or contact with other materials corrosive to copper or copper alloys. For this reason some companies do not allow the use of any copper alloys. The presence of moisture, certain acids, or alkaline materials tends to enhance the formation of copper acetylides.

Pipeline operating pressure and inside diameter are interrelated with respect to the potential for deflagration or detonation. CGA Pamphlet G-1.3 contains a chart showing this relationship and should be used for pipe sizing. For further details on acetylene handling and pipeline design, consult:

- CGA Pamphlet G-1.3-84, *Acetylene Transmission for Chemical Synthesis*
- CGA Pamphlet G-1-90, *Acetylene*
- CEP Technical Manual on Acetylene Handling (AIChE 1963)

6.7.6 *Ethylene Oxide*

Ethylene oxide (EO) is toxic, flammable and explosively unstable. Ethylene oxide vapor decomposes explosively even in the absence of air. Liquid ethylene oxide is very susceptible to polymerization; for this reason, transfer of liquid EO should be done without raising the temperature. Impurities in the inert gas used for pressurizing or inerting may trigger decomposition. For recommendations for piping, pumping, storage, loading and unloading, see FMEC (1992). Some of the recommendations from FMEC include:

- Fire protection systems
- Frequent inspection and maintenance of controls, fire, protection and safety devices
- Design of vessels and storage tanks in accordance with ASME (Sections I, III, VIII)
- Blanket gas and refrigeration systems should be well maintained. Consider monitoring inert gas for impurities
- Materials of Construction: copper, silver, mercury and their allows are potential explosion catalysts in the presence of acetylene
- Selection of appropriate hazardous location electrical equipment.

Recent publications on ethylene oxide include those by Britton (1988, 1991) and Simpson and Minton (1993).

APPENDIX 6A: EXAMPLES OF SAFETY DESIGN CONCERNS

The following concerns are typically included in design of piping systems and valves (adapted from CCPS 1992).

Piping Systems

☐ Has all piping systems handling toxic or lethal materials been identified? (For example, piping handling hydrogen cyanide, nitrogen, etc.)

☐ Does the piping need to be designed to contain a deflagration? A detonation?

☐ Are special monitoring provisions provided for overflow lines which have a tendency to plug? (For example, lines in caustic service)

☐ Has the proper metallurgy been selected for the fluid transported? Has deleterious materials of construction been avoided? (For example, has copper or brass been eliminated from ammonia service? Or has copper or iron been eliminated from benzyl chloride service?)

☐ Have high temperature shutdowns been provided for pumps which handle heat sensitive or reactive material?

☐ Has the proper bolt design been provided for frangible flange systems to accurately control the break point?

☐ Has a surge vessel been provided to contain thermal expansion of a hazardous liquid (like chlorine) instead of a pressure relief valve?

☐ Has special insulation been used on Therminol or high temperature systems to prevent cracking of high molecular weight organics to a lower flash point material with subsequent auto-ignition?

☐ If a bellows type expansion joint is used in flammable and/or pressure relief systems, has this type joint been correctly aligned during installation to maintain integrity?

☐ If a hazardous condition exists when mechanical agitation is lost, has emergency gas agitation via a dip-pipe been provided?

☐ Do dip pipes have weep holes to de-inventory the pipe during a plant shutdown?

☐ Has a "deadman" start–stop station on a pump been provided to prevent overflow of flammable or very hazardous materials from the downstream vessel due to operator inattention?

☐ Has a remote "stop" been provided on a pump which transports flammable material into an operating unit from the outside the battery limits?

☐ Should uninsulated sections of pipe be added for planned heat loss? (For example, the feed water regulator on a boiler).

☐ Have the spring hanger settings for piping used in high temperature or high pressure service been documented during installation?

☐ Has the proper gasket type and material been used in hazardous service? (For example, lethal systems need spiral wound gaskets.)

Valves

☐ Have "air to open" control valves been selected for those remote valves which you want to activate closed during a fire event and has plastic air tubing been provided?

☐ Are the valves which must be manually opened or closed during an emergency capable of remote operation?

☐ Have the valves, nipples (open ended), etc. used in pressurized flammable, lethal gas or oxygen service been capped off?

☐ Have the valves and piping, etc. in chloride or oxygen service been degreased before start up (and/or after repair)?

☐ Have excess flow check valves been installed in pressurized hazardous gas systems such as those involving ammonia, chlorine, hydrogen, etc.?

☐ Has a hole been drilled in a butterfly valve to prevent overpressure due to thermal expansion? If this is not possible, has a pressure relief valve been provided?

☐ Have "deadman' (spring to close) sampling valves been installed in high pressure, flammable, or lethal systems to prevent continued flow of material if the operator becomes incapacitated?

☐ Has a manually activated water flush or quench system (if possible) been provided to stop an uncontrolled reaction or to provide internal fire fighting capability?

☐ Have air-activated valves been locked out (defused) in the field while maintenance is in progress?

☐ Has a hazard analysis of the process been conducted to determine the fail safe position of control valves during a specific or total utility outage (electrical power, instrument air, etc.)?

☐ Has a valve in a tank car and/or truck unloading line been provided which closes on disconnecting, or which must be closed to disconnect?

☐ Have special position indicators been provided for three way valves to clearly indicate which port is active?

Piping and Valves used in ASME Section I Service

☐ Have the piping systems been analyzed for stresses and movement due to thermal expansion?

☐ Are the piping systems properly supported and guided?

☐ Have the piping systems been provided with freezing protection, particularly cold water lines, instrument connections, lines in dead end service such as piping in standby pumps?

☐ Have cast iron valves and fittings been eliminated from piping which subjected to strain or shock service?

☐ Have nonrising stem valves been avoided where possible and has a visual indication of valve position been provided.

☐ Have double block and bleed valves been provided on battery limit piping and/or emergency interconnections to ensure positive isolation and/or to prevent cross-contamination where this is undesirable?

☐ Has a means of draining and trapping condensate from steam piping been provided?

6.8 REFERENCES

6.8.1 Regulations, Codes of Practices, and Industry Standards

The editions that were in effect when these *Guidelines* were written are indicated below. Because standards and codes are subject to revision, users are encouraged to apply only the most recent edition.

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of pilot failure is loss of fuel gas flow; this is often due to a plugged line or filter. Provide a means to ensure that the fuel gas is clean and to verify flow to the pilot. Another cause of loss of flame is blowout on low pressure flares in high winds.

Because uncertainties will always exist that an upset process condition could produce an explosion in a flare or incinerator system, it may be appropriate to install detonation arresters in-line (see Chapter 13).

15.2 BLOWDOWN SYSTEMS

Condensable vapors, contaminated aqueous effluents, and various other liquid streams generated due to plant emergencies require disposal. These "blowdown" systems include plant oily water sewers, chemical sewers, closed drain header systems for flammable liquids or special materials, quench blowdown drums, blowdown drums, effluent disengaging drums or other facilities capable of handling the additional loads. Systems for routine deinventorying are not in the scope of this section.

The method of disposal is determined by the hazardous properties of these fluids, such as toxicity, and temperature, viscosity, solidification, and miscibility. The objective in design of blowdown systems is to not create a new problem while solving the disposal problem. Commonly used blowdown systems are described on the pages that follow.

15.2.1 Equipment Drainage Systems

During upset conditions or shutdowns, process equipment items must be drained of their contents to allow personnel safe entrance. Disposal of small inventories of fluids depends on their volatility and toxicity; frequently discharge is to a sewer or to the atmosphere, provided the material is not hazardous or toxic. Compatibility considerations are of utmost importance.

Disposal of larger inventories depends on properties of the fluid. The following options may be considered:

- For low boiling materials, drain to a closed drain header for further treatment.
- For materials above their flash point, drain to a closed drain header for further treatment.
- For high boiling materials below their flash point, drain to the appropriate sewer.
- For aqueous liquids contaminated with low boilers, drain to water or caustic disengaging drums for subsequent treatment. After pressure

relief, combinations may result in hydrate formation or freezing, resulting in plugging problems.
- For aqueous liquids contaminated with low concentrations of high boilers, drain to a vented section of an oily water sewer.
- For sour water contaminated with spent caustic, drain to an atmospheric tank for subsequent disposal. The tank must be provided with a means to handle any sour off gas.
- For toxic, corrosive or pollutant fluids, drain though a closed drain system for collection and recycle to the plant for recovery or treatment.
- For uncontaminated cooling water and steam condensate, drain to a clean water or oily water sewer.

15.2.2 Disengaging Facilities

Tube failure in heat exchangers using cooling water or steam invariably causes contamination of these utility systems with organics or other fluids, if the process side pressure is higher than utility pressure. These utilities should be treated before they are recycled for further use. Treatment, which entails removing organic vapors or liquids (or other contaminants), is performed in separate disengagement drums for each contaminated utility system. Disengagement drums normally operate at atmospheric pressure; therefore light ends flash and must be safely vented (possibly to a flare). Similar treatment may be warranted.

The following are guidelines for design of disengaging drums:

- The inlet liquid line size is based on the maximum liquid rate to the drum.
- The vapor outlet is sized for the vapor load generated by flashing from the maximum quantity of feed to the drum. This vapor may discharge to a flare or to the atmosphere at a safe location. The minimum design pressure of the drum should be 50 psig (API RP 521).
- High liquid level alarms should be provided.
- Condensed organics should be skimmed and pumped to a suitable recovery system.
- Drum liquid holding time is determined by liquid/liquid (organic/water) separation requirements.

15.2.3 Quench Drums

A quench drum is used to cool and partially condense vapors discharging from relief devices by spraying water or other suitable liquid directly into the gas stream. By condensing organics, this type of drum reduces flare loads and vapor loads to other downstream facilities and reduces the reaction mass carried over. Quench drums are used to reduce the amount of organic emissions to meet federal, local or state regulations. Condensed fluids may be pumped back to the process area for treatment or recovery. The vent vapors (noncondensables) may be discharged to a flare, scrubber, or the atmosphere if appropriate.

A disadvantage of a quench drum is the requirement for a substantial amount of liquid. This will increase the size of the drum and produce large amounts of contaminated quench liquid. Use of this type of drum is limited by the type of organics present in the effluent; that is, it cannot be used for water-miscible organics, liquid low boilers, or fluids below 0°C (32°F).

The following are guidelines for the design of quench drums:

- A single drum may be used for more than one process unit. Consideration must be given to chemical compatibility and continuity of process operation if this drum is out of service.
- Single or multiple headers from various plant locations may enter the drum. Closed liquid headers should be run separately to the drum.
- The quench liquid must not react with the hot relieved fluids.
- The quantity of quench liquid is determined by the heat balance, assuming that the final temperature of the condensed fluid is 10 to 20°F below condensing temperature. Continued reaction in the drum must also be considered in the heat balance.
- The materials of construction must be based upon the corrosive properties of the relieved fluid and the quench medium, and operating temperature.
- A heating coil may be included in the drum to prevent solidification of condensed material at low temperatures or freezing of water by low boiling vapors.
- Instrumentation for pressure, temperature, and level control must be provided.
- Vapor and liquid loads to the quench drums are determined on the basis that all relieving devices from process units will discharge under one controlling contingency only (for example, cooling water or power failure).
- Design pressure of the drum should be a minimum of 50 psig.
- Operating pressure of the drum should be based on the hydraulics of the discharge system and the downstream requirements in order to vent the vapors to a flare stack or other destination.
- If the drum is treated as a pressure vessel, it should be provided with means of overpressure protection.
- The liquid holdup volume of the drum must be sized for expansion of the quench liquid, collected condensate, and collected liquid carryover.

Figure 15-7 shows a typical condensable blowdown (quench) drum.

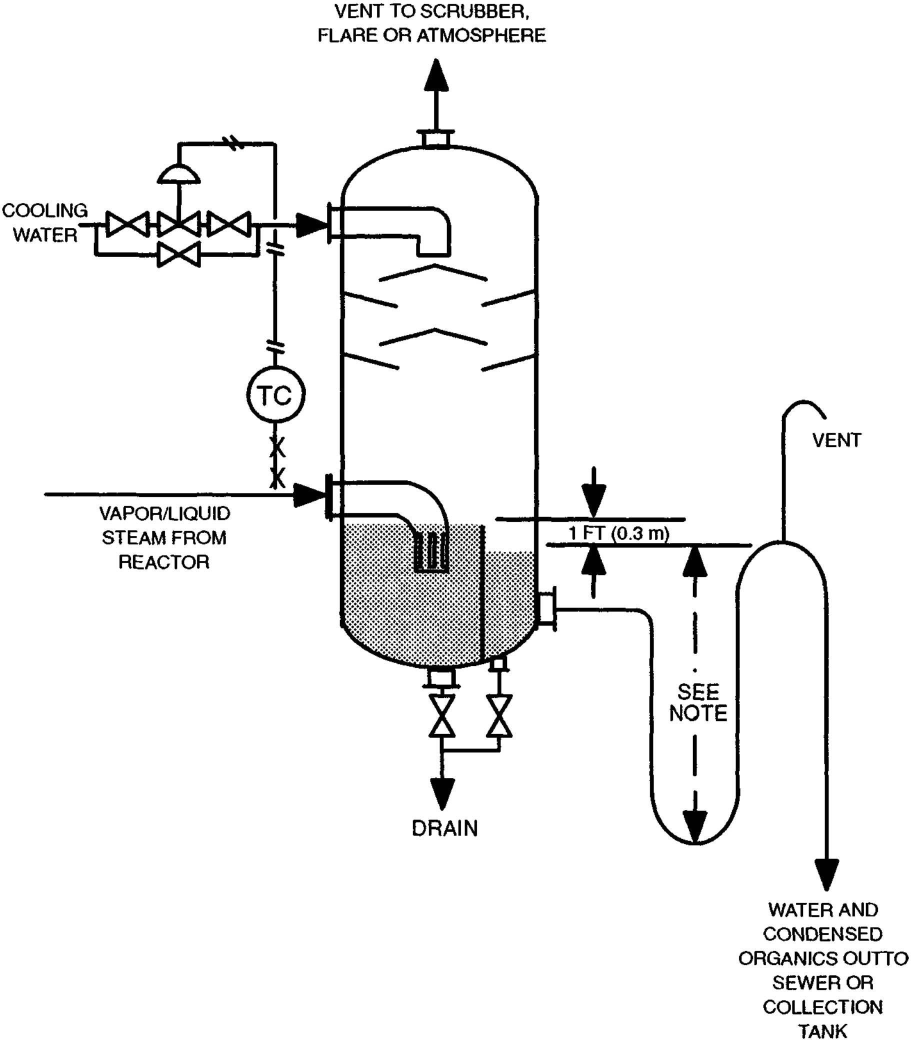

Figure 15-7 Typical condensable blowdown drum. *Note:* It is suggested that the sewer seal be designed for a minimum of 175% of the drum's maximum operating pressure. (API RP 521, Appendix D. Reprinted courtesy of the American Petroleum Institute.)

15.2.4 Other Condensable Blowdown Systems

Quench nozzles consist of an in-line assembly to condense organics using water (or other fluid) as the quenching medium. This system condenses practically all organic vapors that are condensable at 93°C (200°F) and atmospheric pressure. The quench water will be flashed to steam. The flashed steam may be saturated with light boiling vapors. The amount of water required is determined by the heat balance of the system, using available water temperatures.

To reduce the amount of quench water required for high loads, a cooler may be used upstream of the drum to reduce the temperature of the incoming vapor. The design of this system must avoid liquid traps in the safety valve header. This system cannot be used for fluids subject to freezing or solidification.

In some plants where solvents like phenols and ketones are used, special blowdown tanks are often employed (Figure 15-8). These tanks consist of large surge tanks filled with the solvent, as an absorbing medium, with a concentric stack vented to a suitable destination. The vapor enters the bottom of the tank and is distributed through the tank by a sparger. The tank is provided with pumpout facilities to return the solvent/water mixture to the process unit for recovery and treatment. Any vapors exiting the tank must be vented according to federal, state, and local regulations; this often requires treatment in a scrubber, or discharge to a flare.

Fauske and Grolmes (1991) demonstrated that a passive quench tank effectively provides quenching of short duration, high rate releases, given an adequate amount of quench fluid and a suitably designed sparger arm.

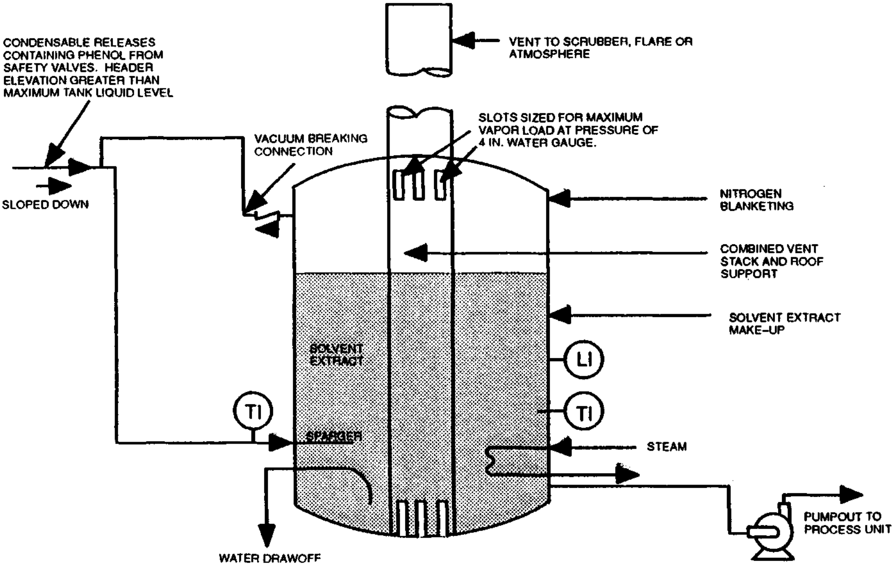

Figure 15-8 Condensable blowdown tank solvent service.

15.2.5 Safety Considerations

The primary safety considerations related to blowdown drums are that they should be designed to handle overpressures that could result from continuing runaway reaction or from an external fire. Design of the vessel to withstand deflagrations is addressed in NFPA 69 and by Noronha et al. (1982). It is good engineering practice to design the blowdown drum for a minimum design pressure of 50 psig (API RP 521); some companies specify a design pressure of 125 to 150 psig (Grossel 1990).

Even if the blowdown drum or tank is designed to withstand higher pressures, pressure relief should be provided in case of external fire or continuation of any runaway reaction in the drum.

Heating equipment may be required if there is any chance that the liquid in the drum could freeze or solidify.

In designing vessel nozzles, attachments, supports, and internals, consideration should be given to shock loadings resulting from thermal effects, slugs of liquid, or gas expansion (API RP 521).

15.3 INCINERATION SYSTEMS

Incineration is the burning of waste in a closed system under carefully controlled conditions, such as a kiln or furnace. The efficiency of the process is measured by destruction of toxic or hazardous components. Incineration technology has been applied to liquid, sludge, solid and gaseous wastes. Federal, state and local regulatory agencies are considering or have already implemented regulations governing safety, design, and limitations on incinerator emissions. These standards are contained in 40 CFR 264 Subpart 0 for incinerators burning hazardous wastes and 40 CFR 761.70 for burning wastes containing polychlorinated biphenyls (PCBs) and 40 CFR 266 Subpart H for boilers and process furnaces burning hazardous wastes.

15.3.1 Basic Design Considerations

The primary design criterion needed to properly specify the system is a waste heat load and material balance showing the number and types of wastes to be incinerated. Each waste should have a detailed description that includes as much of the following as possible:

- State (gas, liquid, sludge, slurry, solid)
- Viscosity
- Mass loading
- Density
- Ultimate analysis (C, N, O, H)

- Percent water, ash, inerts, alkali, heavy metals, sulfur
- Percent Cl, F, Br
- Heat of combustion
- Packaging and delivery of wastes

The heat balance should be as complete as the material balance for the system; however, it must be recognized that incinerator systems handle varying loads both in terms of quantities and composition. In many industrial applications, where high Btu wastes are common, the limiting factor of the incinerator unit will be the heat load on the system, not the material transfer.

The design should include provisions for handling the effluents in case the effluent disposal/treatment facilities are inoperative. Consideration should also be given to the schedule of operations (for example, batch or continuous process) and the procedures for disposal of waste loads from the incineration system.

15.3.1.1 Combustion Chamber

In the design of the incineration system several important factors affect the complete combustion and efficiency of the incinerator; these include the following:

- Combustion air supply and percentage of excess oxygen
- Combustion chamber temperature
- Proper turbulent mixing both inside and outside the flame zone
- Residence time and residence time distribution in the combustion chamber
- Liquid droplet atomization and evaporation rates
- Proper waste feed rate control

15.3.1.2 Monitoring and Instrumentation

Prior to issuing any operating permits and certifications, the regulating agencies require documentation on the sources and rates of emissions, composition of effluents and other pertinent data; therefore, it is required that analytical monitors and instrumentation be incorporated (state and local regulations may apply in addition to the federal Clean Air Act). All incinerators will be required to record combustion zone temperature (primary and secondary), stack flue gas, carbon monoxide, and oxygen. Additional process variables that regulatory authorities may require include waste and fuel feed rates, combustion air, pressure drop across the Air Pollution Control (APC) unit(s), and HCl, NO_x, and/or total organic carbon and particulates. It is suggested that sample taps be installed for stack sampling for particulates and metals; conducting test burns is also required by the EPA.

15.3.2 System Components

Depending on its complexity, an incineration system can consist of a combination of components listed in Table 15-1. The combination of components will depend upon such criteria as analysis of the feed streams, the type of feeds and their handling, the degree of combustion required to achieve the required objective, residue or ash handling, instrumentation and controls, emissions controls and waste heat recovery objectives.

15.3.3 Types of Incinerators

Incineration technology is constantly changing. Several types of incinerators are commercially available and others are being developed. Johnson and Cosmos (1989) compare 12 technologies that can be used for on-site treatment. This section will address some features of both stages of incineration development and the most commonly used types in the industry. Thorough investigation of various alternatives is required to make an intelligent application of this technology.

Table 15-1 Incineration System Components

- For solids and sludges, a waste feed system comprising cart dumpers, ram feeders, etc., including the dust and/or volatile organic chemicals (VOC) collector systems for the conveyers and associated equipment.
- For liquids, storage, feeding, and blending facilities.
- Combustion system comprising primary or primary and secondary chambers.
- Primary or primary and secondary burners with their associated blowers.
- Prime mover including instrumentation and controls. This may be induced draft fan(s) or steam eductors.
- Fuel system (gas or oil) including instrumentation and controls.
- Waste heat recovery system, such as heat exchangers, boiler feedwater supply, and controls.
- Steam collection system.
- Carrier beds handling for fluidized bed incineration systems.
- An elevated stack with monitoring equipment. Air pollution control (APC) system.
- An APC unit is required to reduce particulates, acid gases, toxics and metals emissions. Most APC units are classified as either wet or dry systems. Dry systems may include a partial quench, boiler, or other heat recovery device, dry scrubber, baghouse or electrostatic precipitator. Wet systems normally include a full quench, cyclone, venturi, or impact scrubber, and a demisting device. In certain instances, these two types may be combined into a single system. In either system, a base such as caustic or lime is used to reduce the acid gases to water and salts. The combined particulate salt/particulate wastes, either as a granular solid, or a salt water, must be treated and managed prior to discharge.
- Ash handling system for those units handling sludges and solids and/or with a dry scrubber system. The ash handling system will include a collection system under the incinerator and APC unit, a cooling system, and a covered storage area.

15.3.3.1 Rotary Kilns

A conventional rotary kiln is an angled rotating combustion chamber designed to enhance mixing of solid waste by improving the volatilization process of the solid waste and exposing the waste surface to oxidation (Figure 15-9). It can handle liquids, sludge, viscous and high-solids waste, and fiber drums containing bulk wastes. Supplemental fuel and air are sometimes necessary to help the combustion process. Some new rotary kilns have been developed to burn low-Btu hazardous wastes (2500 Btu/lb) without supplemental fuels (Johnson and Cosmos 1989). New rotary kiln designs may also incorporate the use of lime to neutralize acid gases in the combustion zone to reduce fuel gas scrubbing requirements. Rotary kilns operate usually at 875 to 1100°C (1600 to 2000°F), which is sufficient to allow complete waste destruction.

The pyrolytic rotary kiln operates at much lower temperatures 430 to 600°C (800 to 1100°F) than the conventional kiln. Air below stoichiometric requirements is added and the resulting flue gases are a mixture of nitrogen, combustion byproducts, and unburned and partially burned organic gases. Toxic emissions of sulfur oxides and nitrous oxides are reduced due to reduced combustion temperature. Furthermore, because of low oxygen and temperature, some metals in the residue are not oxidized and, therefore, can be recovered in the ash. The low temperature is sufficient to vaporize and partially degrade the organic compounds without slagging the inorganic ones. Acid gas can be neutralized in the kiln by the addition of lime, thereby reducing the requirements for air pollution controls. Flue gases are incinerated with the addition of air in a secondary combustion chamber. Residue from the kiln must be removed for disposal continuously.

The primary advantage to the rotary kiln is its flexibility both in the types of materials that can be handled and the operational conditions under which the material is burned. The rotary kiln's disadvantages include high maintenance, due to the large rotating system and the problems sealing the mating surfaces. Additionally, ash quality can be a problem for certain types of wastes, particularly sticky, high organic solids such as styrene tars. These materials may form an ash coating on the outside of the waste material which insulates the inside and prevents full combustion of the waste material. Poor material turnover in the kiln may also yield similar partially burned waste in the ash.

15.3.3.2 Indirect Pyrolytic Incineration

A pyrolytic incinerator is designed to handle liquid, solids, or semisolid wastes in either batch or continuous operation. Initial treatment is accomplished in an indirect-fired, reduced oxygen environment at temperatures between 430 and 870°C (800 and 1600°F), where the organic materials are volatilized and partially decomposed. The heat source can be hot, fired gases, infrared radiation, or a thermal transfer fluid. The air-starved combustion also

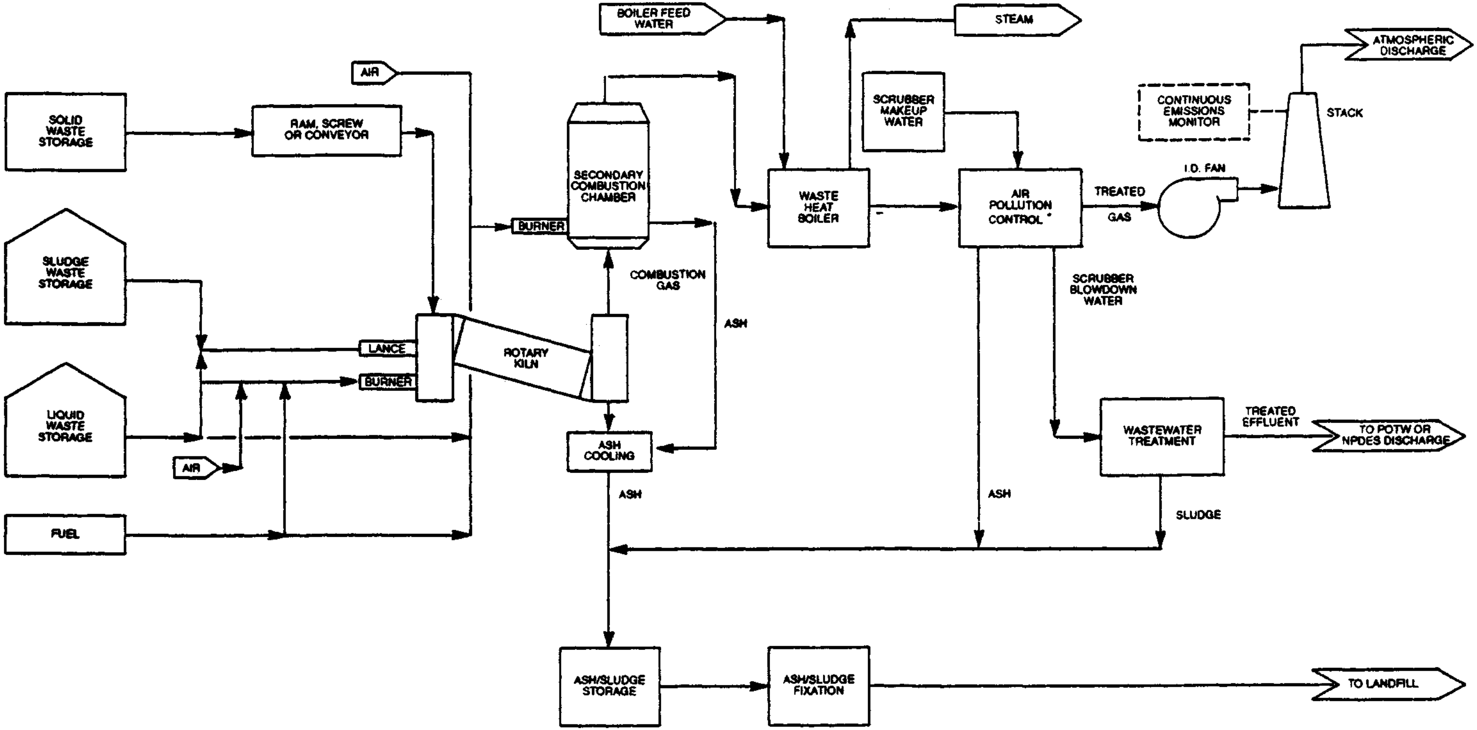

Figure 15-9 Typical rotary kiln incineration unit. Note: Air pollution control is for removal of particulates, metals, and acid gases; POTW = Publicly Owned Treatment Works; NPDES = National Pullution Discharge Elimination System.

reduces the oxidation of any inorganic compounds. The gases leaving the pyrolysis furnace are incinerated in a secondary combustion chamber operating at temperatures between 980 and 1200°C (1800 and 2200°F) where the final destruction of gases occurs. The hot flue gas is then sent to an APC unit with a waste heat recovery section (if desired). Residue ash containing inert metals is continuously removed for disposal.

15.3.3.3 Multiple Hearth Incinerators

This type of incinerator is most commonly used for destruction of a wide variety of sludges. It is comprised of multiple hearths in which the waste flows through progressively hotter combustion chambers (Figure 15-10). This provides a relatively long residence time for the waste and provides good fuel efficiency. Certain types of hearths have the disadvantage of developing cold spots which inhibit complete combustion of the wastes. Mixing inside the hearths may not be thorough, resulting in some gases escaping combustion. Multiple hearth incinerators have high maintenance costs due to high temperature destruction of mechanical components.

15.3.3.4 Fluidized-bed Incinerators

The fluidized bed type of incinerator destroys gases, liquids, slurries, and solids at temperatures between 870 and 1200°C (1600 and 2200°F). It is used for the efficient destruction of waste streams having high moisture content, high concentration of inert materials, acidic compounds or wastes with low heating values. The high degree of turbulence of the bed and use of an air distribution system enhance heat transfer by causing contact between the hot fluidized bed granules and the waste particles. The new types of fluidized beds use a low waste-to-bed ratio thus allowing the incinerator to handle a variation in feed rates and waste heating value without significant variation in combustion temperatures. The thermal mass present in the large volume of the fluidized bed allows complete destruction of the waste in the event the unit is shutdown for emergency. Residue removal is rapid and continuous.

All fluidized bed incinerators work on the same basic principle (Figure 15-11). Combustion air is blown into a bed of fine particles such as sand, alumina particles or similar materials. The air fluidizes the bed and expands it. The wastes, in the form of liquids, sludges, or small solids, and combustion fuel are introduced to the bed and combustion of the materials takes place within the fluidized bed.

Disadvantages of the system include the restrictions on waste size and shape in order to maintain fluidization of the bed and defluidization by low melting salts (NaK salts). At the high rate of air flow required to maintain the fluidization of the bed, the system may yield higher NO_x emissions at higher temperatures. At relatively low combustion rates, NO_x emission is lower.

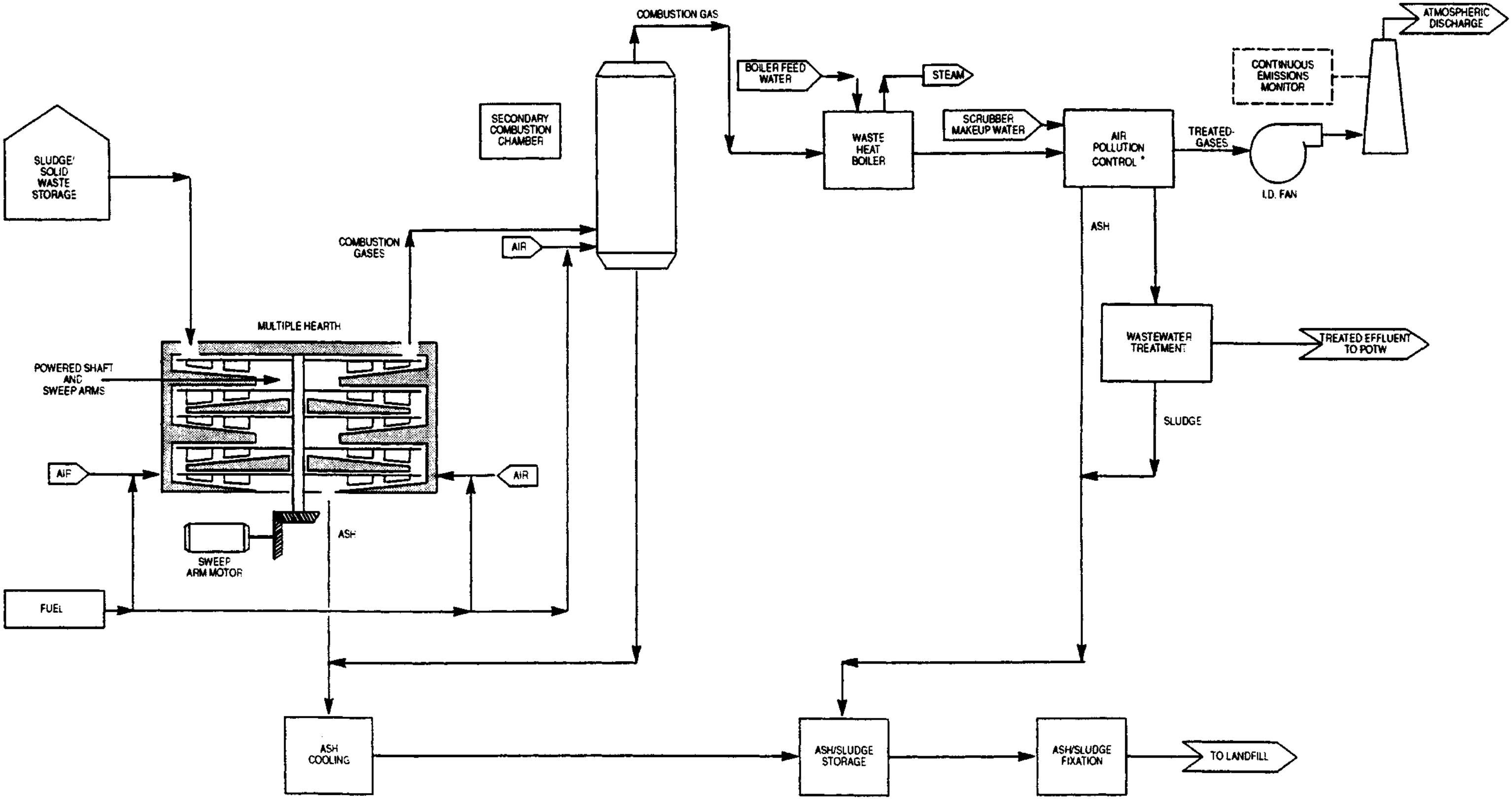

Figure 15-10 Typical multiple hearth incineration unit. *Note:* Air pollution control is for removal of particulates, metals, and acid gases; POTW = Publicly Owned Treatment Works.

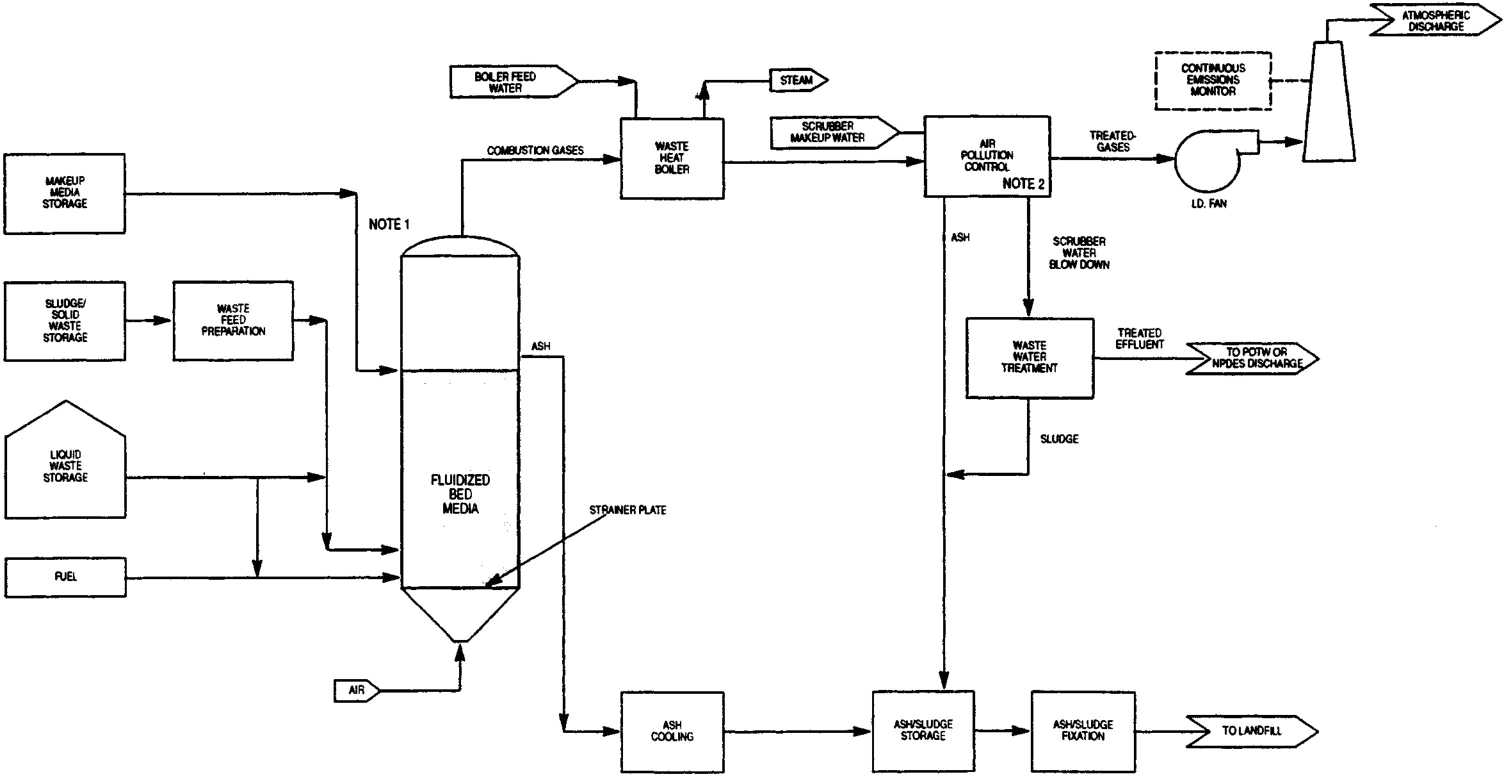

Figure 15-11 Typical fluidized bed incineration unit. *Note 1:* Depending on design, incinerator may or may not require a secondary combustion chamber. *Note 2:* Air pollution control is for removal of particulates, metals, and acid gases.

15.3.3.5 *Liquid and Fume Incinerators*

The primary use of fume incinerators is to control VOCs from low pressure sources. These incinerators are of simple design used for combustion of low pressure effluents from pump vents, separators, dissolved air flotation (DAF) vents, storage tank vents, etc. that would be impractical to route to a normal flare system. Supplementary fuel must be may be needed if the waste does not contain enough heating value. The liquid incinerators are used for low viscosity fluids where special nozzles are required to accomplish atomization of the liquid.

15.3.3.6 *Plasma Incinerators*

The operating principle of this technology is the application of electrical voltage across electrodes to create an arc through which the gas flows. The gas around the arc can reach temperatures of 14,000 to 19,000°C (25,000 to 35,000°F). As the temperature of the gas reaches 3040°C (5500°F), it starts to ionize, forming a plasma that causes the waste to break down to individual atoms and ionize. This type of incinerator has been successfully used in the destruction of toxic baghouse dust and polychlorinated biphenyls (PCBs). In the latter case, the off gases are scrubbed with caustic to remove HCl in the offgas.

15.3.3.7 *Molten Salt*

This is an emerging technology that is potentially applicable for destruction of organic and inorganic hazardous wastes in either solid or liquid form. The basic process is to introduce hazardous waste together with air or oxygen into a pool of molten salt (sodium carbonate) operating at 870 to 980°C (1600 to 1800°F). The molten salt acts as a catalyst to oxidize the waste materials, acts as a mass and heat transfer medium, and reacts with the acid gas produced during oxidation thus eliminating the need for downstream treatment. Inorganic components of the waste form oxygenated salts, and iron is oxidized to iron oxide. These metals are withdrawn continuously from the reaction system. The advantages of this process are that it is energy efficient and has low maintenance costs. Because the gas reacts and is absorbed in the salt, minimum air pollution controls are required. However, salt can cause corrosion problems.

15.3.3.8 *High-Temperature Fluid Wall*

This is an emerging technology applicable in materials processing and synfuels production with emphasis on destruction of hazardous waste. In a typical application, contaminated soil is ground, dried, and reduced in size to a free-flowing solid for feeding the high temperature zone. To be able to handle liquids, the liquid must be atomized or mixed with a carrier prior to treatment. The waste passes through a hollow cylinder carbon core which is surrounded by electrodes. The coil is heated rapidly by radiant heat energy to between 2200 and 2480°C (4000 and 4500°F). The heat is transferred to the waste through an inert gas blanket (nitrogen), which also prevents the waste from contacting the walls of the cylinder and minimizes chemical and physical degradation of the carbon. Several chemical reactions take place that produce hydrogen, carbon, carbon monoxide, and solids. These solids and gases are further oxidized in a downstream reactor at 1094°C (2000°F). Final solids are collected in chambers, and the gases are routed to other treatment facilities.

15.3.3.9 Wet Oxidation

This technology is not an incineration system, but is classified as a thermal waste destruction system. It is primarily used for aqueous organic wastes that are too dilute to incinerate and too toxic to be treated biologically (Figure 15-12). The process includes thermal oxidation of organic and inorganic waste under temperatures ranging between 180 and 320°C (350 to 610°F), at pressures ranging from 300 to 3000 psig. Heat is supplied by an outside source such as steam or hot oils. Theoretically the organics are broken into CO_2, water, Cl_2 and other elementary compounds. In practice, complex compounds may leave incompletely degraded by-products. Oxidized effluents are routed to scrubbers and separators for treatment and disposal. The resulting air emissions may require additional treatment and must be permitted.

15.3.3.10 Supercritical Water Oxidation

This technology is used for destruction of chlorinated aqueous wastes that are too dilute to incinerate. The process relies on the unique physical and chemical properties of water when heated above the critical temperature (374°C [705°F]) at critical pressure (3200 psig). At these conditions, the liquid and vapor phases of the water have the same density and become indistinguishable. High pressure air or oxygen is mixed with the aqueous waste, and the mixture injected into the supercritical fluid. Organics are completely oxidized to water and carbon dioxide. The organic solids are insoluble above 449°C (840°F) and drop out of the supercritical fluid and are removed in solids separators. The high temperature effluent gases containing carbon dioxide, nitrogen, water and residual oxygen are used to generate waste heat steam. The process does produce air emissions which may require further treatment and which must be permitted.

15.3.4 Environmental Guidelines

Hazardous wastes and pollution are regulated in the United States by the EPA and state environmental authorities under the Clean Air Act, Resource Conservation and Recovery Act (RCRA) (for hazardous wastes) or Toxic Substance Control Act (TSCA) (for PCBs). Incineration systems for treating the

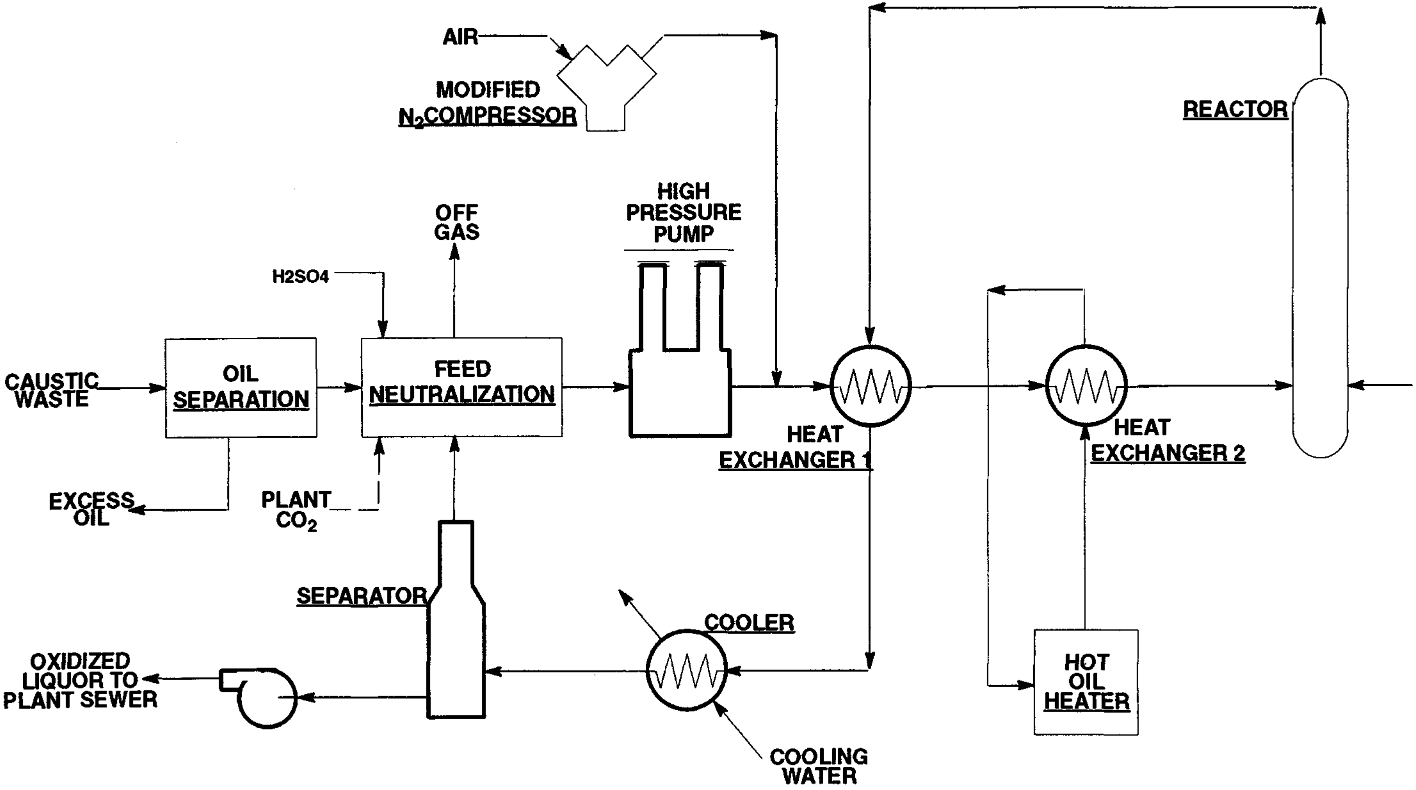

Figure 15-12 Modified wet air oxidation. (DeAngelo and Wilhelmi 1983.)

wastes and resulting emissions are therefore subject to stringent controls and permitting requirements. The exact conditions under which the system will operate, and the resulting pollutant destruction, will be a subject for negotiations between the regulatory authorities and the incinerator builder and operator.

Design criteria and operating conditions typically include the following:

- Organic destruction removal efficiency of 99.99%; 99.9999% for wastes containing dioxins, furans, and PCBs
- Minimum combustion zone temperatures
- Maximum feed rates for wastes and Btu output.
- 99% removal of HCl in the flue gas streams or residual 4 lb/hr whichever is larger
- Minimum of 90% removal of SO_2 in the flue gas stream
- Maximum flue gas particulate of 0.08 grains/dry standard cubic foot (current EPA requirements) or 0.01–0.03 grain/dry standard cubic foot (most state requirements)
- Continuous emissions monitoring requirements
- Interlock requirements to prevent feeding of wastes when the incinerator fails
- Air pollution control conditions including chemical feeds and air pressure conditions
- Stack temperature and flow rate
- Storage requirements for incoming wastes and ash
- A negative draft in the incinerator

Disposal of solid wastes, ash and water will be governed under other appropriate requirements of the RCRA and National Pollutant Discharge and Elimination System (NPDES) regulations (40 CFR Part 60).

15.3.5 Incinerator Safety Concerns

Incinerator hazards are similar to those involved in combustion processes located near flammable materials. Storage areas for materials, particularly liquids and sludges, must be designed to prevent flammable or detonable material from coming in contact with an ignition source, including the incinerator itself. Fire detection and protection equipment should be the same as that used in the rest of the plant. Additional care must be taken to ensure that incompatible wastes are not mixed in one vessel. This has been the cause of several waste storage fires.

Overloading the incinerator, particularly overloading a rotary kiln with a sudden large amount of high Btu solids, can cause the incinerator to overfire, overheating the kiln, and in extreme cases, causing the kiln to go from negative to positive pressure. If only the overtemperature occurs, the temperature control system may be able to handle it, cutting back on fuel gas to maintain temperature below the maximum levels of the incinerator; that is, the interlocks will shut down kiln feed to reduce the thermal load. If high pressure also occurs, the interlocks will shut down the incineration unit. Additionally many kilns have a blowout panel to relieve pressure when the possibility of kiln rupture exists.

One large problem in the operation of solids incinerators is the discharge of partially burned or unburned hydrocarbons in the event of a sudden unit shutdown. The hot solids remain in the incinerator releasing potentially dangerous off-gases. Some kilns deal with this problem by adding an emergency gas burner that activates when the unit shuts down. Using a tall chimney and natural draft the off-gases are sucked up the chimney and burned prior to atmospheric discharge. Other units use the secondary combustion unit burners to continue to burn the gas during shutdown, with the gases being ducted to the atmosphere prior to the air pollution control units.

Variations in Btu value of the waste may cause upset of incinerator operation, therefore, uniformity in feed should be maintained.

In all cases, consideration should be given to installation of detonation arresters for last-resort, passive protection against deflagrations and detonations in vapor lines (see Chapter 13).

The incinerator should be designed to minimize the chance that large pieces of hot slag on the incinerator sides can fall into the quench water at the base of the kiln or secondary combustion unit. Falling slag, at operating temperatures, can cause large amounts of water to flash to steam, potentially rupturing the unit and causing steam to escape into the immediate area.

15.4 VAPOR CONTROL SYSTEMS

Vapor control systems are intended to collect vapor during transfer or storage. Use of these systems is increasing, primarily to meet environmental requirements. Economic factors may determine whether to destroy or recover the collected vapors. Recovery may require additional equipment and piping, for example, to refrigerate and recover the condensed vapor. If the loading system handles a variety of fluids, a separate recovery system might be required for each vapor, or the recovered vapors might be an unusable mixture of compounds.

15.4.1 General

In general, a vapor control system design and installation must eliminate potential overfill hazards, overpressures and vacuum hazards and sources of ignition to the maximum practical extent. Each remaining hazard source which is not eliminated must be specifically addressed in the protective system design and operation requirements. See *Guidelines for Effective Handling of Emergency Relief Effluents* (CCPS, in progress). The point of control of gas to the flare burners is to be considered in accordance with Chapter 9, Process Control.

The vapor control system selected will probably be one of the following:

- Incineration
- Absorption
  —lean oil for hydrocarbons
  —water for acetone or methanol
  —scrubbers
- Adsorption
  —carbon beds
- Refrigeration
- Vapor Balancing

15.4.2 Marine Loading

For illustration, a vapor control system at a marine terminal is described in Figure 15-13. The protective system design (instrumentation, pressure relief, bonding and grounding, etc.) should be considered for other types of loading/unloading facilities.

The EPA and state air quality control boards have recently mandated the collection and destruction or recovery of vapors generated by the loading of some hydrocarbons and chemicals into marine tankers. A recent paper by Babet (1992) provides a review of marine loading vapor control systems.

The potential for a disaster—1000 pounds or more of flammable vapor—is ever present during marine loading of hydrocarbon liquids. Most marine tankers have a very low pressure rating, normally 2 psi pressure to 1 psi vacuum. Because human operations are always required for hook-up and loading rates are relatively high, the element of error is also present. Most vapor control systems utilize an enclosed or open flare, adding yet another source of ignition.

Recognizing the dangers involved in collecting hydrocarbon vapors, the United States Coast Guard (USCG) formulated regulations covering the manner in which vapor control facilities must be installed (33 CFR Part 154, Subpart E—Vapor Control Systems) and certified by a USCG-approved certifying entity.

Regardless of the control method utilized, a USCG-approved flame/detonation arrester must be installed not more than 6 meters from each facility vapor connection. If the collected vapors are being incinerated, the gas must be enriched, diluted or inerted to prevent the gases from being in the flammable range. This conditioning must be initiated within 10 meters of the facility vapor connection. Redundant concentration analyzers must be installed to control, monitor and shut down the system. If vapor balancing is used, each storage tank must have a detonation arrester located within the storage tank containment area as close as practical to the vapor return connection.

If gas is added to the vapor stream, the vapor control system must have high, and possibly low, pressure alarms and a fail-safe vapor shutdown valve which will automatically close under high–high or low–low tanker pressure conditions. A pressure/vacuum relief valve must be installed as close to the facility vapor connection as possible, to protect the vessel from overpressure by the backflow of injected gas or excessive vacuum caused by a blower.

Figure 15-13 shows the flow of collected vapors as they pass through the piping system and the many safety features which are required by 33 CFR, Part 154, Subpart E:

1. The tanker must be equipped with high level alarm (LAH) instrumentation and high–high shutdown (LSHH) instrumentation which are tied into the dockside control system through a 5-pin connector. The tanker high level instrument will activate the dockside audiovisual alarm and the high–high instrument will close both the vapor and, normally, the liquid cargo loading valve. Any blowers which may be operating will be shut down.
2. The vapor collection hose or loading arm must be equipped with an insulating flange. It may be installed on the dockside end of the hose providing that it is impossible for the hose to ground out on the dock. Otherwise, an insulating flange must be installed on the tanker-side end of the hose to ensure that the final "make or break" connection cannot produce a spark. (See Chapter 12, Electrical Hazards.)
3. A pressure indicator (PI) must be installed as close to the vapor connection as possible, to allow the dockman to monitor the pressure in the tanker.
4. A pressure or pressure/vacuum relief valve (PVRV) with flame arrester (FA) must be installed between the vapor connection and the point of enrichment. (Consult the regulations for set points.)
5. Low and high pressure alarms and shutdowns must be installed in a redundant manner (PAH, PAL, PSHH, PSLL).
6. If a blower is utilized, a pressure controlled valve (PIC) must be installed to prevent underpressuring the tanker. This valve can also serve as the emergency vapor shutoff valve.
7. A manual block valve is required.
8. A USCG-approved detonation arrester (DA) must be installed within 6 meters of the facility vapor connection. In most instances, temperature sensors (TSH) must be installed on each side of the arrester to shut down the system if a flame is detected. A pressure differential gauge (DPH) is recommended, but not required, to detect fouling of the tiny passages in

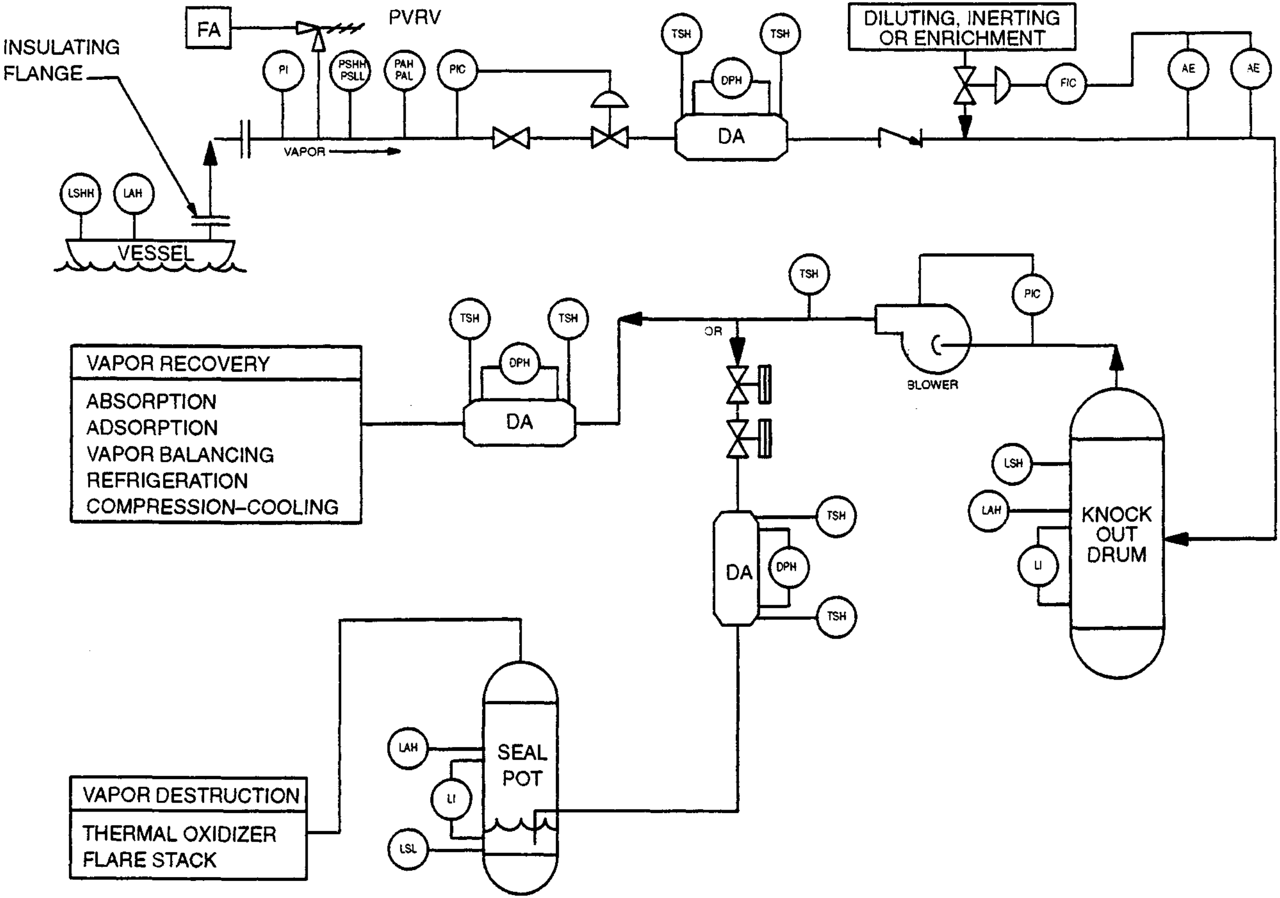

Figure 15-13 Typical marine vapor control system incorporating U.S. Coast Guard regulations (Babet 1992).

the detonation arrester. See Chapter 13 for more information on detonation arresters.

9. A check valve must be installed if gas injection is utilized to prevent overpressuring of the vessel by sending enrichment gas to the vessel. In lieu of this, a differential pressure cell may be installed across the detonation arrester to detect backflow and cause a shutdown.
10. Vapor destruction systems must dilute, inert or enrich the vessel vapor stream within 10 meters of the facility vapor connection.
11. To ensure adequate mixing of the gases within 20 pipe diameters of the injection point, a static mixer is normally required. A well-designed sparger may be used in place of the static mixer.
12. Redundant oxygen analyzers are required to maintain the composition of the gas, either below or above its explosive limits. The worst case of the two readings must be utilized to control the mixing valve.
13. If a blower is utilized, a suction scrubber or liquid knockout drum must be installed to prevent liquid slugs from entering the blower. The vessel must be instrumented to show liquid level (LI) and to provide high level alarm and shutdown (LAH, LSH).
14. If a blower is required, it must be constructed of nonferrous materials or have an internal clearance of one-half inch. Its capacity may be controlled by either variable speed drive or cooled recycle.
15. A temperature sensor (TSH) must be installed immediately downstream of the blower to shut the system down on high discharge temperature.
16. A second detonation arrester (DA) must be installed between the blower and the final means of vapor disposition.
17. In the case of a vapor destruction system, two quick closing valves must be installed between the blower and the destructor.
18. If a thermal oxidizer or flare stack is utilized, a seal pot must be installed with level indication, in addition to level alarms and shutdowns.

This is a brief overview of the main requirements for vapor control systems. The USCG has issued guidelines to assist the certifying entities in ensuring compliance with intended regulations. Because these guidelines are changing, the use of a certifying entity is recommended for the design of the facility to assure compliance with most current regulations.

15.5 REFERENCES

15.5.1 Regulations, Codes of Practice, and Industry Standards

The editions that were in effect when these *Guidelines* were written are indicated below. Because standards and codes are subject to revision, users are encouraged to apply only the most recent edition.

API RP 520. *Sizing, Selection and Installation of Pressure-Relieving Devices in Refineries. Part I, Sizing and Selection, Fifth Edition, 1990; Part II, Installation, Third Edition, 1988.* American Petroleum Institute, Washington, D.C.

API RP 521. 1992. *Guide for Pressure-Relieving and Depressuring Systems.* 3rd ed. American Petroleum Institute, Washington, D.C.

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33 CFR 154 Subpart "E", *Vapor Control Systems.*

40 CFR Part 261, 264, 266. Environmental Protection Agency.

40 CFR Part 761.70. Environmental Protection Agency.

40 CFR Parts 50–99. *Clean Air Act.* Environmental Protection Agency.

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15.5.3 *Suggested Reading*

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LIST OF FIGURES

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INTRODUCTION

The Center for Chemical Process Safety (CCPS) has issued a number of Guidelines aimed at the evaluation and mitigation of risks associated with catastrophic events in facilities handling chemicals. The purpose of this book is to shift the emphasis on process safety to the earliest stages of the design where process safety issues can be addressed at the lowest cost and with the greatest effect.

1.1 OBJECTIVE

The objective of this volume is to help engineers design a safe processing facility with inherently high integrity and reliability.

1.2 SCOPE

This book focuses on process safety issues in the design of chemical, petrochemical, and hydrocarbon processing facilities. The scope of this volume includes avoidance and mitigation of catastrophic events that could impact people and facilities in the plant or surrounding area. The scope is limited to selecting appropriate designs to prevent or mitigate the release of flammable or toxic materials that could lead to a fire, explosion and environmental damage. Process safety issues affecting operations and maintenance are limited to cases where design choices impact system reliability.

The scope excludes:

- Transportation safety
- Routine environmental control
- Personnel safety and industrial hygiene practices
- Emergency response
- Detailed design
- Operations and maintenance

These *Guidelines* highlight safety issues in design choices. For example, Chapter 12, Electrical Hazards, covers the safe application of electrical apparatus and the reliability of power supplies in the process environment required for plant safety, but does not address detailed design of the electrical supply or distribution system required to operate the plant.

It is clear that choices made early in design can reduce the possibility for large releases and can reduce the effects of releases. When considering the variety of mitigation measures used to reduce the severity of the effects of a release, it must be remembered that most of the methods suggested (dikes, curbs, etc.) must also be provided by the designers; it's too late to build them *after* the release.

The ideas presented here are not intended to replace regulations, codes, or technical and trade society standards. Specifically, implementation of these guidelines requires the application of sound engineering judgement because the concepts may not be applicable in all cases. It is not the intent of CCPS to have the contents of these *Guidelines* codified.

1.3 APPLICABILITY

Process safety is a complex subject. These *Guidelines* do not provide all the "answers," but do highlight the safety issues to be addressed in all stages of design. They were written for engineers on the design team, the process hazard analysis team, and the people who make the basic decisions on plant design.

Engineering design for process safety should be considered within the framework of a comprehensive process safety management program as described in *Plant Guidelines for Technical Management of Chemical Process Safety* (CCPS 1992). These *Guidelines* are intended to be applicable to the design of a new facility as well as modification of an existing facility.

1.4 ORGANIZATION OF THIS BOOK

These *Guidelines* have been organized so that the first part of the book deals with catastrophe avoidance through good initial design choices. These chapters deal first with broad design issues followed by more specific design issues.

Chapter 1. Introduction
Chapter 2. Inherently Safer Plants
Chapter 3. Plant Design
Chapter 4. Equipment Design
Chapter 5. Materials Selection
Chapter 6. Piping Design

Chapter 7. Heat Transfer Fluid Systems
Chapter 8. Thermal Insulation
Chapter 9. Process Monitoring and Control
Chapter 10. Documentation

The second half of the book deals with catastrophe avoidance through understanding and controlling chemical processing hazards. The order of the chapters in this section is first) understanding hazards, second) passive catastrophe prevention systems, and third) active protection systems.

Chapter 11. Sources of Ignition
Chapter 12. Electrical Hazards
Chapter 13. Deflagration and Detonation Flame Arresters
Chapter 14. Pressure Relief Systems
Chapter 15. Effluent Disposal Systems
Chapter 16. Fire Protection
Chapter 17. Explosion Protection

During the development of these *Guidelines*, it became clear to the authors that many interrelationships exist. It may be difficult to address a safety issue in one system without affecting several other systems. The difficulty of fixing one problem without creating a problem in another system is frequently encountered. This overlap is also encountered from the perspective of hazard reduction: a single concept can often be applied to several systems. Because of these complexities, it is most effective to build safety into the initial design rather than adding it on.

Specific references and applicable industry standards are listed at the end of each chapter. Additional sources of information are listed under Suggested Reading. It is not the intent of this book to make specific design recommendations but to provide a good source of references where the interested reader can obtain more detailed information. Nomenclature and units are given after each equation (or set of equations); tables and figures adapted from other sources will use the units as originally published. A List of Acronyms and a Glossary are provided.

The readings listed at the end of Chapter 1 are good general sources of information on chemical process safety. They are recommended for use in combination with the CCPS *Guidelines* books.

1.5 REFERENCES

1.5.1 Regulations, Codes of Practice, and Industry Standards

The editions that were in effect when these *Guidelines* were written are indicated below. Because standards and codes are subject to revision, users are encouraged to apply only the most recent edition.

API (American Petroleum Institute) RP 750. 1990. *Management of Process Hazards.* 1st ed. American Petroleum Institute, Washington, D. C.

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1.5.2 Specific References

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15

EFFLUENT DISPOSAL SYSTEMS

A waste gas incinerator at a chemical plant near Houston recently experienced a flashback with a pressure wave in the suction vent gas system, resulting in extensive damage to the flame arrester, fan, valves, and incinerator piping (Anderson et al. 1991). A well-designed system was overcome through an unforeseen combination of failures which defeated the safeguards which were already in place. The air supply normally contained organic emissions at concentrations designed to be less than the lower flammability limit. Through a combination of automatic and operator responses to a trip of the waste gas feed, a fuel-rich stream was suddenly introduced into the incinerator, creating a "slug" of fuel which allowed flame from the burner to blow back into the windbox and the combustion air header. The flame front generated a pressure wave which then blew apart the flame arrestor, fan, valves, and piping. This incident shows that even well-designed systems may be overcome. Determination of actual failure mode is complicated by the safeguards already in place. More importantly, it demonstrates the need to consider the use of in-line detonation arresters or explosion vents for assurance of passive protection of vapor lines in flare, incinerator and blowdown systems.

This chapter addresses containment and disposal of effluents from emergency relief systems, that is, vents, safety valves and rupture disks. Chapter 13, Deflagration and Detonation Flame Arresters, and Chapter 17, Explosion Protection, address related topics. The forthcoming *Guidelines for Effective Handling of Emergency Relief Effluents* (CCPS, in progress) includes "methodology for defining effluent flow rates and calculations concerning fluid dynamics in relief system components and piping" (Huff 1992).

Selection of the disposal system is determined by characteristics of the effluent such as physical state (vapor/liquid/solid), pressure and temperature, and boiling point; quantitative factors such as flow rate, duration of discharge, total quantity of material to be discharged; hazardous properties (toxicity, flammability, buoyancy); nuisance factors (noise, odor); as well as the location of the disposal system (in relation to meteorological conditions, local populations, and local regulations and ordinances). If the effluent is nontoxic, it can be discharged to the atmosphere; however, many nontoxic materials should not be discharged to the atmosphere because of the potential for environmental damage, fire, explosion, odor, or noise. Further treatment may be required in accordance with the Clean Air Act's New Source Performance Standards.

15.1 FLARE SYSTEMS

A flare provides a means for disposing of flammable, toxic or corrosive gaseous effluents by burning them under controlled conditions and converting them to less objectionable compounds.

15.1.1 Description of the System

Flare systems consist of some or all the of following components:

1. Interconnecting collection network, comprising
   - —Discharge piping from individual relief devices and other emergency vents
   - —Laterals connecting several relief device discharges
   - —Relief headers connecting several laterals together
   - —Flare header connecting several relief headers
2. Liquid knockout facilities, comprising
   - —Knockout drums (pots)
   - —Quench drums
   - —Liquid seal drums
   - —Pumpout facilities for drums
   - —Drum liquid heating or winterization systems
3. Flare assembly, comprising
   - —Flare tip or burner
   - —Flare stack or ground flare
   - —Flare stack support
   - —Continuous pilot burners
   - —Pilot automatic ignition facilities
   - —Auxiliary piping for utilities, for example, steam, fuel gas, instrument air
4. Auxiliary equipment which may include
   - —Flame scanners and monitors
   - —Flashback prevention
   - —Smoke suppression control system
   - —Fire protection, insulation, heat tracing
   - —Isolation system (block and diverting valves)
   - —Oxygen analyzers
   - —Instrumentation with alarms
   - —Fluidic sensors
   - —Emission analyzers

Standards for emergency relief system or volatile organic compound (VOC) emissions control are governed by the Code of Federal Regulations (CFR) under the Clean Air Act's New Source Performance Standards. Flares meeting these conditions are assigned a destruction efficiency equal to 98% of the organic materials by the EPA. These standards are detailed in 40 CFR 60.18 and include requirements for:

- Minimum Btu values for the flare gas, for nonassisted and steam- or air-assisted flares
- Maximum flare tip speeds, which vary with the Btu value of the flare gas
- Continuous monitoring for the presence of a flame

Federal, state, and local permits are required to construct and operate flares. The minimum amount of information required for the permitting process includes normal and design maximum flow rates, estimated gas composition and Btu value, normal maximum flare tip velocity, a description of the flame tip monitoring system, and the location and height of the flare. In some cases regulatory authorities may require that the flare emissions be modeled for ambient air effects. Regulatory authorities may also require smokeless (zero visible emissions) operation up to a prescribed percentage of the flare's design maximum emission. Aircraft warning lights may be another regulatory requirement.

15.1.2 Types of Flares

Several types of flares are available in the market for application in process plants. Three of the most common flare types in the process industry are discussed here.

15.1.2.1 Elevated Flares

Elevated flares consist of a stack, flare tip, pilot burners, pilot ignition, and associated facilities for fuel gas and steam (Figure 15-1). The stack, which may be up to 183 m (600 feet) in height, can be self-supporting, attached to a derrick, or steadied with guy wires. An elevated flare is normally used for burning gases containing hydrogen sulfide, hydrocarbons and other corrosive or toxic fluids. Elevated flares provide the best dispersion of malodorous or toxic combustion products.

Disadvantages of an elevated flare are: exposure of plant personnel and facilities to radiant heat during a major release, noise, and annoyance of the public due to the visible flame. Despite its disadvantages, the elevated flare is the most common choice either for total flare loads, or for handling overcapacity releases in conjunction with a multiple burner (multijet) ground flare. For most applications, the elevated flare is the only acceptable means of flaring "dirty gases" that may result in evolution of particulates or corrosive compounds.

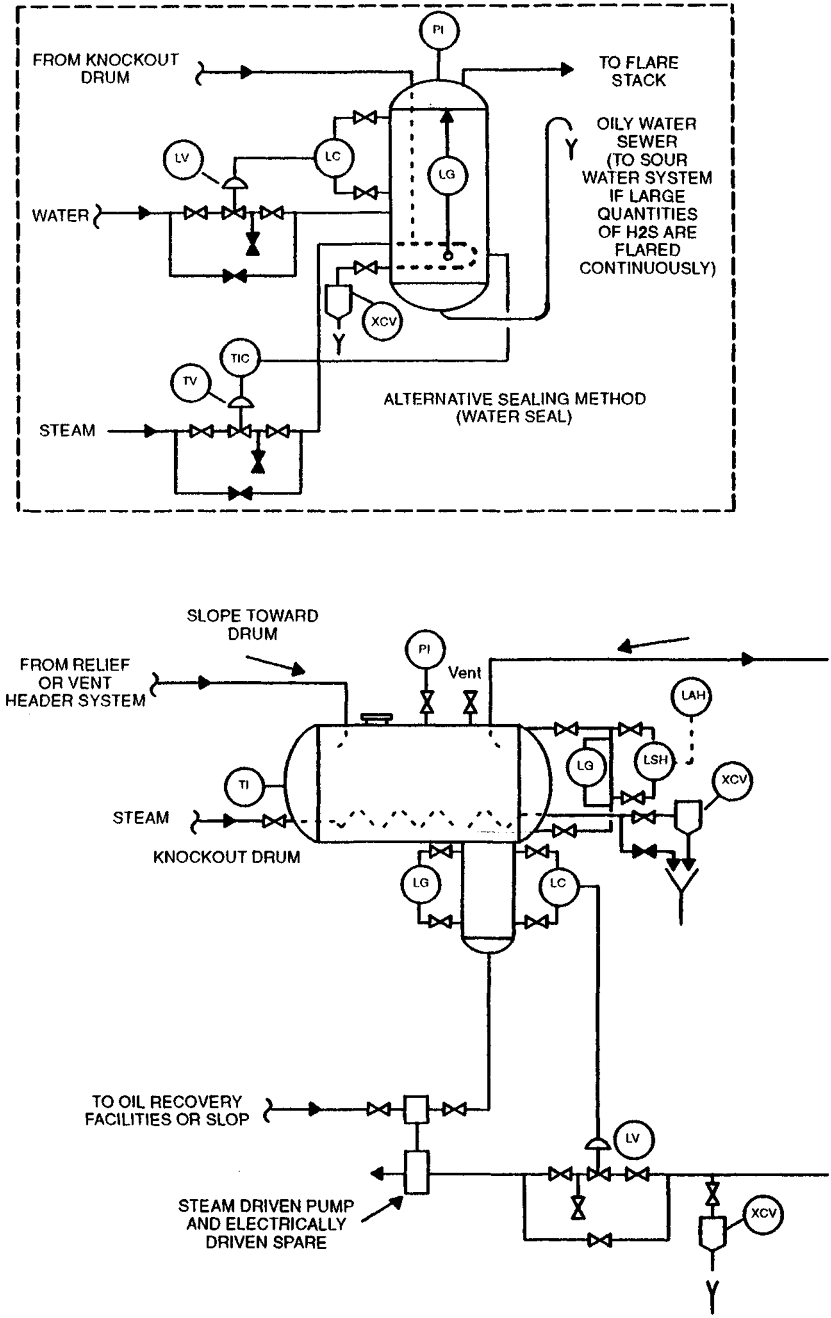
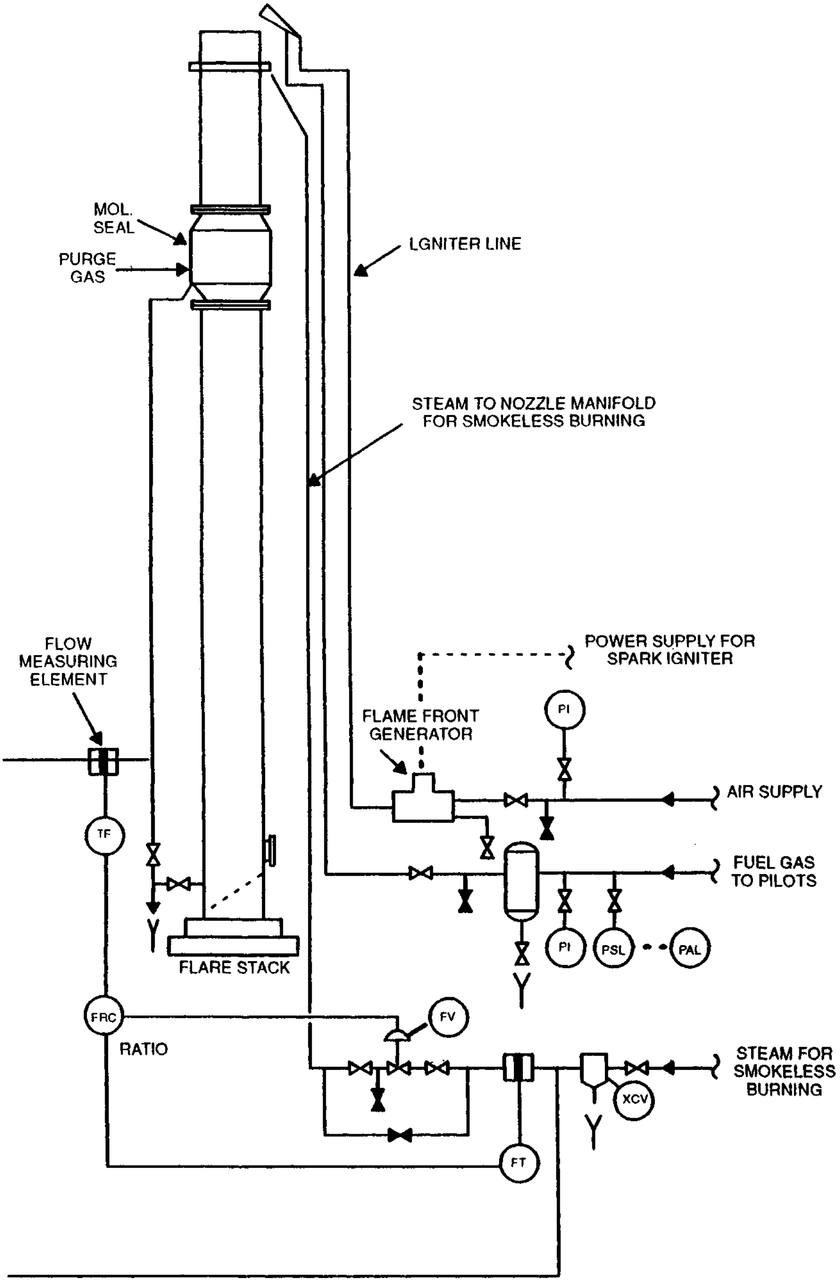


Figure 15-1 Typical elevated fire installation. (API RP 521, Appendix D. Reprinted courtesy of the American Petroleum Institute.)



NOTE: THIS FIGURE REPRESENTS AN OPERABLE ARRANGEMENT AND ITS COMPONENTS. THE ARRANGEMENT OF THE SYSTEM WILL VARY WITH THE PERFORMANCE REQUIRED. CORRESPONDINGLY, THE SELECTION OF TYPES AND QUANTITIES OF COMPONENTS, AS WELL AS THEIR APPLICATIONS, SHOULD MATCH THE NEEDS OF THE PARTICULAR PLANT AND ITS SPECIFICATIONS.

15.1.2.2 Ground Flares

Ground flares are generally used where flare luminosity or noise levels are low, and height requirements are less than 45.7 m (150 feet) (Figures 15-2, 15-3, and 15-4). Because of their proximity to grade, the combustion process must not produce toxic or pollutant by-products. Ground flares may be open or enclosed (to avoid open flame exposure and provide better combustion efficiency). Enclosed flares typically consist of a refractory lined structure that houses the burners.

Low-volume single burner flares are installed in plant areas where space and atmospheric discharges are not limiting. Multiple burner flares can be adjusted to allow staging of burners depending on variations in release rates. Staged burners can be designed to produce smokeless combustion of heavy hydrocarbons by using the pneumatic energy of the flared gas or specially designed air aspirating burners. Ground flares may be installed in combination with elevated flares; normal relief and emergency loads may be distributed in a variety of ways.

15.1.2.3 Low Pressure Flares

These flares usually take off-gases from storage tanks containing VOCs, from American Petroleum Institute (API) separators, dissolved air flotation (DAF), and other wastewater treatment units; and other plant units containing organic vapors that operate at or near atmospheric pressure. In the past these units generally released their VOCs directly to the atmosphere, but under

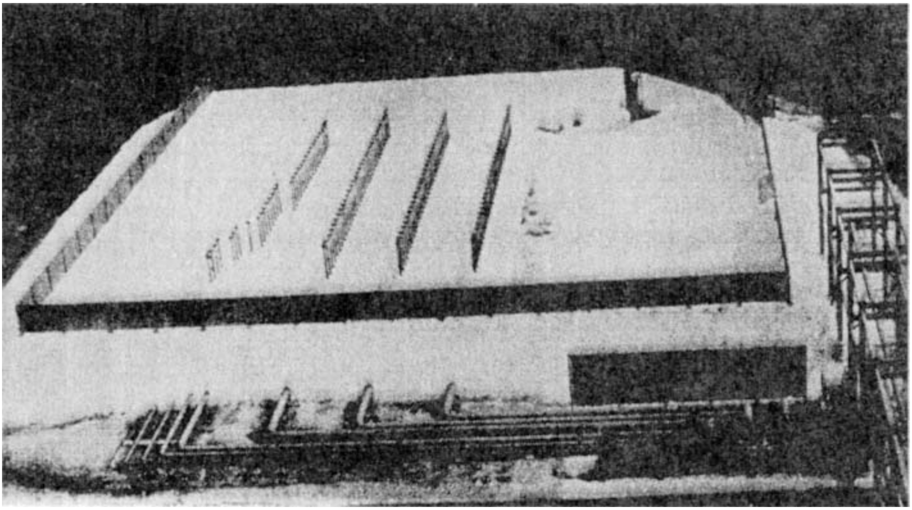


Figure 15-2 Open ground flare. (*Source:* Swander and Potts, 1989)

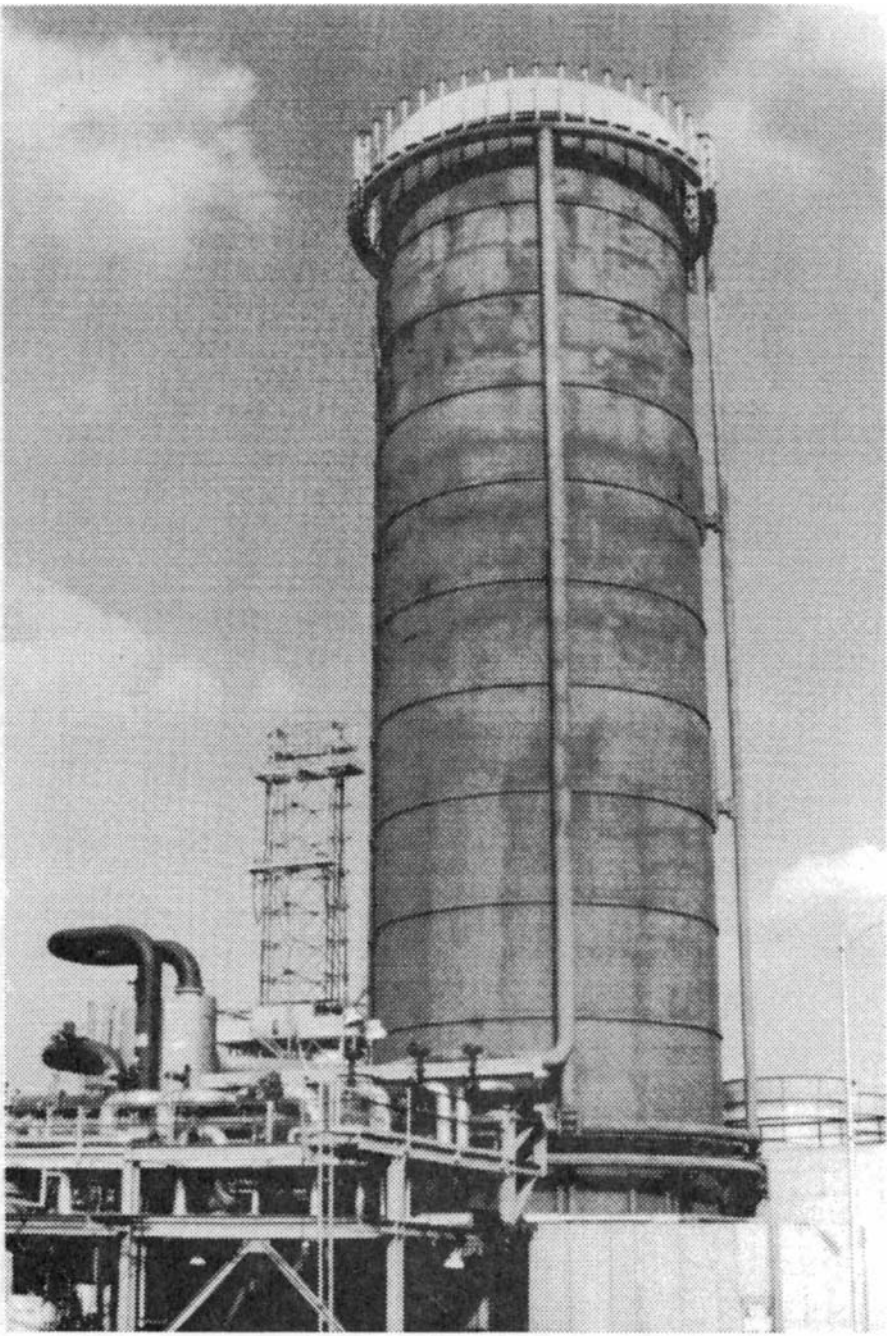


Figure 15-3 Enclosed ground flare. (*Source:* Swander and Potts, 1989.)

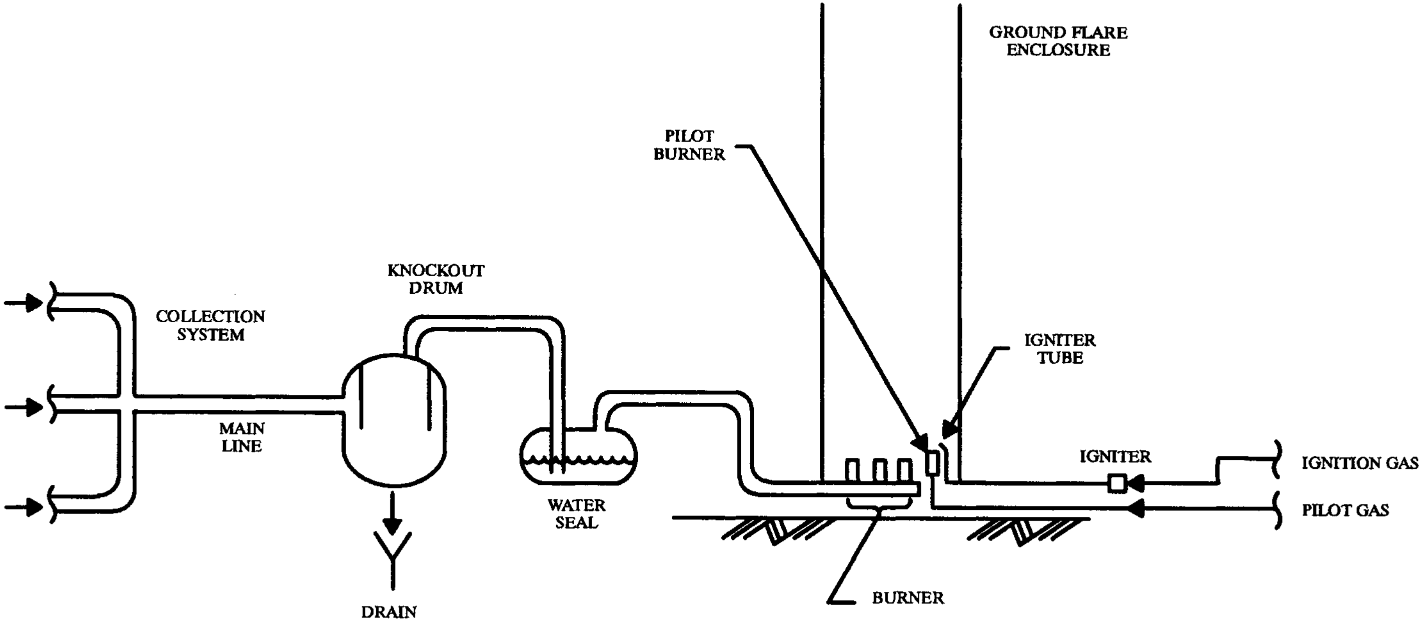


Figure 15-4 Typical enclosed ground flare (Grossel 1990)

current environmental regulations it is becoming necessary to control the emissions. Under certain circumstances, introduction of streams containing oxygen into a VOC flare may be unavoidable. In these cases, careful attention should be given to safe design and operation.

Many of these units create a low flow system that does not require a full size flare assembly. Several vendors market small "stick" flares (an igniter assembly mounted on top of the gas feed pipe) or small ground flares to handle the lower flow rates.

15.1.2.4 Burn Pits

A burn pit is an excavated pit designed to burn either gas or liquid effluent with minimum fuel/air mixing. Its use is limited because it produces large amounts of smoke and must be located at a remote distance from process units, storage areas, and personnel. Under current environmental regulations, it is unlikely that a burn pit would receive an operating permit in the United States. Design considerations include: materials of construction (to prevent leaks and resist fire); size; and location of burners.

15.1.3 General Design Considerations

The following common design criteria for flare systems need to be considered by the designer:

- Regulatory limits on release of toxic, corrosive and flammable substances; noise; smoke (Federal, state, or local venting permits)
- Location and spacing in relation to process units, storage areas, grade level, and personnel (IRI 1991). Criteria are based on radiant heat flux, and ground level concentrations of toxic or corrosive components of the flare gas combustion products.
- Ability to remove liquids entrained in the flare gas
- Prevention of oxygen from entering the system, especially via relief devices Maintenance of relief valves should be performed using procedures that prevent air from entering the system
- Flashback protection to prevent internal explosions in case flammable vapor–air mixtures are generated. Air may be present from backflow through the stack or inlet piping after a release of hot process gas (a hot blow).
- Provision for pilot ignition systems and their controls to be located safely
- Provision for purging the flare header with fuel gas or an inert gas
- A separate flare system for oxygen-containing streams might be preferable to avoid introduction of streams containing air or oxygen into the main flare header. This practice avoids the potential for explosion if flammable concentrations are possible.

- Exit velocity; excessive exit velocity can cause flame detachment or flameout
- Materials of construction should be addressed, especially in regard to low temperatures or corrosive or reactive chemicals.

15.1.3.1 Elevated Flares

Design of elevated flares is dictated by radiation at grade level and the possibility of falling sparks. Sizing criteria and calculations of elevated flares are detailed in API RP 521, Section 5 and Appendix C. Several computer programs, based on API methods, are available to aid in flare system sizing; these programs can be used to calculate flare stack diameter, height, and radiation intensity at various distances from the flare location.

15.1.3.2 Ground Flares

In addition to the general design features, the bottom of the stack should be elevated to allow for combustion air flow into the burning area.

15.1.3.3 Low Pressure Flares

The primary design problem with a low pressure system is in delivering the off-gases to the flare. In many cases the pressure drop involved in moving the gas to a safe area for the flare, combined with the pressure drop across the flashback prevention devices, can easily exceed the total pressure available to the system. In other cases the pressure available may, with care, be sufficient to move the off-gases to the flare.

A low pressure system may be sufficient to feed the flare, provided the header lines are sized adequately to reduce pressure drop. It may be necessary to perform the pressure drop calculations manually as many of the standard computer programs for line pressure drops will not work at such low pressure differentials. Low pressure systems should be checked to be sure that back pressure imposed by the flare header does not interfere with proper operation of relief devices.

When system pressure alone is inadequate, a common solution is to add an off-gas blower to the system after the off-gas source, but prior to any safety device. This allows the system to develop adequate pressure without the need to modify the sources, reduces the size of the flare header and permits the use of the flare safety device of choice. The disadvantage of this method is its inherent safety problem combined with system reliability. The blower is handling flammable or combustible material. Care must be taken in choosing a blower and motor that will minimize the possibility of off-gas ignition. Reliability can be improved by having a blower spare installed and by performing routine preventive maintenance as required. A backup carbon adsorption system may also be used where only short periods of blower downtime are anticipated. The system pressure drop should also be checked to make sure that the back pressure during high release conditions does not exceed the unit's pressure rating. The alternative to adding a blower is to design and operate the system at a sufficient pressure to feed the unit off-gases to the main flare header; or, the low pressure stack can be run separately from the main stack and supported by the same structure.

Another design consideration for low pressure flares is the possibility of extinguishment by high velocity winds. Special flare designs may be required and are available for certain installations (e.g., offshore oil platforms).

15.1.4Smokeless Flaring

Smoke formation is not permitted under EPA (Environmental Protection Agency) regulations (40 CFR 60.18) during normal operations. However, smoking during emergency releases, beyond a certain maximum time (generally 5 minutes) must be reported to the environmental authorities.

Incomplete combustion of hydrocarbons, because of insufficient air caused by poor mixing, leads to the formation of smoke (soot particles). To improve mixing of air and the effluent, turbulence is created by vortex action or injection of steam or fuel gas into the flare area; water spray and air blowers are also used to improve mixing. Steam is generally the most readily available mixing promoter and smoke suppressor and is the only practical way to flare large volumes smokelessly in an elevated flare. However, it may not be available in quantities needed for maximum flaring rates. It can be injected in any one of several locations: at the flare stack just below the burner tip, directly into the flame, or into the flare gas before it reaches the flare tip.

Smokeless flaring is required only for normal flare loads, not for emergency venting loads. API RP 521 contains an equation for calculating the steam injection rate.

15.1.5 Noise

High noise levels in flares are caused by the roar of the actual combustion and the high velocity of injection steam. Noise generated by emergency relief is generally acceptable, even at a high level (up to 125 dBA maximum), because the duration is short (ACGIH 1986). Noise generated by controlled venting and routine releases must not exceed the maximum set by federal, state or local regulatory agencies for operating personnel or the public.

15.1.6 Collection Headers

It may be desirable to combine effluent disposal systems based on similar pressures, process stream temperatures, compositions, and quantities. The materials of construction of the flare collection headers, flare stack and tip are determined by the composition of the flared fluid (especially if corrosive or toxic) and the operating pressure and temperature of the flare system.

Examples of common headers and typical materials of construction are:

- *Cold Flare Header*—austenitic stainless steel is frequently used for ethane and lighter effluents which flash to –45°C (–50°F) or lower.
- *Intermediate Flare Header*—Cold, dry effluents at temperatures from –45°C to 0°C (–50 to 32°F) are frequently collected in a header constructed of killed carbon steel. In an ethylene plant, the streams contributing to the cold and intermediate headers are subjected to vapor/liquid separation in the same knockout drum. Downstream of the knockout drum the vapors are superheated to allow header and stack construction of carbon steel.
- *Hot Flare Header*—Hot, wet effluents above 0°C (32°F) are often collected in a carbon steel header and subjected to gravity separation into a separate knockout drum. Most effluent streams fall in this category.
- *Sour Gas Header*—In certain situations, sour gas streams containing high levels of hydrogen sulfide are collected in a separate header and burned in a separate flare stack. Because of the corrosive and toxic nature of this fluid, it is more economical to provide small stainless steel facilities to handle this stream than to combine it with other effluents in a larger stainless steel header. It also allows for better control of flaring since the sour gas burn rate may be below the minimum burning rate of the larger flare. The flare stack should be high enough to disperse the products of combustion of the sour gas.
- *High and Low Pressure Headers*—Sometimes it is economically warranted to separate the high and low pressure flare systems. Generally, the lower pressure reliefs dictate the size of the relieving system. In some cases, however, the controlling quantity comes from relief devices set at high pressures and in these cases the high pressure system, with a smaller piping network, might be sized separately.

15.1.7 Definition of Relief System Load

Although pressure relief valves are sized to accommodate individual peak relieving loads, the relief system design requires that a cumulative relieving load from valves discharging simultaneously be determined. This load is used to determine the back pressure obtained in the relief system, fluid velocity in sections of the relief header and at the flare tip, and the level of thermal radiation and noise at grade. Since back pressure may affect the performance of a pressure relief valve, the relief header system (PSV tailpipe, subheader and main flare header) is sized to limit the back pressure at the valve outlet and thus maintain the required capacity of the pressure relief valve. The maximum allowable back pressure is a function of the type of pressure relief valve and its set pressure. The actual back pressure obtained at the relief valve outlet is a function of line size and its associated relieving rate in each section of the relief header system. The flow rate in each section of the relief header is different depending on the location, number, and capacity of each pressure relief valve that is expected to discharge into the relief header at the same time.

Typical common mode failures such as fire, cooling water failure, and power failure, are generally involved in the simultaneous discharge of several relief devices. Consequently, the controlling loads generated by one of these emergencies must be evaluated for design of the flare headers as well as the equipment items in the system. These failures must be further analyzed to determine if the effect is plant wide or local, if other standby equipment is available to pick up the service, if automatic startup spares are available, or standby power supplies are provided. The relief loads for one contingency (e.g., cooling water failure or power failure) may not be additive, and therefore proper transient analysis may reduce the overall controlling load.

Special consideration must be given to situations where relief devices can discharge flashing liquids or where a combination of cold liquid and hot vapor discharge may result in vaporization of the liquids. Such situations may generate additional vapor loads, beyond those corresponding to the relieving loads. Mechanical effects due to uneven thermal stress should be considered.

Instrumented shutdowns of equipment and heat sources can appreciably reduce flare design loads. This not only reduces environmental problems associated with flaring or scrubbing, but also reduces the cost of chemicals wasted during plant upsets (Zheman and Early 1992). When considering the relief loads resulting from instrumented shutdowns, it may be assumed that all trips will function. However, it is recommended design practice to assume that the trip on an equipment piece contributing the largest noncumulative relieving load will not function. It is also suggested that this philosophy be supported with a quantitative assessment of reliability.

The disadvantage of instrumented shutdowns is that instrumentation must be of the highest reliability. It is mandatory that the shutdown systems operate as designed and when required, since the flare system is smaller. This will require either redundant protective devices such that the system is always connected to a protective device even when maintenance is being performed on the alternate (redundant) device, or an administrative procedure such as lock and key bypass arrangement that restricts access to the system only to personnel in responsible control.

15.1.8 Design of Flare System

The effluent from an emergency relief device is often a two- or three-phase mixture. Sizing relief devices for two-phase vapor–liquid flashing flows is addressed by the DIERS Project Manual (DIERS 1992) and summarized in Chapter 14. Sizing of relief valves discharging into a flare system is impacted primarily by back pressure considerations.

The flare system includes collection of effluents, phase separation using knockout drums, and combustion in the flare.

Some relief systems include solids, and if carryover occurs, burning material can be expelled from the flare or can plug ground flares. If solid carryover is not cleaned from knockout drums and flare headers after a release containing solids, the next release can result in slugs which can damage the flare headers or flare itself.

15.1.8.1 Headers

Sizing of Headers

The basic criterion for sizing the discharge piping and relief manifolds is that the back pressure, which may exist or be developed at any point in the system, must not reduce the relieving capacity of any of the relief devices below that required to protect equipment from overpressure. Thus, the effect of superimposed and built-up back pressure on the operating characteristics of the valves must be carefully examined. The discharge piping system must be designed so that the built-up back pressure caused by the flow through the valve under consideration does not reduce the capacity or opening pressure of any pressure relief device that may be required to relieve simultaneously. Built-up back pressure will reduce flow through a valve that is sized for subsonic flow, and the design calculations must take this into consideration.

For conventional relief valves, built-up back pressure is limited to 10% of the set pressure. Any increase of back pressure beyond 10% will reduce the valve capacity significantly. For balanced bellows, pilot, and piston relief valves the back pressure can be much higher; however, the manufacturer should be consulted to ensure that sufficient valve capacity remains.

When the maximum vapor-relieving requirement has been established and the maximum allowable header back pressure has been defined, line sizing is based on fluid flow calculations. There are several methods for calculating the size of the discharge piping when the flow conditions are known; for example, see API RP 521, Section 5.

Several computer programs are available to speed up the sizing calculations for flare systems. The programs can rate existing systems, design new flare systems, or rate a portion of a system and design the remaining sections of the system. The programs are capable of calculating heat transfer in the flare system network, using sonic velocity limitations, and performing flash and condensation calculations. The programs can automatically calculate fluid physical and transport properties, vapor fractions, pressure drop, temperature and Mach number for each segment of the network. Several cases can be addressed simultaneously (such as cooling water failure, power failure, etc.). The calculations are performed first on the most critical case followed by other cases in the order of their criticality. This becomes important since back pressures are calculated for each case using the line sizes established from the previous critical case.

Header Design Considerations

The following are general guidelines for flare header design:

- Extensive measures should be taken to avoid pockets in the flare header and associated piping.
- Piping (discharge piping, subheaders and headers) should be free draining to the knockout drum.
- Consider intermediate knockout drums in or near process units if the flare stack is located in a remote area of the plant.
- Sectionalizing is not a requirement and is avoided in some organizations to avoid maintenance problems with valves and possible misoperation or malfunction. Line blinds sometimes are used where sectionalizing is required.
- Flare headers may collapse if a large volume of liquid is inadvertently discharged into the header, exceeding the capacity of the piping supports. To prevent such events, it is advisable to use criteria such as specifying the pipe as half-full of liquid or otherwise ensure that the header can support the weight of the liquid, and absorb the impact of any liquid slugs.
- Pressure relief headers must not be routed from one operating area through another area where operators frequently perform maintenance.
- Flares handling combustible vapors from multiple relief valves must not be used for venting air or steam during startup or at any time loss of flame is likely.
- Avoid freezing or solidification of liquids such as water, high pour point, or high-viscosity oils, polymers or other materials during low ambient temperatures; heat tracing and drains may be required.

Design of the flare system piping should conform to the requirements of ASME B31.3. Installation should conform to API RP 520, Part II.

15.1.8.2 Drums

Knockout drums are used to prevent the hazards associated with flaring gas containing liquid droplets.

Knockout Drums

The flare knockout drum (Figure 15-5) collects relief loads and separates liquid droplets from vapor releases. Depending on its composition, this liquid may

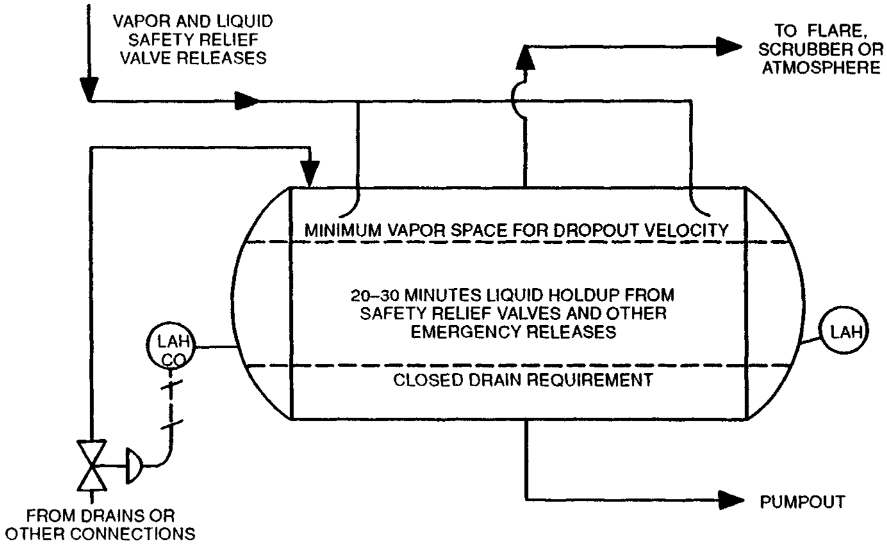


Figure 15-5 Typical flare knockout drum. (API RP 521, Appendix D. Reprinted courtesy of the American Petroleum Institute.)

be returned to the process for further recovery or later vaporized and routed to the flare. An overview of methods of sizing knockout drums and various other types of blowdown/knockout drums and vapor–liquid separators used in the chemical industry is given in the article by Grossel (1990). Sizing method for flare knockout drums is outlined in API RP 521.

Other considerations in the design of a knockout drum are:

- A steam coil, jacket, or other means of heating is sometimes provided in the drum to prevent high viscosity liquids from becoming too viscous to drain or be pumped.
- The drum should be sloped towards the liquid outlet nozzle.
- For cold climate locations, methods for freeze protection are recommended in the event that the knockout drums capture some water.
- Consideration should be given to the reactivity of all chemicals which might be encountered, especially when external heating is applied.

Seal Drums

The purpose of the seal drum is to prevent air ingress into the flare system thus providing flashback protection. A typical flare stack seal drum is shown in Figure 15-6. Typically seal drums are designed for at least 50 psig to withstand internal explosion. The vapor space should be sized to avoid entraining the seal liquid in the flare gas and to prevent surges of gas flow to the flare. API RP 521 presents one method for seal drum sizing. Seal drum

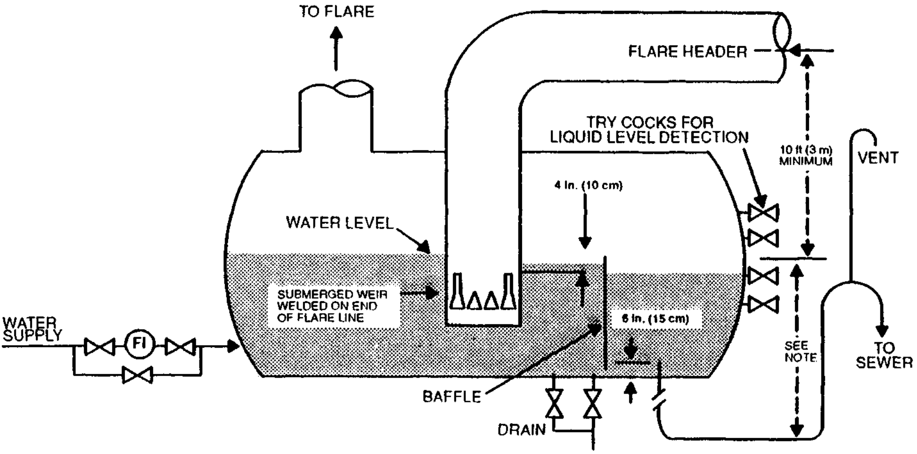


Figure 15-6 Typical flare stack seal drum. *Note:* It is suggested that the sewer seal be designed for a minimum of 175% of the drum's maximum operating pressure. (API RP 521, Appendix D. Reprinted courtesy of the American Petroleum Institute.)

capacity should have sufficient capacity to prevent back flow regardless of the circumstances.

Consideration must be given to the proper disposal of the liquid collected in the knockout and seal drums. The liquid may be flammable, or reactive, and may contain toxic compounds. Consideration should be given to liquid seal integrity, including freeze protection.

15.1.8.3 Flare Stack

The sizing of a flare requires the determination of stack diameter and stack height for the maximum simultaneous load from the source(s). Determination of the maximum simultaneous load is a complex problem requiring an understanding of interactions among loads and an agreement on a philosophy of design. Several factors govern the stack sizing, including velocity, pressure drop available, wind effect, dispersion of flammable and/or toxic gases, and ground level heat flux. A detailed sample calculation for sizing a flare stack is presented in Appendix A of API RP 521.

Flare stack diameter is based on velocity criteria with consideration for pressure drop, particularly in low pressure systems. Depending on the flare gas surge volume, duration and timing, it is recommended that the velocity at the flare stack tip be limited to 0.5 Mach for peak, short term, infrequent flow, and 0.2 Mach for normal and more frequent conditions. Low velocities may result in slow burning that can cause heat and corrosion damage at the flare tip. In addition to API recommendations for tip velocity, 40 CFR 60.18 also specifies maximum flare tip exit velocity as a function of heating value of the gas.

Flare stack height is generally based on the radiant heat flux generated by the flame; recommended maximum heat intensity levels for various conditions are given in API RP 521.

Stack sizing is also governed by the wind effect, that is, distortion of the flame by the wind. As the center of the flame is moved by the force of the wind, heat intensity shifts in relation to plant structures. The variation in heat intensity affects the distance requirements for structures (and personnel) around the flare.

15.1.8.4 Environmental Considerations

The EPA has issued a number of specifications (40 CFR 60.18) relating to flare operation to ensure environmental effects are considered. As recently discussed by Stone et al. (1992a, b), the following points must be complied with:

- Flare exit velocity determines the flare tip diameter. At too high an exit velocity, the flame can lift off the tip and flame out, while at too low a velocity it can burn back into the tip or down the sides of the stack. The EPA requirements for flares used to comply with EPA air emission standards are specified in 40 CFR Section 60.18. The requirements are for steam-assisted, air-assisted, and nonassisted flares. Requirements for steam-assisted, elevated flares state that the flare shall be designed for and operated with:
  —An exit velocity at the flare tip of less than 60 ft/sec for 300 Btu/scf gas streams and less than 400 ft/sec for >1000 Btu/scf gas streams. For gas streams between 300 and 1000 Btu/scf the maximum permitted velocity (V_{max}, in ft/sec) is determined by the following equation:

  $$\log_{10}(V_{\text{max}}) = \frac{B_v + 1214}{852}$$

  where B_v is the net heating value in Btu/scf.

  It is standard practice to use a design velocity of 80% of V_{max} for sizing the minimum flare tip diameter.

- No visible emissions. A 5-minute exception period is allowed during any two consecutive hours.
  —A flame present at all times when emissions may be vented. The presence of a pilot flame shall be monitored using a thermocouple or equivalent device.
  —The net heating value of the gas being combusted being 300 Btu/scf or greater for assisted flares and 200 Btu/scf for nonassisted flares.
  —If nitrogen is used for header flare purging, the effect on Btu value must be considered.

- In addition, owners or operators must monitor to ensure that flares are operated and maintained in conformance with their design.

15.1.9 Header Purging

Another method of flashback protection is the use of continuous purge gas in the flare header to maintain a slight positive pressure in the system. The goal is to prevent air from entering the relief header or flare system and forming an explosive mixture with the organic compounds. Air can be drawn into the flare system under any of the following conditions:

- The gas in the stack is lighter than air (lower in density). The pressure in the bottom of the stack may be substantially lower than atmospheric.
- After flaring hot gases, the vapor remaining in the header will shrink as it cools, causing air to be sucked in.
- Elevation of the flare stack creates a natural draft and air leaks in through flanges and joints.

The purge gas rate depends on whether other sealing devices are used or whether the purge gas is the sole method of flashback protection. Purge gas requirements can be calculated by the method of Husa (1964); the flare vendor should also be consulted. Injection of purge gas at the following locations is recommended:

- At the upstream end of the main header. A flow control device, such as restricting orifice or rotameter, is normally used to control the flow.
- At the end of each subheader servicing the process unit. This application may be used for start-up only.
- At the flare end of the header and upstream of the hydraulic guard to prevent air ingress after a hot release.

15.1.10 Flare System Safety

Safety concerns in flare design involve the risk of explosion or fire due to improper flare design or operation. Routine scenarios encountered during maintenance and operation should be carefully considered to avoid contamination of relief systems with oxygen or reactive materials that may rapidly polymerize, releasing large amounts of heat or plugging the flare. These scenarios should be carefully documented, and training should be provided for operations and maintenance personnel. Some of the concerns listed below have already been discussed:

- *The flare is an open flame and a major source of radiant energy.* The flare must be located to minimize the chance that flammable vapors from a storage tank leak or unit rupture will contact the flare. Flare placement and height should minimize the radiation exposure of storage tanks, process units and personnel working in the area. (See Section 15.1.3.)

- *The entrainment of air into the flare header can cause the vapor in the header to burn or explode, causing fires or rupture in the process systems.* The possibilities of entrainment and the consequent flashback can be minimized by the use of a seal drum, molecular seal, and sweep gas to prevent air from traveling down the line. The options are detailed in Sections 15.1.8 and 15.1.9. Additionally, equipment may be specified with a high enough pressure rating to withstand the pressure transients caused by a flashback.

  In some cases, particularly where wastewater treatment units go to the flare, some air is inevitably included in the flue gases. In these cases, it is common to use an in-line oxygen meter or explosimeter to monitor the air in the system and maintain the flue gas in a nonflammable condition. For example, during shutdown following a process upset in a petrochemical plant, a water seal was interrupted, allowing air to enter the system. When a malfunctioning relief valve was removed for maintenance, natural draft allowed formation of a combustible mixture. The pilot on the flare tip was the source of ignition for the flashback (Kilby 1968).

  Some organizations do not feed air or oxygen-containing streams into the main flare header system; a separate flare system might be preferable.

- *Flashback.* In order to prevent the risk of explosion to the flare, protection can be provided by seal drums; header purging; or use of a dry seal such as a molecular seal, especially when the flare gas is lighter than air, for example, hydrogen. Flame arresting devices may be installed in headers of the flare system to prevent propagation of any flashbacks which might occur. (See Chapter 13.)

- *Some tanks, wastewater treatment facilities, and other units may continuously vent to the flare without the use of relief valves.* Use of direct venting of low pressure tanks and pressure relief devices to flare headers is risky due to potential for overpressure or back mixing during emergency events in other equipment. Care should be taken in the design of flare headers to make sure that these units, and units with low pressure relief valves, cannot overpressure and rupture during high volume relief situations. In some cases it may be necessary to increase the pressure rating of the individual unit to above that seen in flaring situations, or use a separately dedicated low pressure stack.

- *Improperly sized knockout drums can lead to the presence of liquids at the flare tip during high levels of flaring.* This dangerous situation can cause an explosion at the flare tip, extinguishing the flame or ejecting burning liquids into the air. More information on sizing is given in Section 15.1.8.

- *Loss of flame.* A method to monitor the pilot and provide a reliable system to reignite the pilot burners must be provided. The most frequent cause of pilot failure is loss of fuel gas flow; this is often due to a plugged line or filter. Provide a means to ensure that the fuel gas is clean and to verify flow to the pilot. Another cause of loss of flame is blowout on low pressure flares in high winds.

Because uncertainties will always exist that an upset process condition could produce an explosion in a flare or incinerator system, it may be appropriate to install detonation arresters in-line (see Chapter 13).

15.2 BLOWDOWN SYSTEMS

Condensable vapors, contaminated aqueous effluents, and various other liquid streams generated due to plant emergencies require disposal. These "blowdown" systems include plant oily water sewers, chemical sewers, closed drain header systems for flammable liquids or special materials, quench blowdown drums, blowdown drums, effluent disengaging drums or other facilities capable of handling the additional loads. Systems for routine deinventorying are not in the scope of this section.

The method of disposal is determined by the hazardous properties of these fluids, such as toxicity, and temperature, viscosity, solidification, and miscibility. The objective in design of blowdown systems is to not create a new problem while solving the disposal problem. Commonly used blowdown systems are described on the pages that follow.

15.2.1 Equipment Drainage Systems

During upset conditions or shutdowns, process equipment items must be drained of their contents to allow personnel safe entrance. Disposal of small inventories of fluids depends on their volatility and toxicity; frequently discharge is to a sewer or to the atmosphere, provided the material is not hazardous or toxic. Compatibility considerations are of utmost importance.

Disposal of larger inventories depends on properties of the fluid. The following options may be considered:

- For low boiling materials, drain to a closed drain header for further treatment.
- For materials above their flash point, drain to a closed drain header for further treatment.
- For high boiling materials below their flash point, drain to the appropriate sewer.
- For aqueous liquids contaminated with low boilers, drain to water or caustic disengaging drums for subsequent treatment. After pressure

LIST OF TABLES

17

EXPLOSION PROTECTION

17.1 INTRODUCTION

Chemical process systems may contain any number of potential hazards depending on their design, construction, and operation. This chapter deals with the special class of hazards associated with sudden and rapid overpressurization which are usually due to the onset of combustion or exothermic runaway gas-phase chemical reactions. The consequences of such an event are potentially disastrous. Vessel rupture, launching of equipment components as projectiles, discharge of combustion products and fire plumes, initiation of secondary explosions, contamination of the plant and environment, and injury to personnel are the more obvious results of such events. Examples of at-risk systems include solvent storage and pump rooms, aerosol can filling operations, transfer stations for combustible gases and liquids, dust filters, grinders, mills, silos, spray driers, ovens, conveyors, etc. One survey of the frequency of involvement of dust handling equipment in explosions is represented in Figure 17-1. In general, any environment handling combustible gases, volatile liquids, explosible dusts, and mists must be considered a potential explosion hazard.

It is the objective of this chapter to present the background information necessary to understand the conditions and events that can lead to an increase in explosion hazard potential due to combustion processes and to discuss appropriate preventative and mitigative measures that may be applied in process design. Important related subjects are covered in other chapters: ignition sources, Chapters 11 and 12; deflagration and detonation flame arresters, Chapter 13; and runaway reactions, Chapter 14.

17.2 ENERGY RELEASE ON NONCOMBUSTIVE VESSEL RUPTURE

Gases released from an exploding vessel expand isentropically. One method for estimating the amount of energy released to the environment is by integration of the *PdV* work function. The energy release calculated by this method is given by (Crowl and Louvar 1990)

$$W_{\mathrm{I}} = \frac{P_1 V}{(k-1)} \left[1 - (P_2/P_1)^{(k-1)/k}\right] - 10^5 \qquad (17\text{-}1)$$

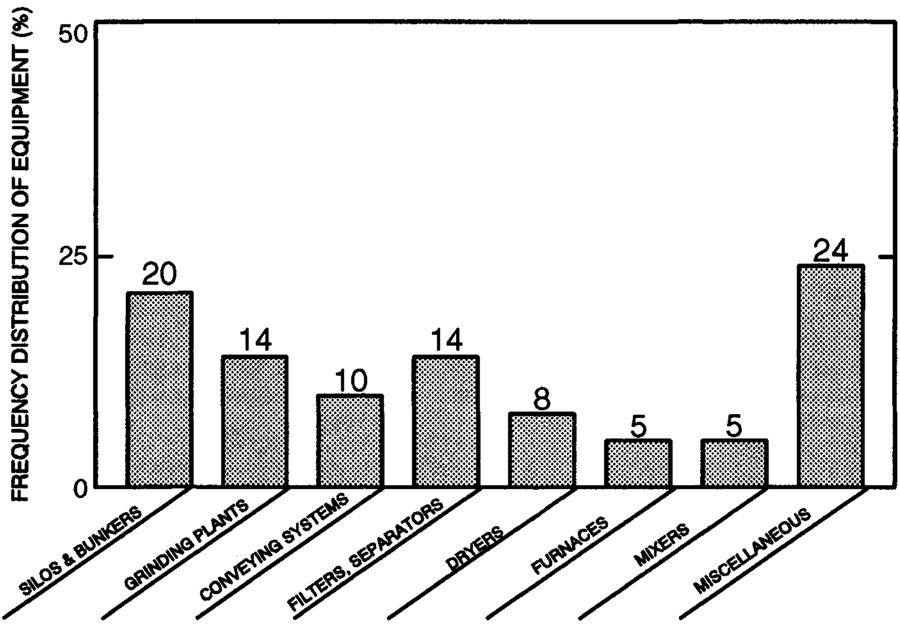


Figure 17-1 Frequency distribution of types of equipment involved in 357 dust explosions, 1965–1980. (From Bartknecht 1989.)

where W_I = explosive energy released based on isentropic gas expansion, J; P_1 is vessel pressure at rupture, bar; P_2 = ambient pressure, bar; V = vessel volume, m^3; k = ratio of specific heats of the expanding gas C_p/C_v, taken as 1.4 for air.

It has been reported that this relation overestimates the energy release for values of P_1 less than about 6.9 bar g. (100 psig) and underestimates the energy release at higher pressures. A more rigorous energy release estimate can be obtained by thermodynamic availability analysis (Crowl 1992) from

$$W_A = nRT[\ln(P_1/P_2) - (1 - P_2/P_1)] \tag{17-2}$$

where n = amount of gas released, mol; R = 8.31 J/mol-K; T = absolute temperature, K; and W_A = the energy released, based on availability analysis, J.

A comparison of the different methods of estimating explosion energy release from expanding nonreacting gases is given in Figure 17-2. One curve in the figure shows the energy release assuming isothermal gas expansion, W_{Iso}, a conservative result obtained using

$$W_{\text{Iso}} = nRT \ln(P_1/P_2) \tag{17-3}$$

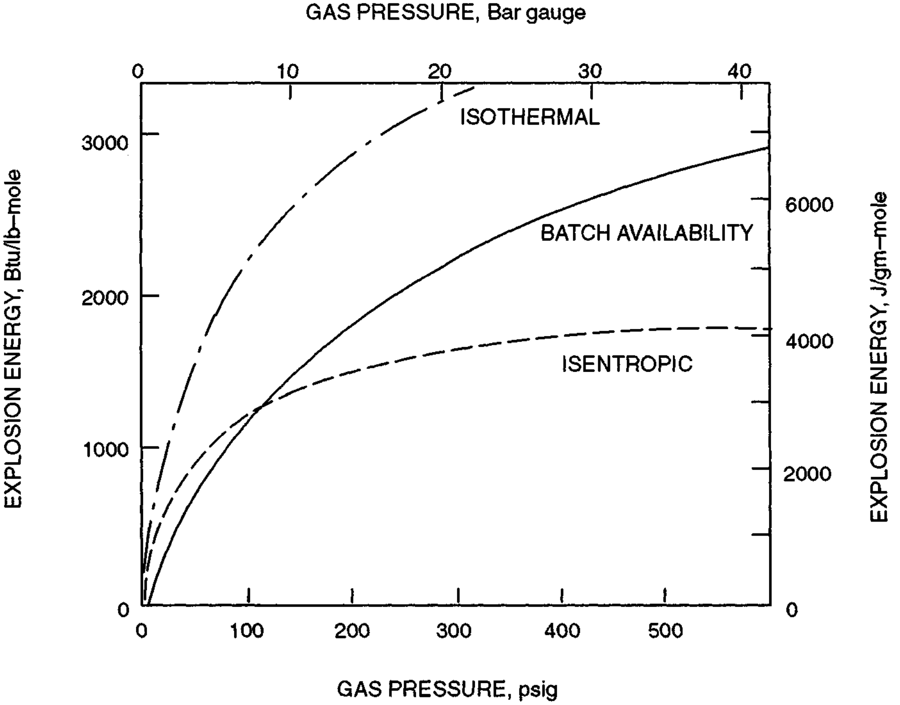


Figure 17-2 Three methods of estimating explosive energy release of nonreacting gases. (From Crowl 1992.)

17.3 FLAMMABILITY

17.3.1 Introduction

An assessment of explosion hazard potential begins with consideration of the possibility of simultaneously bringing together the five essential elements required for an explosion to occur. These are (1) fuel, (2) oxidant, (3) mixing in combustible proportions, (4) ignition, and (5) enclosure. Fuel and oxidant that are not intimately mixed may burn by diffusion flame combustion with energy release rates limited by gross mass transfer rates. Fuel–oxidant mixtures will be unreactive if the mixture ratio lies outside the flammable limits or if there is no possibility of ignition. Ignited flammable mixtures that are unconfined have reduced potential for producing destructive pressures. (However, see discussion of vapor cloud explosions in Section 17.4.3.) This section focuses on the fundamental combustion characteristics of fuels, oxidants, and mixtures.

A mixture of a combustible substance (fuel), such as a gas or dust, and an oxidant, such as air, is considered flammable upon ignition only if certain criteria are met. One method of determining flammability for gas mixtures is given in ASTM E 681. Here, visual observation of flame front propagation is required. Criteria for establishing the combustibility of dispersed dusts are given by Cashdollar et al. (1992). Here, the pressure rise associated with the ignition of a dust cloud in a closed vessel is measured. The authors suggest the pressure attained must be at least twice the initial absolute pressure and that a minimum rate of pressure rise be attained as evidence of sustained flame propagation. Such criteria may be applied in tests for determining limiting fuel or oxidant concentrations for flammability.

17.3.2 Flammability Limits

Gaseous systems capable of supporting an exothermic chemical reaction and giving rise to a deflagration wave may be single-component, binary, or multicomponent in composition. Gases such as acetylene are capable of undergoing single-component exothermic decomposition. Most often a combustion hazard is posed by a fuel–oxygen–inert system. The proportions of fuel, oxygen, and inert that combine to form flammable mixtures at a particular temperature and pressure may be defined on a three component diagram as shown in Figure 17-3 for methane–oxygen–nitrogen mixtures. The figure is further explained in Section 17.5.2.

The lowest and highest concentrations of fuel gas in air that will support combustion are referred to as the lower and upper flammable limits, or LFL and UFL. In the case of the methane–oxygen–nitrogen system we observe the following: LFL and UFL values for methane in oxygen are 5% and 61%; LFL and UFL for methane in air are 5% and 15%. Values of LFL and UFL for a large number of pure vapors are listed in NFPA 325M. When several combustible species are present in the mixture, LFL and UFL values may be estimated using Le Chatelier's rule, Eq. (17-4).

$$L_{\text{mix}} = \frac{1}{\sum(y_i / L_i)} \tag{17-4}$$

where y_i = mole fraction and L_i = LFL or UFL in volume percent of component i as required (Bodurtha 1980).

The influence of temperature on flammable limits can be estimated using Eqs. (17-5) and (17-6) (Zabetakis et al. 1959).

$$\text{LFL}_t = \text{LFL}_{25}[1 - 0.75(t - 25)/\Delta H_c] \tag{17-5}$$

$$\text{UFL}_t = \text{UFL}_{25}[1 - 0.75(t - 25)/\Delta H_c] \tag{17-6}$$

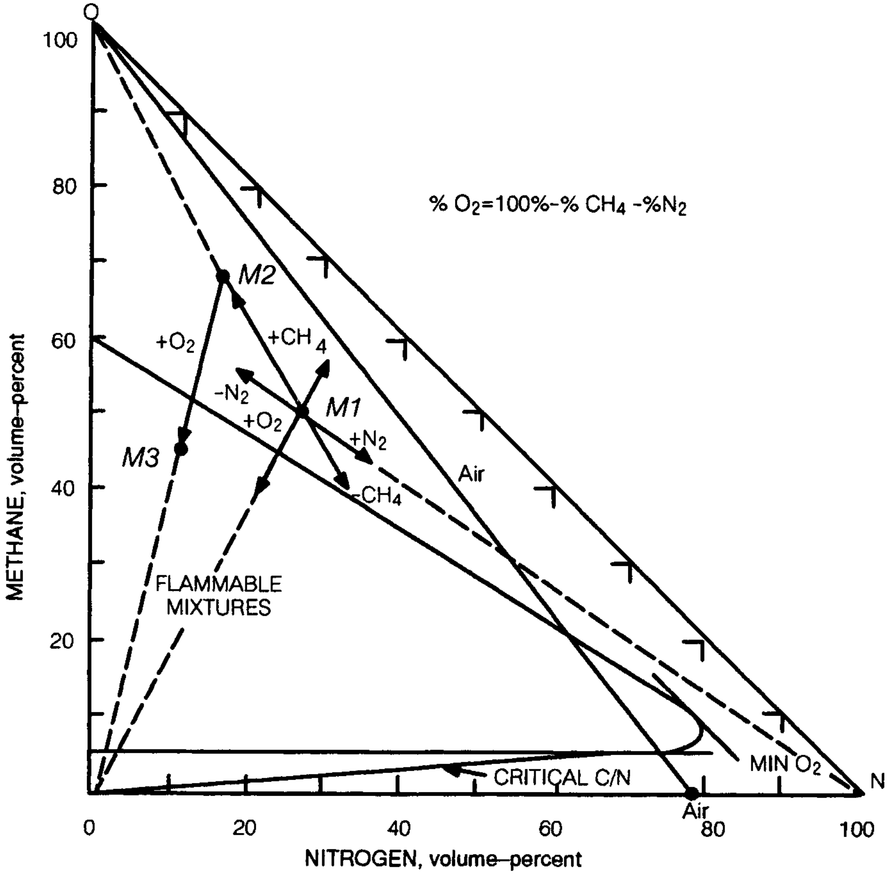


Figure 17-3 Flammability diagram of methane–oxygen–nitrogen system (from Zabetakis 1965a). The condition corresponding to the point *M1* (50%m methane, 30% oxygen, 20% nitrogen) lies outside the flammable region. Mixtures to the right of the line designated MIN O_2 cannot be rendered flammable by ingress of air into the process volume.

where t is temperature in °C and ΔH_c = heat of combustion in J/kg. Most gaseous fuel–air mixtures do not propagate flames at pressures below approximately 0.067 bar (0.97 psia) (Bodurtha 1980). The LFL value is little influenced by pressure. In the range $1 < P < 200$ bar the pressure dependence of UFL for several hydrocarbons was found to be given by

$$UFL_P \approx UFL_{atm} + 20.6 \log_{10} P \tag{17-7}$$

where P = absolute pressure in bar (1 atm = 1.013 bar). Thus, the flammability envelope increases in size at elevated pressure.

17.3.3 Ignition Energy

Initiation of flame propagation in a combustible mixture requires an ignition source of adequate energy and duration to overcome radiative and conductive heat losses to the cooler surrounding material. Methods have been developed for characterizing the lowest spark ignition energy for gases (ASTM 582). Similar methods have been used on dusts. Ignition energy evaluation for dusts, however, is more complex owing to the complications of establishing a reproducible dust cloud, the variables of spark generation (Eckhoff 1975) and the importance of particle size distribution on ignition energy. The theory correlating minimum dust cloud ignition energy with the cube of the particle diameter (Kalkert and Schecker 1979) has been experimentally supported by studies on polyethylene dust (Eckhoff 1991). Ignition and ignition sources are discussed at length in Chapter 11.

17.3.4 Decomposition Flames

Some compounds have very high heats of formation or are otherwise relatively unstable chemically as they may be composed of both fuel and oxidizer components. Such materials can support flames by undergoing exothermic decomposition. Deflagration of ethylene oxide, for example, is discussed by Britton (1990). Examples of gaseous compounds that support decomposition flames are given in Table 17-1.

17.3.5 Liquid Mists

Sprays and mists of fine liquid droplets may have lower flammable limits equivalent, on a mass basis, to vapor LFLs when the droplet size is about 10 m. This is true even for liquids of low vapor pressure (Burgoyne 1965).

Table 17-1 Gases Supporting Decomposition Flames

Gas Species	Decomposition Burning Velocity, m/s
Acetylene, C_2H_2	0.20
Ethylene Oxide, C_2H_4O	0.05
Methyl nitrate, CH_3NO_3	2.50
Ethyl nitrate, $C_2H_5NO_3$	0.10
Hydrazine, N_2H_4	1.10

17.3.6 Dust Suspensions

Dusts suspended in air will support combustion when a minimum mass concentration, designated the lower explosible limit, or LEL, is achieved and sufficient ignition energy is provided. The value of the LEL depends on the composition of the solid phase, its particle size distribution and to some extent on the strength of the ignition source. The LEL for pure vaporizable polymers such as polyethylene can be as low as that observed for hydrocarbon gases as shown in Figure 17-4.

Dusts and mists will exhibit, in principle, an upper flammable limit. In the case of dusts this limit is not usually determined in practice owing to the difficulty of establishing uniform concentrated dispersions. Dispersed dusts readily support combustion at concentrations of several hundreds of grams per cubic meter as shown in Figure 17-4. See Eckhoff (1991) for a comprehensive review of dust as an explosion hazard.

The ignitability of clouds of dust of some materials has been shown to be dependent on the energy density of the ignition source (Cashdollar et al. 1992). Low-volatile dusts, such as anthracite coal, were found to be ignitable in a 20 liter test vessel using igniters with combustion energies of 5 kJ or less. The

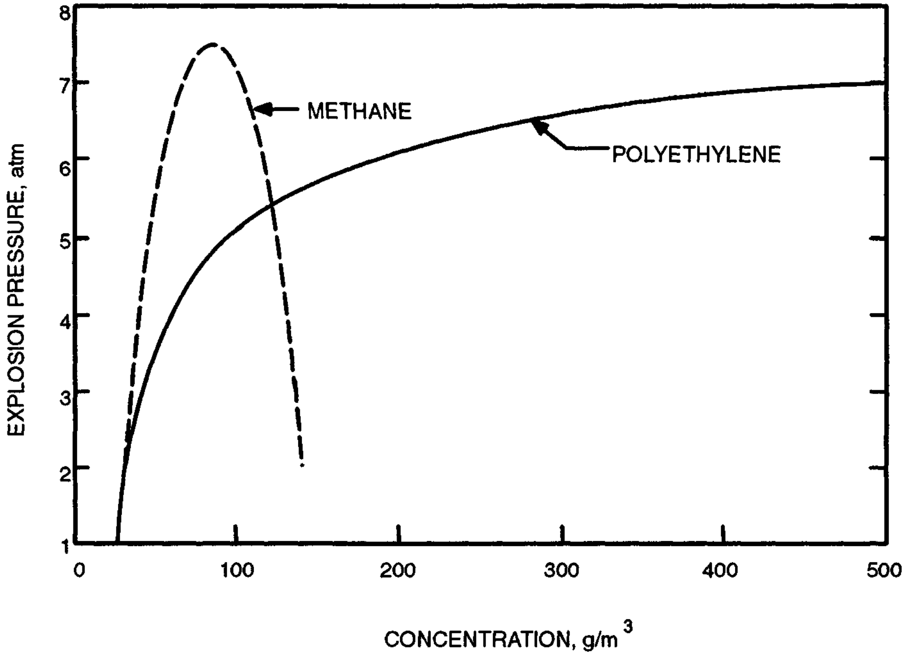


Figure 17-4 Comparison of flammability limits for methane and polyethylene dust in air. (From Hertzberg and Cashdollar 1986.)

same dust was not ignitable at the same concentration in a 1 m^3 vessel using a 10 kJ igniter. Thus, high energy ignition sources in small volumes may overdrive some dust clouds to ignition where in larger volumes ignition may fail to propagate.

17.3.7 *Hybrid Mixtures*

Mixtures containing both a flammable gas and suspended flammable dust are called hybrid mixtures. The LEL of a hybrid mixture is reduced in proportion to the gas concentration up to its LFL value (Bartknecht 1989). This may not be true for a hybrid mixture in which the flammable gas has a high LEL, such as some halogenated hydrocarbons. Further, the ignition energy and burning velocity of a hybrid may be significantly different than that of the dust cloud alone even when the flammable gas component is present in amounts below its own LFL.

17.3.8 *Limiting Oxidant Concentration*

The limiting oxidant concentration (LOC) is that concentration of oxidant below which a deflagration (flame propagation in the gas, mist, suspended dust, or hybrid mixture) cannot occur. For hydrocarbons where oxygen is the oxidant and nitrogen is the diluent the LOC is approximately 9 to 11 vol % oxygen. The LOC for dusts is dependent on the composition and particle size distribution of the solid. Values of LOC for most organic chemical dusts lie in the range of 10 to 16 vol % oxygen, again where nitrogen is the diluent (NFPA 69). The LOC for flammable gases can be estimated as follows (Crowl and Louvar 1990):

$$\text{LOC} \sim (\text{LEL}) \times (\text{moles of oxyden required to completely burn one mole of fuel}) \tag{17-8}$$

17.3.9 *Inert Materials*

Inert components in a fuel–air mixture limit the temperature and pressure rise on ignition or prevent ignition completely. Nitrogen is commonly employed as an inert gas. Water vapor and carbon dioxide are somewhat more effective inerting gases due to their higher molar heat capacities. This is evidenced by the effect of these gases on minimum oxygen concentration. For brown coal the LOC is 11, 12.4, and 13 vol % when the inert is N_2, H_2O, or CO_2, respectively (Bartknecht 1989). Some metal dusts (e.g., magnesium, titanium, and zirconium), which may react with nitrogen or carbon dioxide, must be inerted using a noble gas such as argon.

17.3.10 Inhibitors

Chemicals that prevent ignition or induce extinguishment through chemical rather than thermal mechanisms are called inhibitors. Examples include a number of halogenated hydrocarbons such as bromotrifluoromethane and bromochlorodifluoromethane, Halons 1301 and 1211, respectively. See Section 17.6.5.3 for further discussion on these agents.

17.3.11 Ignitability

17.3.11.1 Flash Point

Flash point (FP) is the temperature, as determined by test, at which a liquid (or solid) emits sufficient vapor to form combustible mixtures with air. The FP may be estimated from vapor pressure data for pure species. The FP of mixtures are best determined using any of several test methods. An extensive listing of FP data is given in NFPA 325M.

17.3.11.2 Autoignition Temperature

Gases

The autoignition temperature (AIT) is the lowest temperature at which a mixture of a flammable gas and air will spontaneously ignite. The AIT, determined at one atmosphere pressure, for many gases and vapors is reported in NFPA 325M. Flammable gases in closed vessels that may become pressurized may exhibit AITs lower than reported in NFPA 325M.

Dust Clouds

The ignition temperature of a dust cloud is designated T_c and is the test temperature at which a dust cloud will ignite. Dust cloud suspensions in test systems are short lived due to settling. Values of T_c are useful in making relative ratings of dust ignition hazard potential. A standard test method for measuring T_c is presently in development by ASTM Committee E-27.

Dust Layers

The ignition temperature of a dust layer is designated T_l (Bartknecht 1989; Nagy and Verakis 1983) T_l is the test temperature that leads to sufficient self heating of the dust layer sample to cause ignition. Dusts accumulated in layers and exposed to hot surroundings or surfaces can ignite at temperatures well below the T_c values. This fact arises from slow oxidation reactions that the dust may undergo when heated. The insulating properties of dust layers may retard the cooling necessary to prevent self-heating to the point of incandescence and ignition. Methods for measuring T_l for both surface layer ignition (Miron and Lazzara 1988) and ignition due to uniform heating are employed.

17.3.11.3 *Spark Ignition*

Dust and vapor clouds may be readily ignited if exposed to electric discharges that exceed the minimum ignition energy (MIE) (ASTM E 582) for the combustible mixture. The energies of sparks that are capable of igniting gas mixtures are usually very much smaller than those required to ignite dust suspensions. A more complete discussion of ignition by sparks of electrical and mechanical origin is given in Chapter 11.

17.3.11.4 *Catalytic Activity*

A number of solid surfaces can act as ignition catalysts in process equipment. Catalytic surfaces, which act to lower the activation energy for key elementary combustion reactions, can result in apparent AITs much lower than for "clean" surface test chambers. Ferric oxide and iron sulfide have been shown to lower AIT values of a number of organic compounds (Bodurtha 1980).

17.4 FLAME EVENTS

17.4.1 *Deflagrations*

Ignition of a flammable gas, dust or mist cloud will result in the propagation of a flame front, or deflagration wave, with the liberation of the heat of combustion into the environment. Deflagrations may also occur in some pure gases having high heats of formation. Acetylene, for example, can decompose explosively at atmospheric pressure (Sargent 1957) while ethylene may also deflagrate at elevated pressures (Scott et al. 1965). The effect of a deflagration is to increase the pressure–volume product due to a large rise in temperature and a change in the amount (moles) of gas present. These relationships are readily quantified by the ideal gas equation of state as follows:

$$PV = nRT \tag{17.9}$$

where P = pressure, bar; V = volume, m^3; n = amount of gas, mol; T = absolute temperature, K; $R = 8.31 \times 10^{-5}$ m^3-bar/mol-K. Four aspects of deflagration behaviors are considered: flame front propagation, and behaviors of unconfined, partially confined, and closed-vessel events.

17.4.1.1 *Fundamental Burning Velocity and Flame Speed*

The fundamental burning velocity, S_u, is the rate at which unburned fuel–air mixture advances into a stationary plain laminar flame front. It is a property of the particular combustible composition at a given temperature and pressure. Values of the best estimates of S_u for a number of gases in air are given in NFPA 68. See Table 17-2. Nagy and Verakis (1983) have shown how effective burning velocities may be estimated for dust clouds. Values of

Table 17-2 Fundamental Burning Velocity of Selected Hydrocarbons in Air[a]

Carbon Number	Burning Velocity, m/s		
	Alkane	1-Alkene	1-Alkyne
1	0.04	n/a	n/a
2	0.47	0.80	1.66
3	0.46	0.52	0.82
n-4	0.45	0.51	0.68
i-4	0.41	0.44	—
n-5	0.46	0.50	0.63
n-6	0.46	0.50	0.57

[a] From NFPA 68

effective S_u reported for clouds of combustible dusts are typically an order of magnitude lower than for gases.

Flame speed, S_f, is rate at which a flame propagates in space. It is equal to the sum of the fundamental burning velocity and the rate at which the flame front is advanced due to the production of high-temperature combustion products. As a minimum

$$S_f = S_u(\rho_u/\rho_b) \tag{17-10}$$

where ρ_u and ρ_b are the densities of the unburned and burned gases, respectively. However, S_f can attain very high values, including detonation velocities, depending on the mixture composition and system geometry. See discussion of detonations, below.

17.4.1.2 Unconfined Deflagrations

The unconfined vapor or dust cloud deflagration presents the hazards of an expanding fireball, with its associated radiant heat emissions and pressure front. The size of the fireball generated can be estimated by assuming that a fixed amount of fuel burns with a stoichiometric equivalent amount of air to yield a burned volume at the flame temperature. The increase in volume of the burned mass is estimated by

$$V_b / V_u = N_b T_b / N_u T_u \tag{17-11}$$

where V_b, V_u = volumes of the burned and unburned gas, m^3; N_b, N_u = number of moles of burned and unburned gas, mol; T_b, T_u = absolute temperature of burned and unburned gases, K.

The ratio of moles of burned to unburned gases can be adequately approximated by writing the stoichiometric combustion equation and comparing the coefficients. The contribution of radicals and equilibrium CO for combustion in air is not generally more than about 1 to 2%. Values of adiabatic flame temperature for a number of common combustible gases are given in Lewis and von Elbe (1987).

Unconfined deflagrations ordinarily do not produce large localized overpressures (see the discussion of vapor cloud explosions for exceptions) because the propagation speed of the reaction zone, or flame speed, is usually much less than acoustic velocity of the unreacted medium. However, deflagration fronts will be accelerated by turbulence that may arise in the flow field by several means. Common sources of turbulence in process spaces are initial velocity gradients, very strong ignition sources, obstacles in the flow path and elongated enclosures such as pipes and ducts. A normal "weak" deflagration can be accelerated and attain speeds approaching the local acoustic velocity. In such circumstances the "strengthened" deflagration can exhibit localized high overpressures. In the extreme case, a strong deflagration can undergo transition to a detonation where the localized overpressures may be extremely high, though brief in duration. Severe damage to process systems is possible, depending on construction. Duct-like enclosures with internal obstacles, such as bucket elevators, are particularly vulnerable to the effects of accelerated deflagrations. See discussion on detonations, below.

17.4.1.3 Partially Confined Deflagrations

A partially confined deflagration is represented by combustion of a vapor or dust cloud in a small volume of a larger enclosure. Lewis and von Elbe have shown that for explosions in confined spherical vessels the total pressure rise is proportional to the volume of gas burned. That is

$$V_b / V_0 = (P - P_0) / (P_{max} - P_0) \tag{17-12}$$

where V_0 = volume of vessel, m^3; V_b = initial volume of combustible that is burned, m^3; P_0 = initial pressure, bar; P = pressure attained on combustion of V_b, bar; P_{max} = maximum deflagration pressure of the combustible, bar.

This relation may be used, together with data on maximum deflagration pressures to estimate the maximum overpressure obtained on the combustion of a small quantity of gas in a large enclosure (NFPA 68; NFPA 69; Eckhoff 1991).

17.4.1.4 Confined Deflagrations

Combustion of flammable mixtures in closed vessels results in a rapid rise in pressure as depicted in Figure 17-5. Key characteristics of a closed-vessel deflagration are the maximum pressure attained, P_{max}, and the maximum rate of pressure rise, $(dP/dt)_{max}$ developed during the event. One measure of the

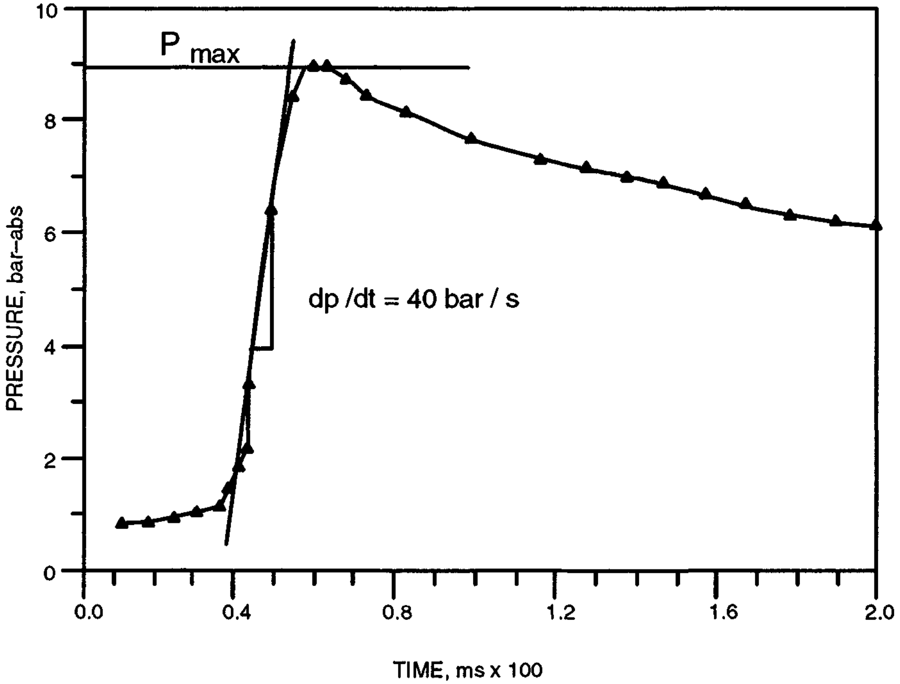


Figure 17-5 Typical pressure versus time data for closed-vessel deflagration. (From D. A. Crowl and F. Louvar, *Chemical Process Safety Fundamantals with Applications*, p. 175. © 1990, reprinted by permission of Prentice Hall, Englewood Cliffs, New Jersey)

explosibility of a combustible material is computed from the maximum rate of pressure rise attained by combustion in a closed vessel. The index of explosibility is defined as

$$K_{\mathrm{St\ or\ G}} = (dP/dt)_{\max} V^{1/3}, \quad \text{bar-m/s} \tag{17-13}$$

where the subscripts refer to dusts (St) or gases (G), V = volume of the test vessel (m^3) and $(dP/dt)_{\max}$ = maximum rate of pressure rise (bar/s) attained over the range of fuel–air ratios tested. The value of $(dP/dt)_{\max}$ will be a maximum for a particular fuel concentration, referred to as the "optimum" concentration, and is characteristic of the particular combustible. K_{St} values for dusts have been found to be nearly invariant with $V^{1/3}$ only for measurements of $(dP/dt)_{\max}$ made in vessels 20 liters or larger in size (ASTM E 1226).

17.4.2 Detonations

Detonation refers to a deflagration wave that is traveling at or over the speed of sound in the unburned medium. A detonation wave is a complex structure consisting of a pressure shock front, that is, an abrupt and large rise in pressure, which is being maintained by the energy release of a closely coupled reaction zone, namely, a flame front (Nettleton 1987). The distance separating the shock front and the reaction zone depends on the composition of the combustible mixture and whether the medium is gaseous or two-phase (dusts and mists). All other stages of development of a combustion wave, from laminar propagation to just prior to the coupling of the reaction zone and the shock front, are deflagration waves of varying strength or intensity. The composition limits of mixtures that will propagate detonations are narrower than the flammability limits for either fuel–air or fuel–oxygen systems.

The development of detonation waves poses special problems in explosion protection. The propagation velocities of fully stable detonation fronts attained in most hydrocarbon fuel–air systems, initially at ambient conditions, are about 1800 m / s. Note the speed of sound at ambient conditions in about 335 m / s. Very high static pressure pulses are associated with the passing shock front, typically about 20 times the initial absolute pressure. The high-velocity gas possesses significant momentum that will cause the reflected pressures experienced by obstacles in the flow path to be still higher, approximately 50 times the initial pressure. Some characteristics of shock waves in air are given in Table 17-3.

Calculated values are with $T_0 = 273$ K and where P_1 = initial pressure, bar; P_2 = static pressure of shock front, bar; w = gas velocity behind shock front, m / s; D_s = shock front velocity, m / s; T_{ac} = temperature that would be achieved by adiabatic compression alone, K; T_{sh} is temperature attained in the shock wave, K; I = impact pressure imparted by shock front to an obstacle in the flow path, bar.

There are certain conditions that can give rise to deflagration to detonation transition (DDT). One means of establishing DDT in a detonable mixture is the discharge of an ignition source of sufficient power to lead directly to detonation. An alternate means of achieving DDT results from the traverse of a deflagration in a detonable mixture in a pipe or duct. Flame acceleration will occur due to flame stretch and turbulence developed as a consequence of wall drag. Transition to detonation can occur if the duct diameter is larger than

Table 17-3 Properties of Shock Fronts in Air[a]

P_2/P_1	w	D_s	T_{sh}	T_{ac}	I/P_1
2	175	452	336	330	1.63
5	452	698	482	426	11.4
10	725	978	705	515	34.9
50	1795	2150	2260	794	296

[a] From Lewis and von Elbe 1987

about one-third the detonation cell size, λ, which is a property of the combustible mixture. The distance traveled by a deflagration front from the point of ignition to the point of DDT is referred to as the "run up distance." The run up distance depends on several factors including the mixture detonation cell size, ignition energy, initial gas turbulence intensity, and the presence of turbulence enhancing obstacles in the flow path. For flames of near stoichiometric mixtures of aliphatic hydrocarbon gases in air which are initially quiescent but which must pass over a standard turbulence promoting obstacle path the run up distance is frequently found to be about 100 pipe diameters. See Table 13-1 for data on a propane–air system. Run up distances are shorter for mixtures of smaller cell size such as for near stoichiometric ethylene–air or hydrogen–air mixtures.

Propagation of the detonation into unconfined space at the pipe exit can occur if the pipe diameter is larger than about 13λ. Wide rectangular ducts may issue propagating detonations if their narrow dimension is greater than 3λ. Detonation energies and cell widths for several stoichiometric gas–air mixtures is given in Table 17-4.

17.4.3 Vapor Cloud Explosions

Vapor cloud explosions (VCEs) can be extremely destructive events. They may be prevented through avoidance of the massive releases of flammables. In particular, tanks containing liquified flammable gases must be protected from being over pressurized due to overfill or overheating.

Table 17-4 Detonation Characteristics of Select Stoichiometric Gas–Air Mixtures[a]

Gas	Cell Size λ, mm	Direct Initiation Energy, kJ
Acetylene	9.8	5.3
Hydrogen	15	4.7
Ethylene	28	43–63
n-Butane	50–62	210–340
Ethane	54–62	130–170
Propylene	54	53
Propane	69	210–340
H_2S	100	>80
Methane	280	93,000

[a] From Sulmistras et al. 1985. Copyright held by the British Crown. Reprinted with permission of the Government of Canada.

A VCE is the result of the ignition of a cloud of flammable vapor or gas. The resulting fireball may propagate with very high flame speeds releasing explosive energy. The energy release may be estimated by (Zalosh 1990)

$$E = \alpha \Delta H_c m_f \tag{17-14}$$

where E = the blast wave energy release, J; α = yield, that is, the fraction of available chemical energy released in generating the blast wave; ΔH_c = low heat of combustion of the vapor, J/kg; and m_f = mass of flammable vapor released, kg. The yield α, is typically of the order of 0.01 to 0.05 depending on the fuel and event scale.

The energy release from TNT ($\alpha = 1$) is equivalent to 4.69×10^6 J/kg. The TNT equivalence of blast energy is therefore

$$m_{\mathrm{TNT}} = E / 4.69 \times 10^6, \quad \mathrm{kg} \tag{17-15}$$

The overpressure produced by a blast wave varies in proportion to the cube root of the blast energy release and in inverse proportion to the distance from the center of the blast. Thus, the scaling law is

$$z_c = R_b m_{\mathrm{TNT}}^{1/3}, \quad \mathrm{m/kg}^{1/3} \tag{17-16}$$

where R_b = distance from blast, m; z_c = scaled blast distance, m.

Figure 17-6 contains an illustration of overpressure and damage effects as a function of the scaled blast distance, z_c.

Example: Estimate the overpressure at a distance of 30 m from the center of a VCE involving sudden release and subsequent ignition of 45 kg of propane. Assume the yield is 3%. The ΔH_c for propane is 46.3×10^6 J/kg

$$E = (0.03)(46.3 \times 10^6)(45) = 69.5 \times 10^3 \ \mathrm{J}.$$

$$m_{\mathrm{TNT}} = (69.5 \times 10^3)/(4.69 \times 10^6) = 13.3 \ \mathrm{kg}$$

$$z_c = (30)(3.28 \ \mathrm{ft/m})/[(13.3)(2.2 \ \mathrm{lb/kg})]^{1/3} = 32 \ \mathrm{ft/lb}^{1/3} \tag{17-17}$$

Realizing that an interpretation of a log–log scale requires care, based on Figure 17-6 the overpressure is estimated as 2.2 psig.

17.4.4 BLEVEs

Boiling liquid expanding vapor explosions (BLEVEs) can result from the sudden loss of containment of a liquid above its normal boiling point. Blast energy is released upon rupture of the pressurized vessel. At atmospheric pressure the liquid phase will have enthalpy in excess of its equilibrium value. Equilibrium is reestablished by flash evaporation of a portion of the liquid to form a vapor cloud. In the case of a flammable vapor the added threat of a

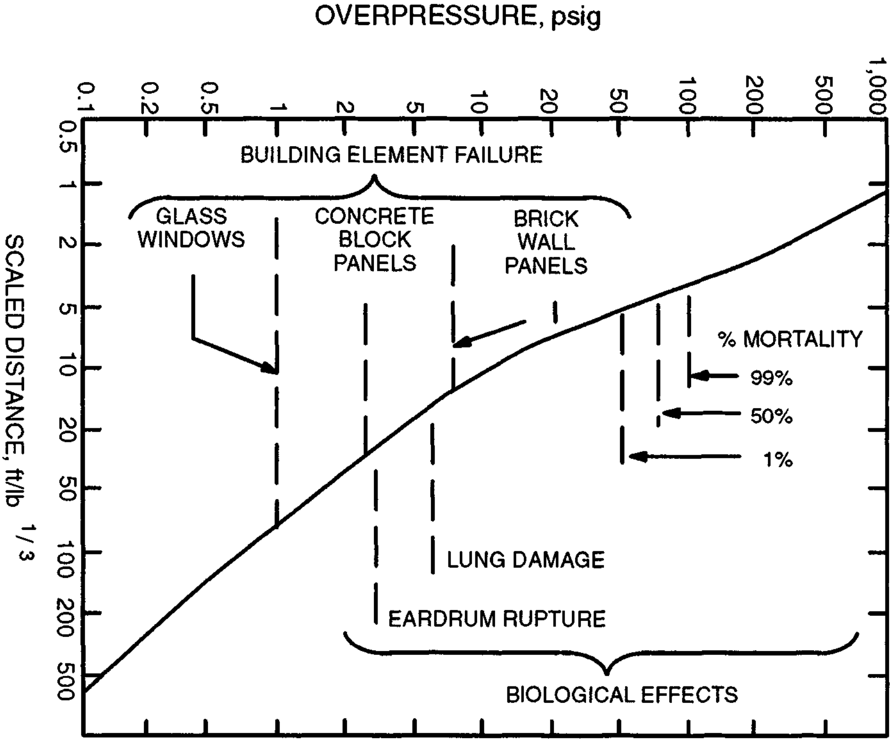


Figure 17-6 Ideal blast wave overpressure versus scaled distance. (From Baker 1983.)

fireball is present. The fraction of superheated liquid that flashes to vapor can be estimated by

$$\chi_v = (T_0 - T_b)C_p / \Delta H_v \tag{17-18}$$

where

χ_v = mass fraction of liquid that flashes to vapor;
T_0 = initial liquid temperature, K;
T_b = atmospheric boiling point of liquid, K;
C_p = specific heat of liquid, kJ/kg-K;
ΔH_v = heat of vaporization of liquid, kJ/kg.

In addition to the vapor cloud created by a BLEVE, a substantial amount of the unevaporated liquid is also cast into the air as a fine mist. On ignition this fine mist of combustible droplets will also participate in the development of the overall flame ball. In the case of liquified gases similar to propane and butane it may be assumed that the entire mass of material would have the potential to burn in a VCE.

The main characteristics of BLEVE fireballs, which can have implications on equipment spacing and building designs, may be estimated as follows (Fay and Lewis 1977):

$$z_p = V_{vap}^{1/3} \tag{17-19}$$

$$D_{max} = 5.25 m_f^{0.314} \tag{17-20}$$

$$\tau = 1.145 m_f^{0.362} \tag{17-21}$$

$$q_{r,max} = 828 m_f 0.771 / R^2 \tag{17-22}$$

where z_p = plume height, m; V_{vap} = volume of fuel vapor, m^3; D_{max} = plume diameter, m; m_f = mass of fuel in vessel, kg; τ = fireball duration, s; $q_{r,max}$ = radiant heat flux, kW/m^2; and R = distance from fireball, m.

A more complete discussion of VCEs and BLEVEs can be found in *Guidelines for Evaluating the Characteristics of Vapor Cloud Explosions, Flash Fires, and BLEVEs* (CCPS in progress).

17.5 FLAMMABILITY CONTROL MEASURES INSIDE EQUIPMENT

17.5.1 Combustible Concentration Reduction

The first of the several considerations in explosion prevention design is the identification and management of potentially combustible materials in the process environment. Specifically, such materials should be managed to maintain their airborne concentration outside the limits of flammability, preferably below the LFL. An extensive tabulation of flammability limits for gases and vapors is given in NFPA 325M.

Designs for maintaining low flammable concentrations are discussed at length in NFPA 69, *Explosion Prevention Systems*. Important guidelines are that:

- The concentration of the combustible should be maintained at or below 25% of the LFL where combustibles concentrations are not continuously monitored.
- Temperature or pressure elevation may result in broadened flammability limits.
- Equipment design should incorporate appropriate components to prevent flame propagation back into process spaces.
- Combustible dust concentrations can be kept low through use of cyclonic separators, filters or precipitator systems. Incidental airborne dust found in inhabited work spaces can accumulate on surfaces. Surface dust may

become airborne to form combustible concentrations. Regular attention to housekeeping in such environments is essential in removing a potential fuel source.

17.5.2 Oxidant Concentration Reduction

There are many cases where the presence of flammable vapors or explosible dusts cannot be practically maintained outside the flammable limits. In such instances it is essential that the concentration of oxygen, or other oxidant, be maintained below the minimum oxidant concentration that will support combustion, LOC. When continuous oxidant monitoring instrumentation is used the concentration should be maintained at least 2% below the LOC. Further provisions, plus listings of LOC values for a variety of flammable vapors and explosible dusts, are given in NFPA 69.

In the design of inerting systems one must provide sufficient inerting gas to assure not only that the normal process conditions are rendered nonflammable but also that any credible alteration of the process environment remains outside the combustible limits. Flammability diagrams are useful tools for this purpose. Figure 17-3 is an example of a flammability diagram for the methane–oxygen–nitrogen system. It is clear from this diagram that the condition corresponding to point *M1* (50% methane, 30% oxygen, 20% nitrogen) lies outside the flammable region. However, should air leak into the process equipment the overall mixture composition will move along the line between the initial condition and the point 79% nitrogen and 21% oxygen. Since this line passes through the combustible region the initial condition is not as safe a choice as one lying to the right of the line designated Min. O_2. These mixtures cannot be rendered flammable by ingress of air into the process volume.

17.5.3 Inert Gas Selection

Nitrogen is commonly used as an inert gas as it will not react with most materials. Nitrogen may not be suitable in some instances, as in processing some metal dusts, with which it can react. Magnesium dust is such a material. Similarly, carbon dioxide and water vapor can serve as oxidizers in metal dust systems. Water vapor condensation in metal dust systems poses a special hazard in that its slow low-temperature oxidation of metal dusts yields hydrogen gas. Hydrogen formed this way may accumulate in bulk or simply reside as an adsorbed phase within a dust layer causing the dust to become susceptible to ignition. Argon is usually used in these cases.

Furnace flue gas is sometimes employed as an inerting gas. It usually contains less than 3 vol % oxygen.

Halogenated hydrocarbons are employed successfully as combustion inhibiting agents. Due to economic considerations these are usually employed in on-demand batch inerting applications. Examples of such applications are pump rooms handling petroleum products and aerosol fill rooms. The principal halogenated agent employed for this purpose has been bromotrifluoromethane, known commonly as Halon 1301. Due to adverse environmental impact (high reactivity with stratospheric ozone) Halon compounds are soon to be prohibited from production. Fluorinated compounds are now being considered as replacements where Halon 1301 was once used.

17.5.4 Ignition Source Control

An important means of preventing industrial explosions due to combustion processes is the identification and management of potential ignition sources in areas that may feasibly contain combustible atmospheres. The ignition sources are discussed at greater length in Chapter 11.

17.6 FLAME MITIGATION INSIDE EQUIPMENT

17.6.1 Introduction

While the application of explosion prevention measures, as discussed in the previous section, *should* ordinarily be sufficient to minimize risk of initiating a closed-vessel deflagration in a well engineered process system, it is a sad fact that industrial explosions can and do occur, even when preventative measures are practiced. Process systems, including safety systems, are imperfect owing to (a) undetected flaws in design, construction, and installation and (b) use of improper procedures in plant operation and maintenance. Frequently, unanticipated circumstances lead to violation of fundamental assumptions made in creating a process system. The application of good engineering practice and explosion prevention measures can reduce the probability of bringing together simultaneously the necessary ingredients for an explosion—confined fuel / oxidant mixture in the presence of an ignition source—but cannot reduce the probability to zero. Given this position it must be decided whether the consequences of catastrophic failure of all explosion prevention measures can be accepted. Should the answer to this proposition be *no* then the potential benefits of further investment in systems that can reduce the damage potential of explosions must be considered.

Methods that can mitigate the effects of explosions fall into four basic categories:

- Pressure relief with flame ejection
- Isolation with or without flame ejection
- Pressure containment
- Suppression

Pressure relief systems usually consist of relief valves, rupture disks or larger venting panel systems. Only deflagration venting will be discussed here. Relief valves and rupture disks are discussed in Chapter 14.

Isolation systems may be passive (flame arresters), active (fast closing valves and chemical barrier systems), or may have both active and passive characteristics (rotary valves and flame front diverters). These systems serve to prevent the communication of combustion zones between process units. Pressure containment (passive) relies on vessel design to withstand the forces imposed by a deflagration or runaway reaction given that pressure relief is not feasible.

Suppression systems contain components for early detection of combustion conditions, such as sparks or flame fronts, and subsequent extinguishment of the burning matter in a time frame that avoids the development of unacceptably high pressures.

Application of explosion mitigation systems to a given process may employ one or more of the concepts described here. The requirements of the safety system design will depend entirely on the design and operating details of a given process and the safety objectives to be addressed.

17.6.2 Spark Detection and Extinguishment

One method of preventing deflagrations is the early detection and extinguishment of sparks being transported from the point of their generation. Processes employing milling, grinding, or other highly energetic mechanical action on materials may generate sparks. This may arise due to overheating of a combustible material. Alternatively, foreign matter, such as a metal fastener, may enter the process unit leading to generation of sparks. Unextinguished sparks that are conveyed to a process unit containing a combustible material above its LEL, such as a silo or dust collector, may initiate a deflagration. Sparks may be detected using infrared optical detection systems. Sparks detected in a dust laden air stream may be extinguished by action of an automatic system that sprays water, or other agent, into the dusty air stream.

17.6.3 Containment

Explosion protection of process units must include consideration of the strength of the enclosure itself. A process vessel must be strong enough to contain either the pressure of an unmitigated deflagration or that of a vented or suppressed deflagration. Guidance in the design, construction, and testing of pressure vessels can be found in VDI 2263, the ASME Boiler and Pressure Vessel Code, and in NFPA 69. The latter standard recommends that the required vessel design pressure be calculated as follows:

$$P_r \text{ or } P_d = 1.5\{R(P_i + 14.7) - 14.7)\}/(F_r \text{ or } F_d), \quad \text{psig} \qquad (17\text{-}23)$$

where P_r and P_d are the design pressures to prevent *rupturing or deformation*; R is the ratio of the maximum deflagration pressure to the initial pressure at which the determination is made and may be taken as 9 for most gas mixtures and as 10 for dust–air mixtures; however, actual deflagration data should be used if available; P_i is the initial process pressure in psig: F_r is the ratio of the ultimate stress to permitted stress of the vessel and is taken as 4 for low carbon and low carbon stainless steels; F_d is the ratio of the yield stress to permitted stress of the vessel and is taken as 2 for low carbon and low-alloy stainless steels.

Example: Unvented carbon steel vessel—A dusty product, which has a maximum deflagration pressure of 125 psig, is to be air conveyed into the vessel at a maximum operating pressure of 7 psig. The minimum design pressure to prevent rupture will be:

$$P_r = 1.5\{([125 + 14.7]/14.7)(7 + 14.7) - 14.7\}/4 = 72 \text{ psig} \qquad (17\text{-}24)$$

17.6.4 Combustion Isolation in Pipes and Ducts

17.6.4.1 Introduction

Combustible vapors and dusts are commonly conveyed between process units. Dust or powdered materials are frequently transported together with air in dilute or dense phase pneumatic conveying. Ducts or pipes carrying combustible mixtures can, if ignition should occur at one end, act as fuses. The ignited mixture can propagate flame through the pipe leading to ignition of the process unit at the other end. If possible, flame propagation should be blocked near the inlet of a pipe or duct. Otherwise the speed at which a flame propagates in the duct can steadily increase. If the mixture composition is in the detonable range the flame front can undergo deflagration to detonation transition developing pressures pulses of about 20 times the initial pressure and reflected pressures (that experienced by an object in the flow path) of up to 50, or more, times the initial pressure.

Prevention of flame propagation through pipe and duct systems is an important aspect of total protection of a process plant. Several approaches are used in prevention of flame propagation in pipe and duct systems. These include use of:

- flame arresters
- backflash interrupters
- isolation valves
- chemical inerting systems

17.6.4.2 Flame Arresters

Flame arresters are devices that intercept and extinguish flames propagating in flammable gas mixtures in pipes. They are constructed so as to cause the gas flow to pass through small channels thereby causing the flame to be cooled and quenched to extinguishment. In one application flame arresters are located in the breather vents of tanks of flammable liquids. Flame arresters that are intended for use well away from a pipe opening may be subject to accelerated deflagrations or even detonations. A more complete discussion of flame and detonation arresters is given in Chapter 13.

17.6.4.3 Backflash Interrupters

One method of preventing flame propagation in a pipe is to cause the pipe to open in such a manner as to discharge the burning material to the ambient while impeding flame from further propagation past the vent point. A schematic diagram of a design to prevent the vented flame from flashing back into the pipe is shown in Figure 17-7. There is at present no standard for the design

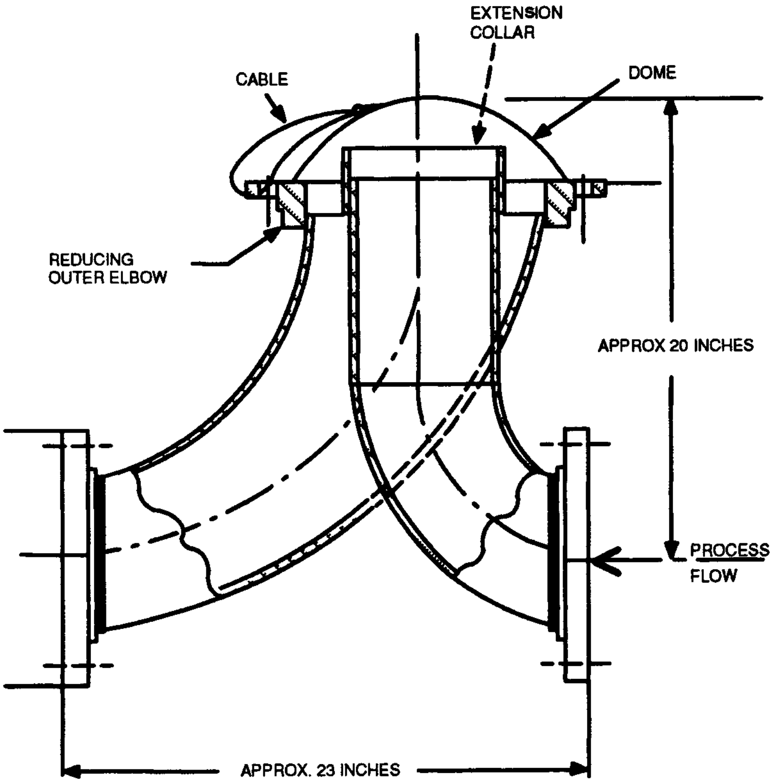


Figure 17-7 Backflash interruptor. (From Chatrathi and DeGood 1991.)

of these devices. Thus, before backflash interrupters are specified they should be tested with the applicable flammable mixture that would be present over the expected range of operating conditions.

17.6.4.4 Isolation Valves

Positive mechanical isolation of a pipe system is another way to prevent passage of flames or pressure pulses from communicating between process units. Unlike flame arresters and backflash interrupters which are passive devices, a valve is part of an active protection system. They are used in conjunction with detection and control devices. One arrangement of an isolation valve system is shown in Figure 17-8. A flame sensor is located at a sufficient distance from the valve such that, on detection of flame, the valve has adequate time to close. It was noted above that flame propagation in pipes can accelerate to very high speeds. Thus, the spacing of the valve and detector and the closing time of the valve must be well understood and, if necessary, demonstrated by test. High-speed knife gate valves have been used successfully to intercept detonations in progress (Senecal and Meltzer 1992).

17.6.4.5 Chemical Isolation

Rather than completely blocking a pipe or duct by a valve an alternative approach is, upon detection of flame, to discharge a chemical extinguishing

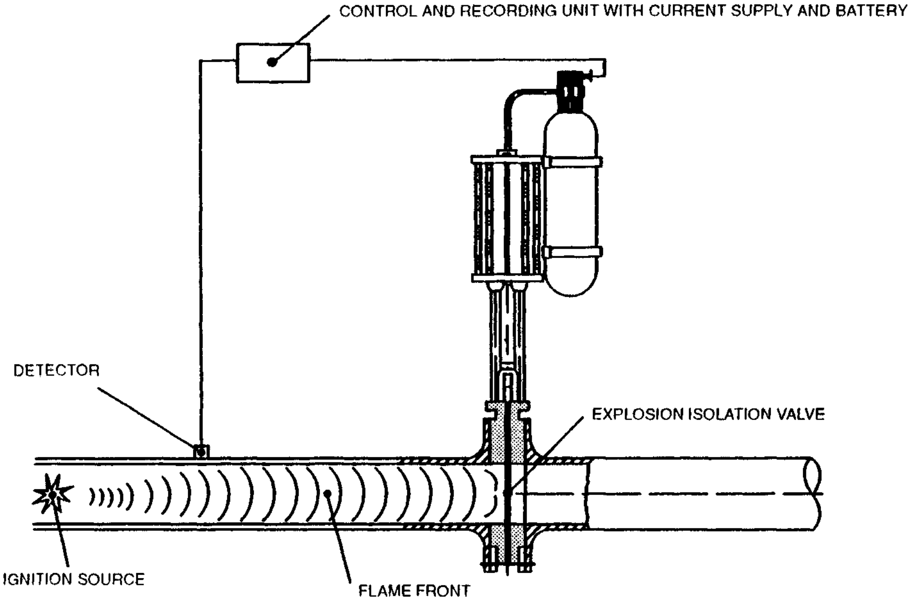


Figure 17-8 Explosion detector and isolation valve in a pipe (Fenwal 1992).

medium into the pipe. Extinguishing compounds such as sodium bicarbonate or ammonium dihydrogen phosphate, chemicals commonly used in fire extinguishers, have been found to be very effective (Chatrathi and DeGood 1991). Halogenated hydrocarbons with low boiling points may be particularly useful as they provide complete vapor blocks in pipes. Examples of chemicals of this type are HFC-23, HFC-125, HFC-227ea. These are three of several compounds suggested as substitutes for Halons 1301 and 1211. Halogens leave no residue after discharge but may form halogen acids upon interacting with flame fronts. These acids may be harmful to mechanical components as well as personnel. Both dry chemical and gaseous agents have been used successfully in industrial pipe and duct explosion protection systems applications.

17.6.5 Deflagration Suppression

17.6.5.1 Introduction

In many cases deflagration waves can be extinguished before unacceptable pressure rise if the onset of combustion can be detected early and an appropriate extinguishing agent is rapidly delivered to the protected volume. Suppression systems are active systems involving detection, agent delivery, electrical supervision to assure readiness to operate, interlock functions to shut off key process equipment. Suppression is the only explosion mitigation method that stops the advance of the combustion process. Discussion of the application of these systems to suppression of dust deflagrations is given by Moore (1986).

17.6.5.2 Fundamentals of Deflagration Suppression

Deflagration suppression is a competitive process between a rising rate of combustion heat release and a delayed, but rapid, delivery of extinguishing agent. The deflagration will be suppressed when

1. the unburned fuel–air mixture has been rendered inert or inhibited due to the addition of extinguishing agent, or
2. the combustion zone has been cooled to the point of extinguishment.

At the onset of ignition there is some minimum uniform concentration of agent that renders the protected space noncombustible. This is usually referred to as the inerting or inhibiting concentration for a given agent. As an example, a stoichiometric mixture of propane and air at standard temperature and pressure can be rendered inert, against weak ignition sources, by adding carbon dioxide to a concentration of 43 mol%.

Once the deflagration has evolved, a proportionally larger quantity of agent is required since unburned material must be inerted and the burned volume must be quenched to prevent it from serving as a "strong" ignition source. The amount of agent that must be dispersed within the protected space to effect suppression increases with the progress of the deflagration. Should delivery of agent be delayed too long the deflagration will pass the point of suppressibility. The result may be the attainment of normal deflagration pressures or even higher pressures depending on the choice of suppressant.

The time available for action of a suppression system will increase with vessel volume and decrease with the fundamental burning velocity of the material being processed. For example, the time available to undertake suppression in the 1.9 m^3 deflagration event depicted in Figure 17-9 is about 100 ms. Beyond this time the rate of pressure rise increases rapidly. By application of the explosion scaling law, Eq. (17-13), the same event occurring in a 25 m^3 vessel would be expected to have a time window to effect suppression of about 250 ms.

17.6.5.3 *Elements of a Suppression System*

A deflagration suppression system consists of three basic subsystems for (a) detection, (b) extinguishment, and (c) control and supervision. Incipient defla-

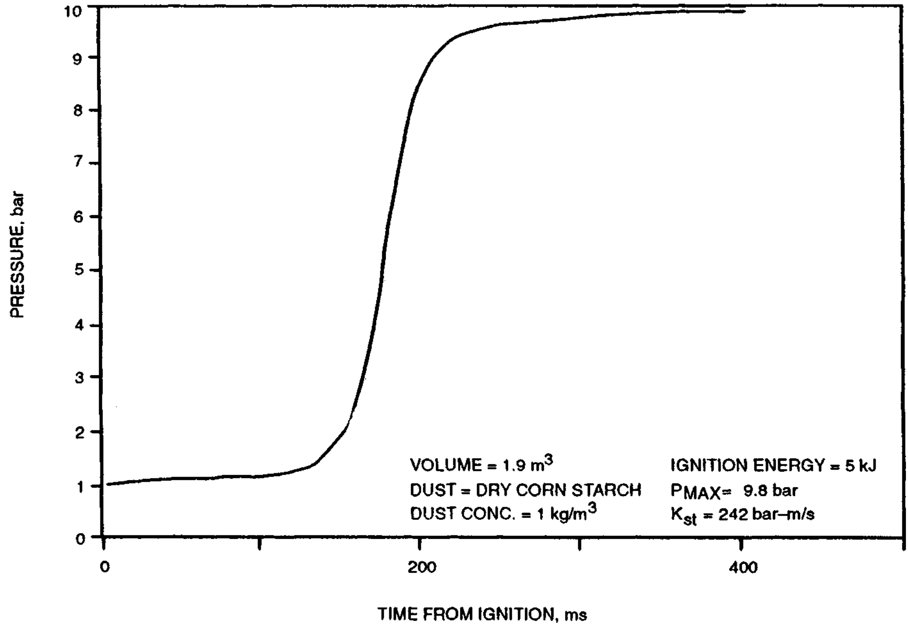


Figure 17-9 Dust suppression in a spherical vessel: Pressure–time plot of a closed-vessel dust cloud deflagration (Fenwal 1992).

grations are detected using pressure detectors, rate of pressure rise (or "rate") detectors, or optical flame detectors. Optical detectors, employing UV radiation sensors, are preferred in unenclosed environments with nonabsorbing UV atmospheres. Examples of such environments are solvent storage, pump, and aerosol can filling rooms. Pressure detectors are employed in closed process equipment and particularly where dusty atmospheres prevail. Rate detectors find use in processes that operate at pressures significantly above or below atmospheric.

The extinguishing subsystem consists of one or more high rate discharge (HRD) extinguishers charged with agent and propellant. Normally dry nitrogen is used to propel the agent. The propellant overpressure is normally in the range of 2 to 6 MPa (300 to 900 psig) depending on the supplier. Explosively opened valves provide rapid agent delivery that is critical to effective suppression. Common extinguishing agents are

- Water
- Dry chemical formulations based on sodium bicarbonate or ammonium dihydrogen phosphate
- Halogens: Halons—1011, 1301, 2402, or 1211; perfluorocarbons; hydrofluorocarbons.

The extinguishing mechanism of each agent is a combination of thermal quenching and chemical inhibition. The selection of the agent is usually based on several considerations such as effectiveness, toxicity, product compatibility, residual inerting, and volatility. Halons are particularly versatile agents but are now subject to production phaseout due to their adverse effect on stratospheric ozone. Alternative environmentally safe chemicals are being developed by several chemical manufacturers but these remain to be proven effective in explosion protection applications. As such, dry chemical agents are more commonly specified in suppression applications.

Control of these systems is achieved using an electronic power supply with battery back up power. This unit supervises the suppression system circuitry to assure integrity and supplies the current to discharge the explosive actuators to open the high rate discharge (HRD) extinguishers. Normally the process being protected by the suppression system is automatically shut down upon detection of an incipient deflagration. A simple deflagration suppression system is represented in Figure 17-10.

The protection afforded by a suppression system is measured by the maximum pressure attained in the suppressed event, P_{red}, as compared to the unsuppressed event, P_{max}. The pressure–time profile of a suppressed deflagration of dried corn starch is shown in Figure 17-11. As long as the strength of the process equipment is greater than P_{red} then no damage will occur.

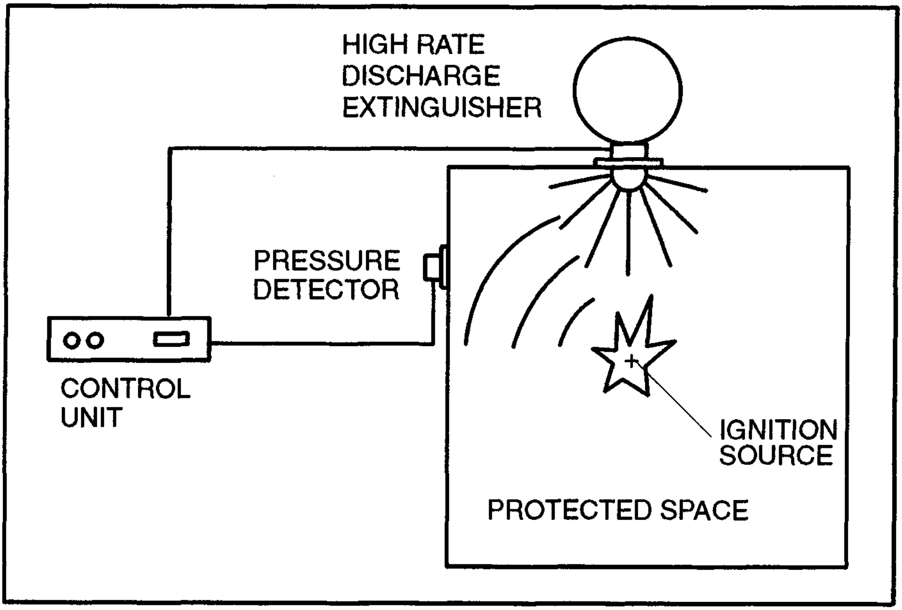
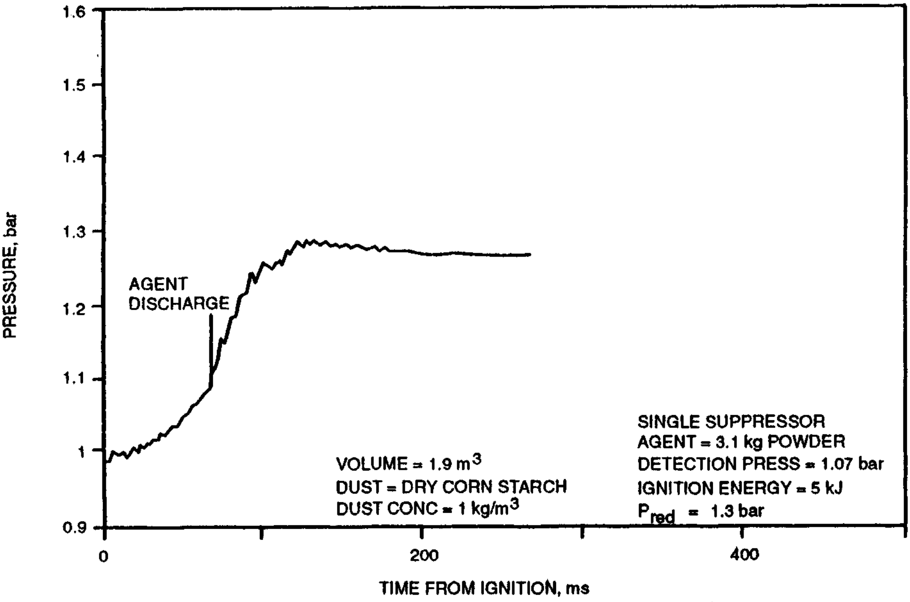


Figure 17-10 Schematic of a deflagration suppression system (Fenwal 1992)



Suppressor Agent: Dessikarb ($NaHCO_3$) @ 7.0 lbs w/Conical spreader. Pmax = psig

Figure 17-11 Pressure–time plot for suppressed dust cloud deflagration (Fenwal 1992)

17.6.6 Deflagration Venting

17.6.6.1 Introduction

A deflagration vent is an opening on the wall of an enclosure designed to allow escape of process gases quickly enough to prevent a greater rise in pressure than the enclosure can withstand. Venting is usually the simplest and least costly means of protecting process equipment from damage due to pressure rise from an internal deflagration. Pressure rise due to a confined deflagration is typically in the range of 8 to 10 times the initial absolute pressure. Process enclosures are seldom designed to bear the stresses of a confined deflagration. There is, for a given process unit, a definable pressure at which the enclosure will likely rupture spewing contents and vessel parts. This pressure is referred to simply as the plant strength, P_{ps}, and represents the absolute limit of pressure tolerable for any appreciable length of time in a failure scenario. A lower pressure at which inelastic deformation of equipment begins to occur may be designated as P_{ed}.

The maximum pressure attained in a failure scenario in which an explosion mitigation system is employed is referred to as the *reduced* pressure, P_{red}. The actual pressure history in a process enclosure protected by a venting system will typically have the form represented by the lower curves in Figure 17-12. Important characteristics are (a) the static pressure at which a closure that covers the vent opening operates, P_{stat}, (b) the maximum pressure attained, P_{red}, and (c) the duration of the pressure pulse.

If the amount of vent area available, A_V, is large enough and P_{stat} is small the value of P_{red} and the pressure pulse duration will be small. Practical considerations, however, often place limits on P_{stat} and A_V. An actual vent system design must employ operating parameters sufficient to assure attaining an *acceptable* value of P_{red} under the least favorable conditions credibly attainable. What constitutes an acceptable value of P_{red} may vary from plant to plant and is a function of the level of economic risk willing to be assumed by the plant manager. Distorted sheet metal (i.e., $P_{red} > P_{ed}$) may be an acceptable outcome of a loss scenario, but ruptured equipment (i.e., $P_{red} > P_{ps}$) may not be acceptable.

The design of a deflagration vent, specifically the specification of the total amount of vent area required for a given P_{stat}, is not an exact science. A number of different approaches have been employed both in the United States and in Europe (Eckhoff 1989). The most commonly referenced guideline for vent design in the U.S. is NFPA 68, *Venting of Deflagrations*. The German standard for the venting of dust cloud deflagrations is VDI 3673. These documents cited should be consulted on the design of vent systems. A complete discussion of this subject is beyond the scope of this chapter. Only a brief discussion of the most basic considerations is given below.

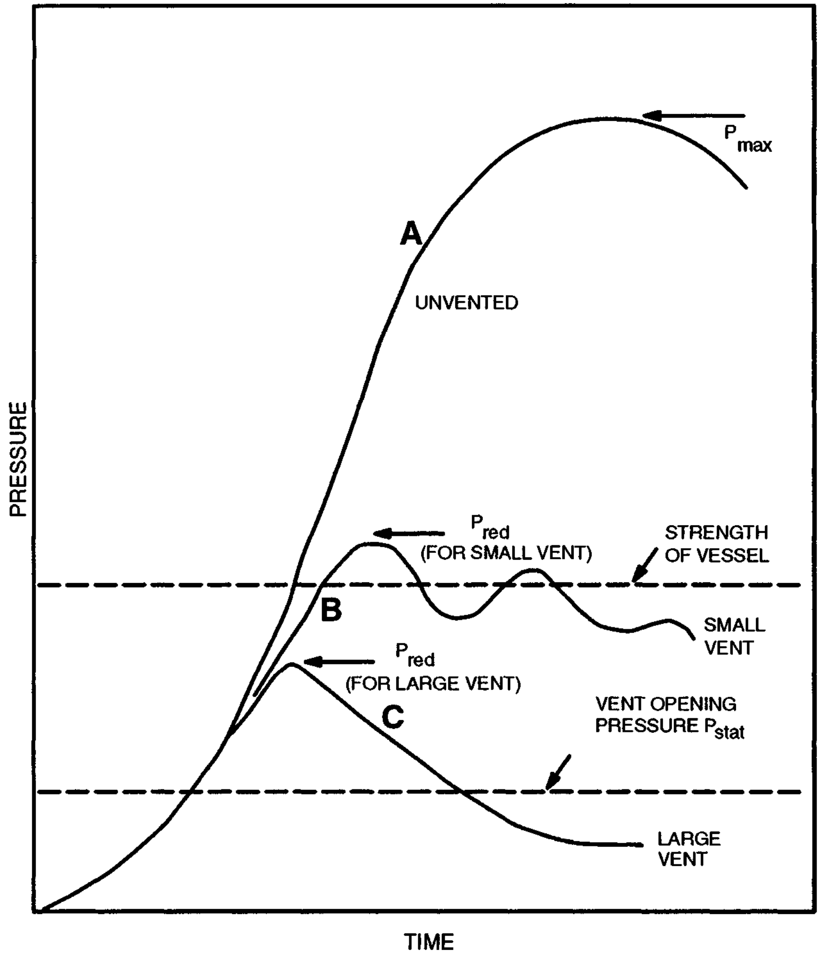


Figure 17-12 Pressure–time characteristics of vented and unvented deflagrations form initially closed vessels. (From Fire Research Station, reprinted in Lunn 1992.)

17.6.6.2 Fundamentals of Deflagration Venting

The following factors should be considered when designing a deflagration vent system:

- The basic combustibility characteristics of the materials being processed should be quantified. Where different materials may be processed in the same equipment the design must be adequate to the demands of the worst case material. Uncertainty about the combustibility of a material being processed should be clarified by reference to the literature or by test. In particular, the explosibility parameters of the worst-case material being processed in the volume in question must be known in order to apply the vent design models correctly. The basic explosibility parameters are the maximum deflagration pressure, P_{max}, and the volume-normalized maximum rate of pressure rise represented by K_{St} for dusts and K_G for gases. It is important that the K value be determined for the material being processed in the most hazardous form that it could credibly assume in the process.

- The volume of the protected space bears directly on the vent area required.
- The inertia of a vent closure will tend to retard its opening. Thus, it is preferred that the total mass of any movable components on a vent be kept low.
- The action of a vent in relieving pressure is to open and discharge the contents of the protected volume. The material ejected may include burning matter, combustion products, and as yet unburned material which may ignite on exposure to ambient air. The combustion of ejected material will be vigorous due to the high turbulence intensity of the discharged mass. The rapidly discharged mass will also create a pressure front ahead of it that may stir up available combustible matter originally external to the vented equipment that may in turn ignite to cause a secondary deflagration.
- For dust processing areas a high level of housekeeping is in order around vented equipment to avoid a secondary deflagration or the creation of missiles by the action of a pressure front on loose objects.
- Vented equipment is preferably located outdoors away from habitated spaces. Vent openings, in particular, must be oriented to direct the discharge away from locations where personnel may be working or passing.

17.6.6.3 *Enclosure Considerations*

Low-Strength Enclosures

For the purposes of deflagration vent design low-strength enclosures are those that cannot withstand internal pressures greater than 0.1 bar g (1.5 psig) above the ambient pressure. All structural elements must be considered in making a strength assessment including walls, ceilings, doors, and windows. A simple design equation for determining the area of vents for these enclosures is

$$A_v = CA_s/(P_{red})^{1/2} \tag{17-25}$$

where A_v = vent area, ft^2 or m^2; C = combustible-dependent constant [Table 17-5]; A_s = internal surface area of enclosure to include walls, floor, and ceiling, ft^2 or m^2; and P_{red} = maximum overpressure tolerable by weakest structural element, bar or psi.

Table 17-5 Combustible-Dependent Constants for Low-Strength Enclosures[a]

Combustible	C (psi)$^{1/2}$	C (bar)$^{1/2}$
Anhydrous ammonia	0.05	0.013
Methane	0.14	0.037
Gases with $S_u < 0.6$ m/s	0.17	0.045
St-1 dusts	0.10	0.026
St-2 dusts	0.12	0.030
St-3 dusts	0.20	0.051

Note: S_u = fundamental burning velocity. See Table B-1 of NFPA 68 for values of S_u for a number of gases.

[a] Adapted from NFPA 68.

A single vent should be located near the middle of an enclosure. Multiple vents should be distributed along the longest dimension of the enclosure.

High-Strength Enclosures

Structures capable of withstanding an internal overpressure of more than 0.1 bar g (1.5 psig) are designated high-strength enclosures. Deflagration pressures developed in vented high-strength enclosures may be considerable. A vent design should be such as to assure a value of P_{red} that is no more than 66% of the expected failure strength of the enclosure. In this regard bulging of the enclosure walls is not considered failure.

Calculation of vent area for these enclosures is more complicated than for low-strength enclosures. Nomograms have been developed that take into account the enclosure volume, the static opening pressure of the vent closures, the maximum value of reduced pressure that can be accepted, and the burning characteristic of the combustible gas or dust. Nomograms specific to methane, propane, hydrogen, and coke gas are given in NFPA 68. Nomograms are also given for dusts. The latter include use of the dust cloud explosibility parameter K_{St}. The reader is referred to NFPA 68 for further details.

Bins, Silos, and Hoppers

Vents on these enclosure types must be located above the highest possible level that may be attained by accumulation of solids. Otherwise operation of the vent will be hindered.

Pipes, Ducts and, Elongated Vessels

Enclosures with length to diameter ratio greater than five need special consideration. When confined to elongated enclosures, such as pipes and ducts, initially quiescent deflagrations undergo rapid development. Transition to detonation may occur. The pressure front advancing ahead of the combustion reaction zone may be prevented from achieving very destructive levels by providing pressure relief vents at strategic locations. Venting of ductlike systems is less well understood than for more regular enclosures. The following guidelines are recommended by NFPA 68:

- The total vent area at each vent position should at least equal to the cross sectional area of the duct.
- Vents should be located as close as possible to potential ignition sources.
- Ducts containing an obstacle should be vented on both sides of obstacles such as elbows, tees, valves, and blockages that reduce the duct area by more than 5%.
- When several vents are employed in long ducts certain spacing requirements should be followed.

17.6.6.4 Other Considerations

Turbulence

The combustion of a mixture of a flammable substance in an oxidant will be greatly accelerated by turbulence in an enclosure. Turbulence is caused by velocity gradients due to normal fluid flow. It is also caused by flow around obstacles. Flame propagation in a dust–air mixture initiated in a bucket elevator may be accelerated due to flow over buckets and velocity gradients developed between the buckets and the walls. Additional vents may be required to alleviate pressure rise in such applications.

Vent Duct

Vented process enclosures are preferably located outside of buildings. When this is not practical a duct leading to a safe location for vent discharge should be attached at the vent opening. Vent ducts will add resistance to the fluid flow during discharge. Special considerations are required (NFPA 68; Lunn, 1988).

Discharge of Flames

A deflagration inside vented equipment will issue out of the vent opening at high velocity spewing burned gases, burning gases and dust, and unburned material (gas or dust) which will find adequate oxygen to complete combustion in the ambient air. Flames issuing from vent openings can extend a distance equal to six times the cube root of the enclosure volume.

Thrust on Venting

A force will be applied to the vented enclosure due to the thrust of the material discharged from the vent. The equivalent static force applied to the structure can be estimated as

$$F_s = 173 A_V P_{red} \tag{17-26}$$

where F_s = thrust force, lbs; A_V = vent area, in^2; and P_{red} = reduced pressure, psig (NFPA 68). A coefficient value of 89.3 (with area in ft^2), is correct for use of a new correlation to appear in the 1994 revision of NFPA 68, which estimates the static force to be resisted by a venting structure.

17.7 REFERENCES

17.7.1 *Regulations, Codes of Practice, and Industry Standards*

The editions that were in effect when these *Guidelines* were written are indicated below. Because standards and codes are subject to revision, users are encouraged to apply only the most recent edition.

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ASTM E 582. 1988. *Standard Method for Minimum Ignition Energy and Quenching Distance in Gaseous Mixtures*. American Society for Testing and Materials, Philadelphia.

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9

PROCESS MONITORING AND CONTROL

9.1 INTRODUCTION

Great strides are being made in process monitoring and control instrumentation. As instrumentation systems have grown, from the Distributed Control System (DCS) and Programmable Logic Controller (PLC) to the Programmable Electronic System (PES), the chemical process industry has become increasingly automated. As control systems become more complex and more automated it is even more important that process engineers and instrumentation and control specialists understand each other's disciplines to ensure instrumentation and control are fully integrated with process design to provide inherently safer plants.

This chapter focuses on several major aspects of process monitoring and control:

- consideration of monitoring and control problems inherent in both specific types of instruments and specific types of process equipment; these issues will need to be addressed regardless of *how* control is carried out.
- some practical considerations that go into the development, design, checkout, operation, and maintenance of a process control system.
- recognition that development of the PES requires a team approach, requiring input from many disciplines
- the application of risk analysis techniques to the development of computer-based safety interlock systems. The issues which were once raised under the concept of "redundancy" are now examined in the framework of risk assessment and the development of safety layers.

This chapter highlights the significant role the process engineer plays in the implementation of the process control system and the role of other disciplines such as hazards analysis, materials engineering, plant operations and plant maintenance. For the purposes of this chapter, process control is considered an umbrella term that covers the equipment, systems, personnel, and know-how that maintains chemical process operations in an efficient, productive, safe state. Both the equipment and systems for normal process control, the Basic Process Control System (BPCS), and the equipment and systems for mitigating hazardous events, the Safety Interlock System (SIS), will be addressed.

9.2 INSTRUMENTATION

Regardless of the methods used to exercise control, the accuracy and reliability of the field instrumentation also needs to be carefully considered. Reliable measurement of pressure, temperature, flow and level, as well as analysis for specific gases (e.g., oxygen or toxic gas composition) is critical to safe plant operation. Reliable process measurement begins with proper installation of the process measuring device. Guides to the installation of process measurement equipment include *Instrument Engineers Handbook* (Liptak, 1982) and ISA *Standards and Recommended Practices for Instrumentation and Control*. Reliable measurement also depends on proper maintenance to ensure accuracy and reliability.

9.2.1 Temperature

Temperature is frequently measured and controlled because of the effect temperature has on the rate of a chemical reaction. Often the rate doubles or triples with a temperature increase of less than 10°C (FMEC 1974). Most substances change from solid to liquid to gas at precise temperatures. If these properties are used as a basis of separation, temperature control is critical. Other properties, such as solubility, are also temperature dependent. Temperature controls are also imposed to meet material limits.

Temperature measuring devices should be located in process lines and vessels where there is a continuous movement of fluid and not in stagnant pipe or vessel sections. Temperature sensing elements should normally be installed with a thermowell or protection tube to shield the sensor from the harmful effects of the fluid stream, such as erosion, corrosion, oxidizing or reducing atmospheres, and to allow removal for maintenance. Thermowell stresses resulting from the fluid dynamics should not be overlooked. When installed at right angles to the fluid flow, vibration fatigue failures can occur above certain flow velocities. For differential temperature measurement, differential sensors are preferred to reliance on the difference between absolute measurements from two different sensors.

Fractionation tower tray temperature points should be located at the bottom of the tray downcomer, if liquid temperature is of interest or just below the tray above if vapor temperature is to be measured. Temperature points for the bottom liquid or overhead vapor should be located in the piping from the bottom or top of the vessel. For packed towers the temperature sensors should be located so as to detect temperatures in the bed. Resistance temperature devices (RTDs) may be more precise than thermocouples, but their use may be limited by a narrow functional temperature range.

9.2.2 Pressure

Pressure measurements should be located as close as possible to the pressure points of interest and should be located in process piping or in top connections of level instruments or bridles if possible. They should not be located in piping that can be blocked-in during normal operation of the plant or process. Safety considerations may include:

- using a diaphragm seal to prevent the measured fluid from entering the chamber of the gauge (if a chemical seal is used, consider compatibility of fluids)
- using a damper or a gauge designed for pulsating service
- ensuring safe working temperature and pressure of the gauge
- preventing process fluid from entering the pressure switch housing
- preventing vapors from condensing or freezing in the gauge during operation
- using a differential pressure gauge, instead of the difference between two absolute pressure gauges, to obtain differential pressure.
- locating the sensing tap outside the area of high turbulence (typically ten diameters downstream of the reducing valve)
- blow out plugs

9.2.3 Flow

The most common method of measuring flow rate uses an element inserted into a flowing stream that will generate a differential pressure (d/p) that is proportional to the flow. The differential pressure is then measured by instruments that are calibrated in terms of flow rate. Each d/p type device requires sufficient upstream and downstream piping in order to produce a fully developed flow velocity profile and an accurate and repeatable differential pressure that can be measured and read in terms of flow rate. Some sources of information on d/p type flow elements are: *Flow Measurement Engineering Handbook* (Miller 1989) and "Orifice Metering of Natural Gas and Other Related Hydrocarbon Fluids (AGA 1985)."

Orifice plates are commonly used and are relatively easy to apply, but their range is limited. For certain applications, caution must be exercised. A vapor stream may carry a considerable amount of entrained liquid or ambient conditions may cause condensation which can collect on the bottom of the pipe. A liquid stream may carry entrained gases which collect on the top of the pipe in horizontal meter runs. These conditions will cause inaccurate flow measurement because the geometry of the entering fluid stream is affected by the collection of liquid or gas on the inlet face of the orifice plate. However, the adverse effects on accurate measurement can be minimized by correct installation. Installing the meter run in a vertical line, with vapor flow down or liquid flow up, is one solution. The use of one of the other differential flow elements which do not have a buildup problem may be a better solution. As a last resort, weep holes will allow the liquid or vapor accumulation to pass down the line and not build up behind the orifice plate (Miller 1989).

Other flow devices include load cells, mass flow meters, positive displacement meters, variable area meters (rotameters), turbine meters, vortex meters, doppler effect meters and magnetic flow meters. Some of these devices, particularly the positive displacement meter and the turbine meter can offer high accuracy and reliability. Other meters, such as the doppler effect and nuclear meters are placed on the surface of the pipe being monitored. This makes them extremely safe, but at the cost of lower accuracy and more difficult calibration. Additionally some materials may not register with the nonintrusive types of flow meters. The choice of the flow meter used in a particular application will depend upon a set of tradeoffs involving the material being measured, the flow range, the pressure drop, the accuracy required, and the safety required. Avoid meters with glass tubes in hazardous or high pressure service; rotameters should be of all metal construction.

9.2.4 Level

Level measurement is often accomplished by displacer/float instruments and level glasses. Other choices include differential pressure gauges, gas bubblers, and noncontact level instruments, such as ultrasonic, microwave, and fiberoptic instruments. The use of differential pressure gauges is discouraged in tanks or vessels where the specific gravity of the stored material is variable since the change in the weight of the material column will change the pressure at the level instrument. Level glasses are not recommended for materials that are highly flammable or toxic, unless they are armored or high pressure design. IRI (1990) has published recommendations on the use of sight glasses and gauge glasses in hazardous and flammable liquid service.

In order to minimize fabrication complexity and expense, the use of level bridles or standpipes is recommended when more than four vessel connections are required. Bottom level connections should never be located in such a manner that the level measurement will be affected by liquids flowing out of the vessel, i.e., connected to the bottom outlet piping. Additionally, the connecting piping should not form a liquid trap that does not drain back into the vessel.

Dedicated service level switches may be necessary on suction vessels to protect pumps from losing suction caused by low liquid level and to protect compressors from liquid carryover caused by high liquid level. Level switches intended to protect rotating equipment are often directly connected to the vessel and not to level bridles. This prevents them from being blocked-in and rendered ineffective if the bridle is blocked-in to service an instrument in a less critical service.

Often, correct level control and indication is critical to safe and secure operations and in these cases redundant level controls are typically installed. Examples include deaerators, steam drums, or certain distillation tower overhead accumulators. Redundant level indication should be considered on any vessel containing hazardous materials, including storage tanks.

9.2.5 Vibration (Rotating Equipment)

Monitoring of vibration is applied mainly to rotating equipment. Vibration is measured by either displacement, velocity, or acceleration. Much information on the condition of machinery can be gained by vibration monitoring if vibration modes have been correlated with particular fault conditions (e.g., misaligned shaft, bent shaft). Critical items such as turbines, centrifuges, compressors and large pumps, may have to be monitored continuously. Both Industrial Risk Insurers (IRI 1991a,b) and Factory Mutual (FMEC 1988b) address vibration monitoring.

9.2.6 Other Methods to Monitor Condition

By monitoring equipment condition, one may detect faults that might result in failure (Lees 1980). Many methods have been used to monitor condition, such as:

- performance monitoring (e.g., efficiency of a pump or heat exchanger)
- acoustic emission monitoring (e.g., pump cavitation, pressure vessels, high pressure leaks)
- thermal image monitoring [thermography] (e.g., condition of insulation, furnace hot spots, process flow abnormalities)
- speed and torque measurement

Use of monitoring requires consideration of the appropriate methods, frequency of measurement, and determining the criteria for action.

9.2.7 Gas Analysis Systems

Gas analysis systems in chemical plants are used for many purposes: to control and monitor process reactions, for product quality control, to detect the leakage of flammable or toxic gases into the environment, to detect and control the buildup of potentially flammable or explosive gas mixtures and to monitor environmental compliance. All gas detectors have the same basic components—the gas capture/transfer unit that gathers the gas for measurement, the analysis unit that uses one of several possible analytical methods to measure the concentration of the monitored component in the gas and transform it to an electric signal, and the signal/control unit that shows or records the concentration or uses the concentration to adjust process controls, to activate an alarm or to initiate a process shutdown.

Several of the design criteria for gas analyzers are summarized below:

Use of the analysis results: The detection limits and range of various types of gas analyzers will determine the basic type of system that may be installed; an analyzer that detects in the percent range cannot be used to monitor ambient conditions where the Threshold Limit Valve (TLV) for the chemical is in ppm. Where the analyzer controls a safety function, such as an alarm, unit shutdown, or process interlock, the safety system may need to be totally independent from the analyzer that performs the process control function.

Capture/transfer unit location: The unit should be located in an area where the monitored gas may collect; for light gases the unit should be placed high; low placement areas should be used for heavy gases. For units located in process piping, the detectors should not be located in a portion of a pipe where the mixing of gases is expected to occur. If possible the unit should be placed where there is easy access for maintenance. Analyzer houses must be adequately protected by ventilation and/or detection of flammable or toxic material.

Real time analysis: Some types of gas detectors, such as catalytic combustion or nondispersive infrared detectors for organics, operate on a "real time" basis, that is, the analysis of the captured gases is completed in a very short period of time and the electrical signal output is ready for use in control or recording circuitry. Other types of analyses require periods of up to several minutes to complete a single analysis and convert the results to an electrical signal. The type of analyzer that can be used for a particular requirement will depend upon the action and time needs of the process.

In-unit versus remote analysis: The analysis unit for the detection system can be placed in the unit or it may be placed in a remote location, with the sample pumped from the process to the analyzer. The in-unit location allows for a more immediate analysis of the sample with little or no time delay created by the transport of the sample to the analyzer. In control situations, such as a unit shutdown, an excessive time delay may create a problem. In-unit placement may have some drawbacks; if it is hard to reach, it is difficult to maintain. In-unit placement may require means to protect the analyzer from the harsh chemical conditions normally present in an operating unit. The potential for the analyzer to cause safety problems in the unit may require the analyzer to be intrinsically safe or to be placed in explosion-proof enclosures. The remotely placed unit can be located in a safe area, where it is away from the process and easy to access; the cost is the additional time required to draw the gas sample, combined with the requirement for line tracing to prevent condensables from dropping out of the gas.

Single versus multiple collectors: Many analyzers can examine a gas from several collectors by pulling the gases through a manifold system that draws a sample from each collector on a rotating basis. This capability can save significant amounts of money on expensive analyzers, but the lag time between two samples of a single point may be too large to allow for adequate process control or alarm.

Gas contamination: The gas stream being analyzed may require treatment prior to being sent to the analyzer. Treatments can include heating or cooling the gas and the removal of particulate matter or condensables such as water. Additionally, contaminants in the gas stream may poison the catalysts in some types of analyzers or cause the analyzer to give false readings.

9.2.7.1. Oxygen Analyzers

Oxygen analyzers have several process safety functions. These functions include:

- The detection of oxygen levels to ensure flammable concentrations are avoided in flare lines, storage tanks, sewer lines and open areas in the plant, reactors, centrifuges, grinders
- Combustion control in furnaces and heaters
- The detection of oxygen levels below human support levels in tanks, sumps, and other confined spaces

Most commercially available oxygen analyzers are of two types: electrochemical cell or paramagnetic resonance. Both types work equally well if properly installed and maintained. Quite often a gas sample must be pretreated to remove harmful components such as water, acids, dust, etc., to prevent damage to the analysis cell. Also, gas sample lines should not be oversized as a time lag can result which would be detrimental to using the analyzer to trigger an alarm or shutdown.

A problem common to electrochemical cells is that when the electrochemical cell goes bad, the analyzer still indicates a safe oxygen level when in reality it isn't. Adherence to the manufacturer's recommendation as to how frequently the cell should be replaced will minimize the problem. It is possible to purchase an electrochemical cell oxygen analyzer with two cells in tandem, and an alarm to indicate when the first cell is going bad. To keep oxygen analyzers properly operating, they should be calibrated and maintained on a regularly scheduled basis. The IChemE (1983) has published useful guidelines on the safe application of oxygen analyzers.

9.2.7.2 *Combustible or Toxic Gas Monitors*

Dailey (1976) reviews analytical principles for a variety of methods (nondispersive infrared, catalytic oxidation, and chemical types) and summarizes a number of other methods. The selection of the method of sensor depends on a number of factors, including: "sensitivity, application, range and methods of analysis, stability, reliability, maintainability, and availability of vendor training and service" (Dailey 1976). The simplest instrument is the common combustible gas detector, which operates by measuring the heat produced by catalytic reactions.

Other important considerations or components of the monitoring system include:

- sampling methods
- alarm requirements
- data handling
- remote annunciators
- interlocks and controls
- NEC hazardous area requirements. "Designers of instruments must consider the ultimate usage of the sensor and install flashback arresters, explosion-proof housing, and use other design criteria to meet the requirements of the NEC, USBM, UL, FM, etc., for instrument usage in hazardous areas." (Dailey 1976).
- operational reliability. Factory Mutual (FMEC 1987) outlines system maintenance and testing.
- requirements to condition the sample, e.g., trap condensates or filter particulates. In sampling from drying ovens, consider the need to filter particulates or heat the lines to prevent solvent condensation
- sample reacts with the analyzer, e.g., silicone vapors (such as in a drying oven) can inactivate (poison) the catalytic filaments in a combustible gas detector (FMEC 1987). Consider another method, such as nondispersive infrared.
- sample point locations: e.g., for gases higher or lighter than air sample between hydrocarbon holdup areas (tanks and columns, etc.) and ignition sources; sample at point of release, such as pumps, valves, rupture disks, vents, or pressure relief valves.
- requirements for calibration of the instrument: calibration gases must be chosen carefully. Consider exactly what is to be monitored; "Special consideration must be given when fuel gas (methane) must also be detected" (Johanson 1976)
- maintenance of sample lines, filters, etc.

Other analytical instruments may be used to determine quantities such as vapor pressure, titration end point, flash point, Btu content (GPSA 1987). These installations also require consideration of sample probe location, sample lines, filters, etc.

9.2.8 Backup Instruments: Redundancy and Diversity

Redundancy refers to providing two or more methods to achieve the same function. A good review of the topic is provided in a recent paper by Englund and Grinwis (1992). The question of redundancy should be addressed because the components of a process control system will eventually fail. "The system must be designed so that when an instrument or control component fails, the plant is still safe and continues to function in a normal manner" (Englund and Grinwis 1992). Different levels of redundancy affect both process operability and safety. Englund and Grinwis illustrate how operability and safety are related in terms of redundant outputs (Table 9-1).

Table 9-1 Ranking of Process Operability and Process Safety[a]

Number of Inputs to Cause Action and Number Available	Process Safety	Process Operability
1 out of 3 can cause action	Very safe. False trips likely	Poor. Failure of sensor can cause shutdown.
1 out of 2 can cause action	Safe. False trips likely.	Poor. Failure of sensor can cause shutdown.
1 out of 1 can cause action	May be poor. No way to detect failure; no second chance	Poor. No way to detect failure; no second chance.
2 out of 2 can cause action	Fair. If there is failure, operator can vote if there is enough time. Operator may make a wrong decision if there is not enough time.	Good. Few false trips. If there is failure, operator can vote if enough time, but may make wrong decision if pressed. Significant probability the process will not shut down when it should.
2 out of 3 can cause action	Very safe. Action can be taken quickly. Computer can decide action if there is disagreement. Wrong decision is unlikely.	Very good. Few false trips, yet will shut down the process when it should shut down.
3 out of 3 can cause action	Poor. Requires that all 3 sensors be functional and agree before shutdown occurs.	Very good. Few false trips. Process does not shut down unless all agree.

[a] Englund and Grinwis 1992

Table 9-2 Characterization of Process Sensitivity and Process Hazard[a]

High Hazard, Low Sensitivity —Two or more devices —2 or more than 2 inputs used for alarm —1 out of 2 (or more than 2) "OR" logic used in alarm —Either single or redundant inputs used for control —Plant strategy: If you think there is a safety problem, shut down. There will be false trips. *Examples:* —chlorine tank car unloading station —parts of tank farms for flammable materials	**High Hazard, High Sensitivity** —Triple redundant —2 out of 3 voting used in alarm —More than one input used in control (auto select) —Control system decides if alarm condition exists —Alarm sounds if redundant inputs disagree —Operator initiates repair —Plant Strategy: Need to minimize false trips but shutdown if needed. Control failure can cause safety problems and economic loss. *Examples:* —parts of ethylene plants —parts of ethylene oxide plants
Low Hazard, Low Sensitivity —Single device —Single input for alarm —1 out of 1 —Single input used for control —No spare equipment —Plant strategy: False trip is not a problem except for downtime and minor product loss. *Examples:* —calcium chloride dryer —plastics granules extrusion and packaging line —water treatment plant (unless it affects downstream plants)	**Low Hazard, High Sensitivity** —Dual device —2 inputs used in alarm —2 out of 2 "AND" logic used in alarm —More than one input used in control (auto select) —Sound alarm if redundant inputs disagree —Operator initiates repair and/or shutdown if input disagreement —Plant strategy: minimize false trips; control failure causes only minor safety problems but significant economic loss —Operator has time to make a decision —Operator can make the wrong decision *Examples:* —lime kiln —blast furnace

[a] Englund and Grinwis 1992

Determination of the appropriate degree of redundancy is based on process hazards and process sensitivity (Englund and Grinwis 1992). Process hazards are characterized by preliminary hazard analysis or other methods. A matrix (shown in Table 9-2) was developed by Grinwis (Englund and Grinwis 1992) to help determine the level of redundancy required.

After an analysis of which components in such loops should be redundant, consideration should be given to the use of diversity in the backup hardware. "Diversity" refers to the fact that a different principle of operation is designed into the backup device. Diverse design can be accomplished for analog or discrete loops; control or indication only; and for the process sensor, controller, and/or final control elements. Examples of diversity include:

- pneumatic as backup for electrical
- vapor pressure as backup for temperature
- mass flowmeter as backup for turbine meter
- nuclear instrument as backup for sonic or d/p level instrument

A comparison of pneumatic and electrical instruments is shown in Table 9-3.

9.2.9 Preconditioning and Other Considerations

The physical properties of the fluids being measured must be fully understood. Viscosity and polymerization are important considerations for the proper application and sizing of flow meters and control valves. Operating temperature and pressure extremes are needed to specify instrumentation

Table 9-3 Comparison of Instrument Type Features[a]

Pneumatic	Electronic
Advantages	
1. Intrinsically safe, no electrical circuits	1. Greater accuracy
2. Compatible with valves	2. More compatible with computers
3. Reliable during power outage for short time period, depending on size of air surge vessel	3. Fast signal transit time
	4. No signal integrity loss if current loop is used and signal is segregated from ac current
Disadvantages	
1. Subject to air system contaminants	1. Contacts subject to corrosion
2. Subject to air leaks	2. Must be air purged, explosion proof, or intrinsically safe to be used in hazardous areas
3. Mechanical parts may fail due to dirt, sand, water, etc.	3. Subject to electrical interference (shorts or ground loads)
4. Signal boosters often needed on transmission lines of over 300 feet	4. More difficult to provide for positive fail-safe operation
5. Subject to freezing with moisture present	5. Requires consideration of installation details
6. Control speed is limited to velocity of sound	6. Backup power supply required

[a] Adapted from GPSA 1987, Fig.4-2

rating and materials of construction. Proper chemical identification of fluids is required to select metallurgy and seal elastomers. Freezing points are used to determine if heat tracing or winterization of measurement impulse lines is required.

When installing flow, level, and pressure instruments in dirty fluid streams such as slurries and streams with entrained solids, steps must be taken to prevent instrument plugging. The pressure taps for all three types of measurements can be purged with a process compatible fluid or installed with special seal fittings to prevent the dirty fluid from entering the instruments.

Harsh plant environments containing H_2S, SO_2, Cl_2, NO_x, or airborne contaminants, are destructive to electrical components; filtration of pollutants may be required. Field instruments may be protected by either purging or hermetic sealing, not to satisfy electrical classification requirements, but to extend the life of the instrument.

Calibration is especially important for instruments and control devices critical to safety; therefore, these devices should receive priority in maintenance.

Samples should be representative of the process, that is, not changed while being sampled or measured. For example, it may be necessary to inhibit monomer formation in the sample line or provide for continual flushing of the line (Lovelace 1979). The Lovelace paper also discusses methods to improve the safety of manual sampling operation (both direct and indirect line sampling methods).

Classification of instrument systems should be in accordance with the National Electric Code. Intrinsically safe instruments may be used in classified areas.

9.3 PROCESS MONITORING USING COMPUTER-BASED SYSTEMS

The types of computers involved in process control in today's chemical plants range from minicomputers to microcomputers and can be found in the basic process control system as well as in sensors and final control elements (Figure 9-1). (Terminology for process control is presented in Table 9-4.) Transition from conventional safety interlocking to programmable electronic technology brings new concerns for the process engineer. While increased automation can reduce the potential for operator error, new types of faults may be introduced by the application of computer-based control technology. These safety issues are receiving serious consideration throughout the industry.

A summary of current practices in the area of safe automation is provided in *Guidelines for Safe Automation of Chemical Processes*, known as the *Safe Automation Guidelines* (CCPS 1993). This book provides information on im-

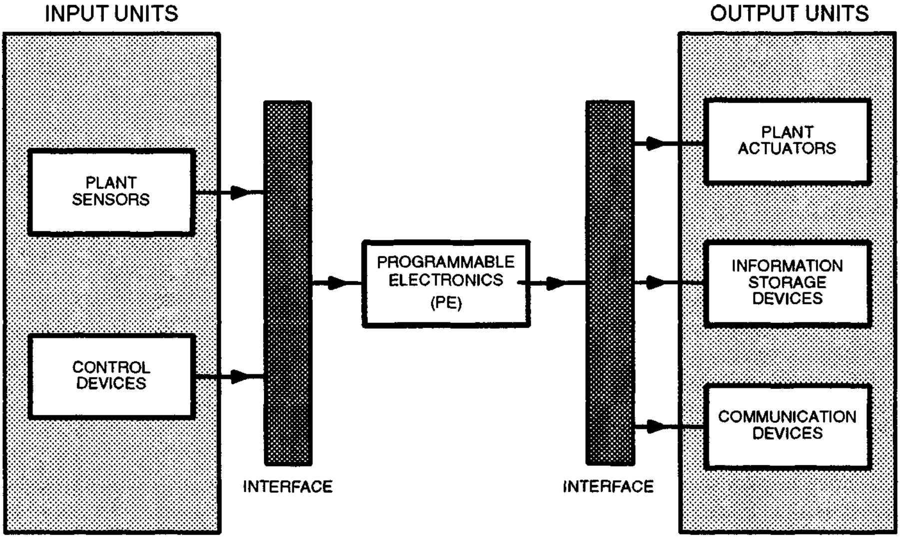


Figure 9-1 Schematic diagram of the structure of a programmable Electronic System (PES). Whatever their size and role in a particular installation, PESs all have the same basic structure (Source HSE 1987, Part 1).

proving safety in the process control systems and safety systems. The primary emphasis is on application of programmable electronic systems (PESs), but the principles may be applied to all types of control system hardware. The *Safe Automation Guidelines* are intended to cover the entire control system, from field-mounted process sensors through the control modules, the human-machine interface, and the final control elements. The book presents techniques to evaluate the types of failure modes that can exist in control systems components and the effects of these failures on the overall safety of the process. The design philosophy expressed in the *Guidelines* was summarized in a recent paper by Drake and Thurston (1992); parts of this chapter draw heavily from that paper.

Although the *Safe Automation Guidelines* recommend that the Safety Interlock System (SIS) and the Basic Process Control System (BPCS) be physically and functionally separate, there are some disadvantages to this complete separation that must be considered. Physically and functionally separate process control systems may aggravate the problems of human interaction, communication between, and coordination of, these diverse systems. Also, diverse systems, because of their complexity, may impose a limit on employing the best safety strategy due to the increased level of knowledge required for their implementation and operation. With the SIS completely separate from the BPCS and not involved in the normal operation of the process, plant personnel may look at it as a "black box" that they do not understand.

Table 9-4 Process Control Terminology

Process control includes both the systems that monitor the process and regulate it, and the systems that implement safe shutdown if the process cannot be controlled.

Control System refers to the complete system of instrumentation, algorithms, and logic used to control a process, including field instrumentation, basic process control systems(s) and safety interlock system(s).

Basic Process Control System (BPCS): the system which controls the basic process, such as a DCS, by performing the regulatory, sequencing, process interlocking, and diagnostic functions. While it does have protective functions, the primary purpose of the BPCS is automatic regulation of day-to-day process operation. This system may contain interlocks designed to reduce the opportunity for misoperation (Maggioli and Stike 1990).

Distributed Control System (DCS): microprocessor which controls a limited number of control loops, thereby distributing the processing.

Interlock: a system that detects out-of-limit (abnormal) condition or improper sequences and either halts further action or starts corrective action (Maggioli and Stike 1990).

Safety Interlock System (SIS): same as Interlock, except a failure to control an out-of-limit condition can cause personnel injury, property damage or unacceptable environmental contamination; a system that can be separate from the BPCS or can be integrated and redundant with the BPCS. The SIS monitors the process for prescribed abnormal conditions and takes action to alleviate or mitigate the condition. This system is sometimes called the Emergency Shutdown System.

Programmable Electronic System (PES): an industrial control system which uses analog and digital input/output (I/O) circuitry to control field devices based on a programmed or configured set of instructions and algorithms; includes distributed control systems and programmable controllers. This term was coined by the British Health and Safety Executive (HSE) and is being adopted by the standard-making bodies. The term PES applies to all types of digital control systems: distributed control systems, programmable logic controllers (PLC), single station digital controllers, and other microprocessor-based equipment that may be used for control applications (HSE 1987).

"A PES is a computer-based system which controls, protects or monitors the operation of plant, machinery, or various types of equipment. The PES is linked to the plant by sensors and actuators [input and output units]" (HSE 1987, Part 1). See Figure 9-1 for schematic diagram of a typical PES.

Maintenance personnel must be familiar with testing and repair procedures for diverse hardware and software. A process control system that provides separate hardware and separate control software for the safety systems, but is integrated into the overall control system with a common control language and common user interface can be a feasible option for facilities that possess the necessary support functions to ensure the highest level of safety analysis. No matter what process control system is used, the philosophy and concerns discussed in the following pages are pertinent and need to be addressed.

Hazard evaluation techniques must address software as well as hardware when applied to an electronic system. These techniques, qualitative and quantitative, can be applied to the programmable systems used for both basic process control and in the safety systems used to mitigate risk. Chemical plant management provides leadership by establishing risk control guidelines and setting criteria for the sound management of safety systems throughout the life of the facility. When PES-based control systems are used for risk reduction, particular care is needed in implementing safety guidelines.

9.3.1 Programmable Electronic Systems

"When evaluating safety, it is important to realize that programmable electronic equipment is fundamentally different from other equipment. For example, it is not always easy to predict the effects of the failure of a PES, or even to find out where the fault lies" (HSE 1987); consequently, it is "essential to follow systematic steps to make sure that adequate safety precautions have been taken. . . ." The steps include:

- Hazard analysis
- Identification of the safety-related systems
- Determination of the required safety level
- Design of the safety-related systems
- Safety analysis

Because PESs provide process interlock functions to the BPCS, the process control and safety engineers have had to consider the impact of PESs in reliability analysis. This is complicated by the fact that most of the instrument safety protection schemes provided in chemical plants today have been combined with instrument protection layers using non-PES technology (Maggioli and Stike 1990).

Programmable and nonprogrammable instrumentation share some failure modes, such as failures of sensors and final control elements and human error. The introduction of programmable electronic technology introduces some new safety concerns, such as:

- How to identify and prevent new failure modes
- How to detect errors in software, either in original programming or by "corrupted" data
- Loss of operator knowledge of the process and how to control abnormal conditions arising from equipment/computer failure or unanticipated process excursions. It is critical that the designer carefully evaluate proper allocation of supervisory function between the operator, the computer controls and interlock systems in order that the operator maintains the knowledge and commitment to respond effectively to process upsets.

- How to define battery limits, when "there is virtually no way to isolate sensors and final elements from the PES safety analysis" (Maggioli and Stike 1990).
- How to modify control rooms for electronic equipment and to modify the electrical distribution system

Failures encountered in PESs may be characterized as random hardware failures and systemic failures, including software (HSE 1987). One effective precaution against random hardware failures is to employ redundancy. Equipment reliability is not easy to evaluate, due to the rapid changes in computer hardware. Systemic failures are particularly troublesome because they may remain hidden for long periods of time; as noted in HSE (1987), it is not feasible to test a system under every possible combination of operating conditions, and faults may remain hidden until a particular set of circumstances arise and the system breaks down. Several types of errors can cause systemic failures:

- Specification errors. These are the mistakes and omissions made when the tasks to be performed by the installation were originally planned.
- Equipment errors. These occur at any stage in the design, manufacture, installation, or operation of the equipment.
- Software errors. These may occur during programming, during subsequent modifications, or by corruption of the data following installation.

There are several options for providing additional safety to the system if the failure of one particular hardware channel could cause the whole installation to break down. As listed by HSE (1987) these may include providing

- Additional nonprogrammable hardware
- Additional programmable electronic hardware of a different design, i.e., diversity
- Additional programmable electronic hardware of a similar design. This option requires the highest levels of safety analysis
- Software diversity

One of the more significant considerations related to the PES is that the failure of a single input/output module could simultaneously disable as many as 16 instrument loops, thereby impacting the control of a significant fraction of a process. Such a failure can result in common cause failures of parallel equipment pieces if not properly considered in the design.

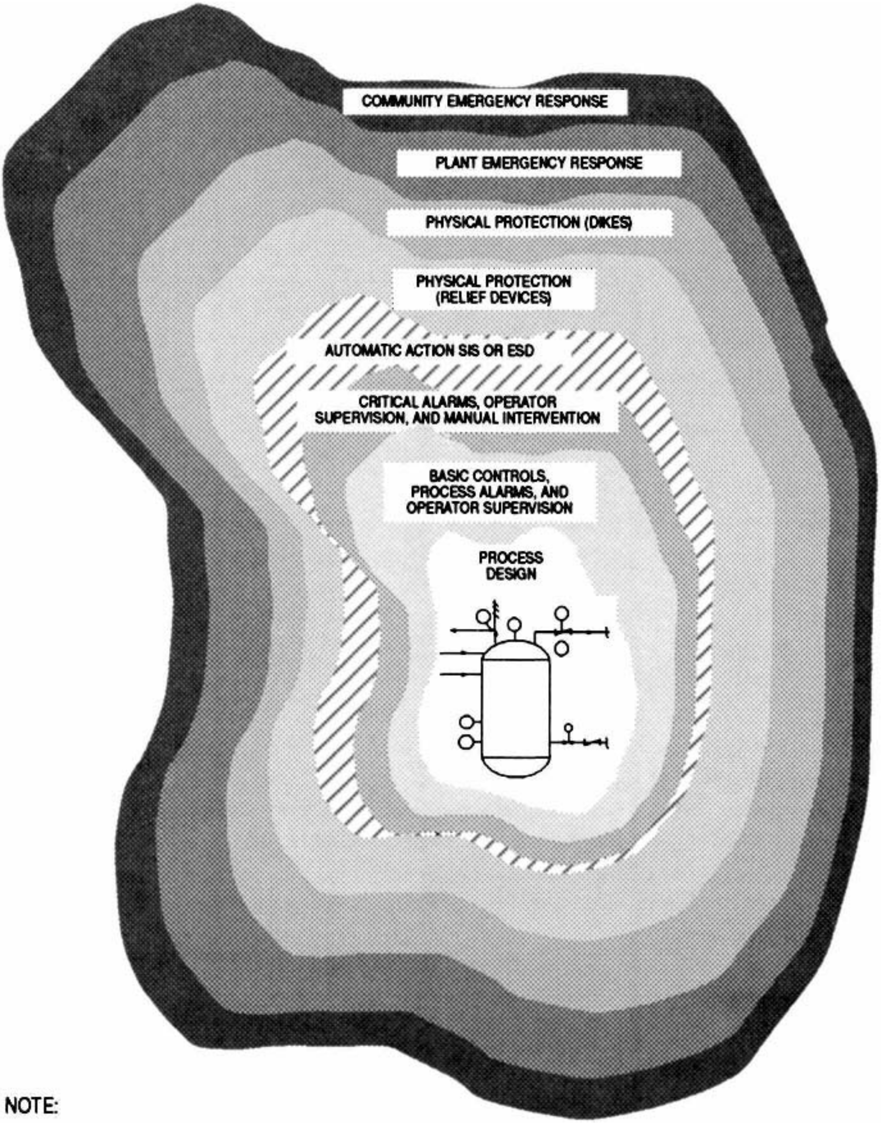
9.3.2 A Safety Evaluation Framework

Process hazards management provides the framework for evaluating the safety of PESs, just as it does for other systems. "Many of the hazard identification and risk assessment methodologies used today are based on techniques that assume independence of failures. However, possibilities for common mode failures and covert faults are greatly increased in PESs for process control which may be interconnected through data highways, software, central supervisory control computers, and subtle deficiencies in design" (Drake and Thurston 1992). Plant safety today calls for a safety evaluation framework in which to address input from all design disciplines, including safety and risk specialists. The integrated approach emphasizes applying risk analysis techniques to programmable electronic monitoring and control systems. This important concept is receiving considerable attention from standards-issuing organizations and industry groups.

9.3.2.1 *Application of Safety Protection Layer Philosophy*

The concept of layers of protection (see Chapter 2) also applies to design of control systems. "Facilities which process hazardous materials should be designed with multiple safety layers of protection. Each safety layer prevents or mitigates an undesirable event, and multiple layers addressing the same event are often necessary to achieve high levels of certainty that protection will be available when needed. Events with more serious potential hazards usually require more layers of protection than events with lesser potential impact. Further, there is advantage in taking action to prevent escalation of a developing accident at the earliest possible step in its development" (Drake and Thurston 1992). The concept of concentric layers of protection is presented schematically in Figure 9-2. When significant hazards cannot be avoided by developing an inherently safer process or by selecting inherently safer process equipment, instrumented protective functions become more important.

As described in earlier chapters, the first layer of protection is provided by detailed process design: selection of the process itself and minimization of hazardous material inventories. The next layer is the basic process control system, which includes operator supervision and regulation. Further protection is provided by the alarm system and operator-initiated corrective actions. Subsequent layers of protection are added to meet the levels of risk determined by plant management. A Safety Interlock System (SIS), or the emergency shutdown (ESD) system, may be the next level of protection. The SIS "provides automatic action to correct an abnormal plant event which has not been mitigated by actions in the inner layers" (Drake and Thurston 1992); an SIS functions only "when normal process controls are inadequate to keep the process within acceptable bounds," that is, when the basic process control system fails. Subsequent layers may include physical means to mitigate or contain the event, such as venting devices, to prevent equipment failure due to overpressure, and dikes to contain a liquid release. If all these protective layers fail, emergency response plans at the plant and in the community are the final opportunities to mitigate the effects of the hazardous event.



NOTE:

Protection layers for a typical process are shown in the order of activation expected as a hazardous condition is approached.

ESD – Emergency Shutdown
SIS – Safety Interlock System

Figure 9-2 Layers of protection in a modern chemical plant (CCPS 1993).

Since these protection layers are generally quite different in nature from one another, they often can be considered independent; however, establishing the independence of these layers becomes more difficult in programmable electronic systems.

Safe Automation Guidelines includes a method to establish qualitative criteria and the ranking of risks, by estimating the severity and likelihood of a hazard. The *Guidelines* provide a risk matrix for selecting the integrity level required for the safety interlock system after completing risk evaluation; this process is also illustrated in Section 9.6.

9.3.2.2 Application of Process Hazards Analysis

The focus of recent developments in process control is the application of qualitative and quantitative analysis techniques to evaluate both BPCS and SIS. This is not only an issue in new construction, but throughout active operation. The chief purpose of a process hazard review is to ensure that the total process control system design meets all safety criteria; those established by relevant codes, standards and regulations, as well as the safety goals set by corporate policy. Formal methods of safety evaluations, such as process hazards analysis (PHA) may be used in safety system design as well as at other stages of the plant life cycle (CCPS 1992a, Greenberg 1991, HSE 1987).

Identification of significant process hazards must occur *early* in the selection of process technology so that the instrumentation/electrical designers can consider these potential hazards in developing the basic process control strategy. It is essential to create interaction between process designers, control system designers, risk evaluators, and experienced operators.

Qualitative techniques for risk assessment include:

- Engineering judgement. This includes input from process engineers, instrument specialists, risk specialists and experienced operators. The single-discipline approach should be avoided.
- Safety codes and company or vendor design specifications, including the new standards being developed (for example, ISA SP84)
- Formal hazard analysis, for example:
  —What-if analysis or checklist (in early design stages)
  —Failure Mode and Effect Analysis or Hazard and Operability Study (in later stages)
  —other techniques such as fault tree or event tree techniques used without quantification

Quantitative techniques are discussed in detail in *Chemical Process Quantitative Risk Analysis* (CCPS 1989). These techniques need to be used carefully, realizing their capabilities and limitations. Types include Fault Tree Analysis, Event Tree Analysis, Quantitative Risk Analysis, Markov Models, and Human Reliability Analysis.

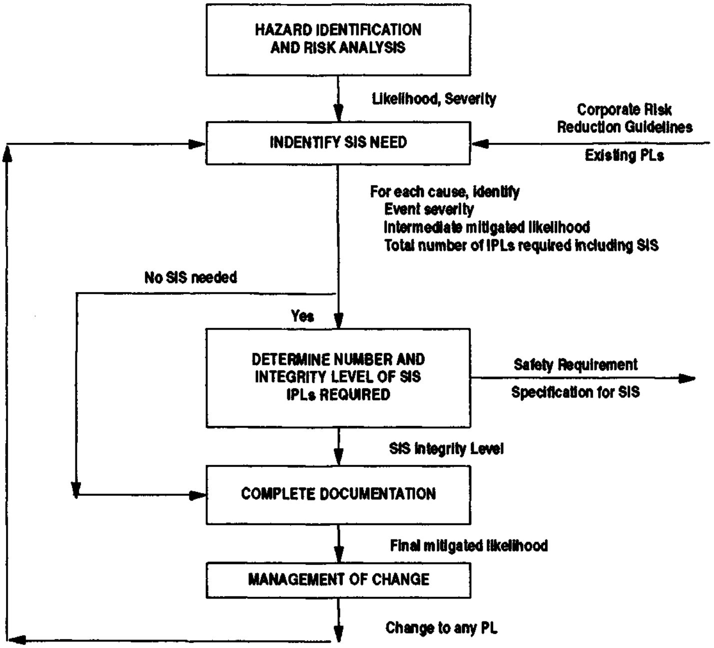
Human reliability analyses need to be included in quantitative methodologies because the human/machine interface is particularly important in process control systems. For example, humans may fail to design the system properly or to respond properly, or commit errors in calibrating, testing, or interpreting output from control systems. In particular, the structure and content of the graphical displays to which an operator must respond should be reviewed. A more fundamental problem generated by the use of automated systems can be the loss of operator knowledge of the process and lack of commitment to controlling the process when his experience has been that the process runs fine by itself. Serious consideration needs to be given to providing the operator with a significant portion of the supervisory control function. These studies are addressed in *Guidelines for Improving Human Performance in Chemical Process Safety* (CCPS in progress).

9.3.2.3 *A Format for Identifying SIS Design Requirements*

After the initial process design and the basic control strategy are developed, a more detailed risk review should be conducted to determine qualitatively what level of risk exists. This analysis results in identifying the specific safety interlocks and alarms to be included in the safety interlock system, and defines the level of integrity required in the performance of each interlock. For example, in a Hazard and Operability Study (HAZOP) or in a process design verification review, failure scenarios might be developed that require additional safety layers to reduce the likelihood of a hazardous event to an acceptable level (as defined by plant management). Best results can be achieved when options for mitigation begin in the innermost layer (process design) before working outward. If risk is not acceptably low after three inner layers, the option to further reduce event *likelihood* is the basis for adding either a safety interlock or mechanically independent protective layer (CCPS 1993). The risk review must include human factors.

Two points to emphasize are: (1) the risk should be reduced as much as possible in the innermost layer, before adding the next layer; and (2) the independence of the protective layers must be clearly understood. In certain hazard analysis techniques, notably fault tree analysis, establishing the independence of the "branches" of the tree is almost impossible when examining programmable electronic system controls, "which may share data highways, have programming done by a single individual, have the same vendor, or be susceptible to other common mode failures" (Drake and Thurston 1992).

There may be a number of alternative ways to assess total system safety. The method described in *Safe Automation Guidelines* highlights the importance of designing independent protection layers into a risk control design strategy and the limitations of certain types of analyses in assessing safety of PES-based control systems. Figure 9-3 presents the sequence of steps used to establish safety interlock system requirements. Implementation of this strategy requires



NOTE: IPL = independent protection layer; PL = protection layer; SIS = safety interlock system

Figure 9-3 Sequence of steps in establishing SIS requirements (adapted from Drake and Thurston 1992).

establishment of corporate risk levels (Balls 1987) and a method to rank event likelihood and severity (CCPS 1993). These parameters may then be used to set priorities for mitigation efforts; these parameters are also helpful in classifying the integrity level of a safety interlock system (CCPS 1992a).

A format to systematically identify and document protection layers is presented in *Safe Automation Guidelines*. This format identifies the protective layers that already exist; it represents a method to track the assessments required to develop a protective layer and then to estimate the layer's effectiveness in risk mitigation. Industry experience suggests that an SIS independent protection layer alone may not be satisfactory to protect against events of extensive severity.

The first step in identifying additional mitigation measures is to look for additional protection opportunities in the innermost layers. Every possible option should be considered to reduce risk in the process itself as much as possible. At this point, if the intermediate event likelihood is not acceptable, use of an SIS is indicated.

Subtle common mode failure possibilities are often present in SISs even when independent and diverse system elements are selected. Consequently a separate review of all control-related protection layers is suggested after the SIS design is complete to ensure that the designers have not overlooked any of the critical attributes of the system. The review is conducted systematically, starting with the highest integrity level interlocks (Drake and Thurston 1992). This verification may be performed with the help of checklists addressing availability, separation, diversity, fail-safe characteristics, testing, etc. In programmable systems, questions regarding development of software and methods for testing are particularly important.

9.3.3 General Guidelines

General guidelines for applying process hazards management to PES-based controls are developed in *Safe Automation Guidelines* (CCPS 1993):

- Identify, early in the project, the impact of the equipment technology being considered for the BPCS and SIS on the design and maintenance of the facilities
- Consider the BPCS and SIS as integral parts of the process, not as "add-ons."
- Include operations, maintenance, and safety personnel as well as BPCS and SIS designers in early project discussions. This is particularly important if the process is complex. The potential influence and interactions of the BPCS and SIS should be examined so that any design problems are resolved prior to beginning of detailed design. If multiple groups are participating in control system design, their efforts must be integrated as early in the project as possible.
- Ask probing questions early to establish what the BPCS and SIS are intended to do, and what *not* to do, to prepare a clear and usable functional description for a new BPCS or SIS. Early discussions, including requirements for integrity, separation, diversity, etc., will raise common awareness among members of the project team and will be a good basis for proceeding with a systemic approach to the design.
- Remember that the technical versatility, interactive capability, complexity, and failure modes of PESs are different from those of other devices. There should be a requirement for a formal management of change procedure once the control system has passed the last functional validation step before plant startup. "Fix-it changes to PES-based BPCS and SIS may easily be made without realizing that unexpected hazards are being introduced." (Drake and Thurston 1992).
- Clearly document the software so that subsequent analysis may be easily accomplished and the thinking applied in generating the application will not be lost.

Next Page

- Complete prestartup training and assure that all documentation and spare parts are onsite prior to startup.
- Develop a systematic review and evaluation scheme that will validate the integrity of the BPCS and SIS through its life cycle.

9.4 ALARM SYSTEMS PHILOSOPHY

Development of the alarm system includes determining what parameters should be alarmed, how they should be alarmed, and how they should address operator response. Guidance is provided in publications from the Instrument Society of America, the Institute of Electrical and Electronic Engineers, the American Institute of Chemical Engineers, and the Institute of Chemical Engineers.

The need for stand-alone dedicated alarm systems, even where modern PES controls are implemented, continues for two primary reasons. First, with modern distributed control systems there is a tendency to overalarm. This overalarming tendency compromises the reliability and safety of an alarm system. Unless an alarm condition exists only rarely, it is almost certain to be disconnected or ignored. Dedicated annunciators help to ease operator comprehension of process unit status, particularly in a critical upset situation. Consequently, a dedicated, stand-alone annunciator has the ability to draw attention to specific alarm information and provides an important advantage over a corresponding cathode ray tube (CRT) alarm display. Priority alarm or time sequencing of alarms in PES time history is also useful to show the sequence of process variations.

The second primary factor contributing to the survival of stand-alone alarm systems is the desire to provide redundancy for critical alarm functions. Even if displayed on a CRT console, a separate annunciator display offers added security in the event of a CRT workstation failure.

9.5 SAFETY SYSTEM MAINTENANCE TESTING

Reliability and availability goals of safety systems should be taken into consideration during the design phase of the safety system when redundancy and failure modes are addressed. However, no safety system can be presumed to perform its intended function under abnormal conditions every time. In a normally operating continuous process, the safety components remain in one position over an extended period of time and may become fixed. It is therefore mandatory to conduct regularly scheduled testing to exercise these components periodically and thus ensure operation.

3

PLANT DESIGN

This chapter discusses ways to maximize process safety in the conceptual design and layout stages of plant design. The quality of the basic design is more critical in determining the safety of the plant than specific safety features added to minimize the hazards. As F. P. Lees (1980) points out, the aim is to eliminate the hazard rather than devise measures to control it. The focus of this chapter is avoiding and mitigating major releases of process materials by implementing safety reviews at all stages of design from conceptual design to process design, site selection and plant layout, and civil and structural design. Safety issues relevant to equipment selection and piping are addressed in subsequent chapters.

Decisions made at the conceptual stages are crucial in forming the basis for process design. Before beginning the design of the plant, safety elements should receive consideration by the product and process research and development team, designers and management. As illustrated by Figure 3-1, the timing of design changes can greatly influence their impact. The opportunity for maximum inherent safety is greatest during early stages of design.

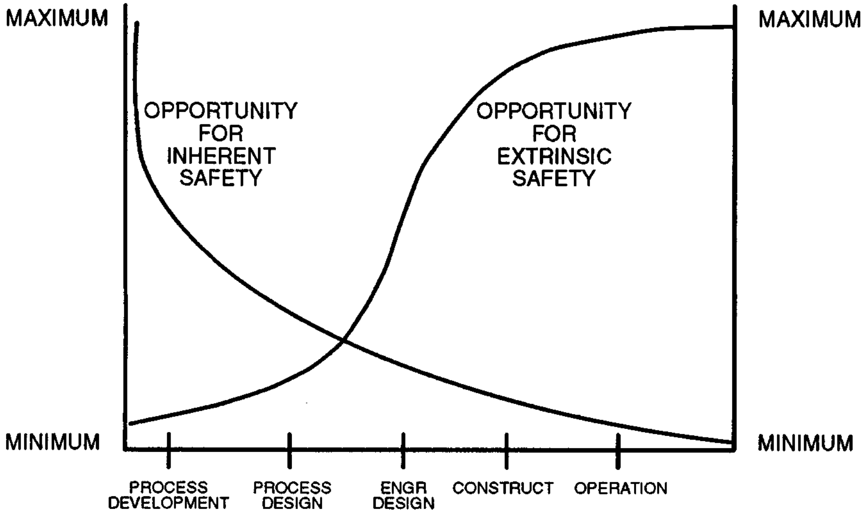


Figure 3-1. Effects of timing of design changes (Greenberg 1991).

3.1 PROCESS SAFETY REVIEW THROUGH THE LIFE OF THE PLANT

The purpose of hazard evaluation is to identify, evaluate and control hazards involved in chemical processes. Hazards can be defined as characteristics of systems, processes, or plants that must be controlled to prevent occurrence of specific undesirable incidents. Hazard evaluation is a technique that is applied again and again throughout the plant design, construction and operation (Figure 3-2). Hazard evaluation is synonymous with process hazard analysis and process safety review. No single ideal method of hazard evaluation applies to all of the stages of a project from conceptual design to decommissioning. Different methods are required for different phases of a project such as research and development, conceptual design, start-up and operation. Table 3-1 presents some of the development stages and typical corresponding process hazard evaluation techniques. The list is presented to illustrate the variety of study methods available. A technique shown for one project stage may be applicable to another.

Basic principles of safe design such as inherently safer design and multiple safety layers are discussed in Chapter 2. Methods of hazard analysis and

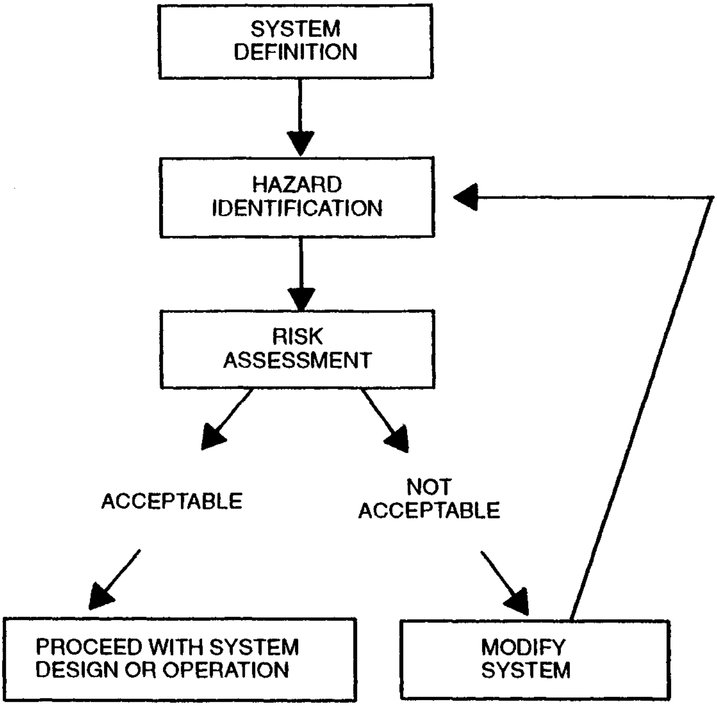


Figure 3-2. Hazards evaluation.

Table 3-1 Typical Hazard Evaluation Objectives at Different Stages of a Process Lifetime[a]

Process Phase	Example Objectives
Research and Development	Identify chemical interactions that could cause runaway reactions, fires, explosions, or toxic gas releases Identify process safety data needs
Conceptual Design	Identify opportunities for inherent safety Compare the hazards of potential sites
Pilot Plant	Identify ways for toxic gas to be released to the environment Identify ways to deactivate the catalyst Identify potentially hazardous operator interfaces Identify ways to minimize hazardous wastes
Detailed Engineering	Identify ways for a flammable mixture to form inside process equipment Identify how a reportable spill might occur Identify which process control malfunctions will cause runaway reactions Identify ways to reduce hazardous material inventories Identify safety-critical equipment that must be regularly tested, inspected, or maintained
Construction and Start-Up	Identify error-likely situations in the start-up and operating procedures Verify that all issues from previous hazard evaluations were resolved satisfactorily and that no new issues were introduced Identify hazards that adjacent units may create for construction and maintenance workers Identify hazards associated with the vessel-cleaning procedure Identify any discrepancies between the as-built equipment and the design drawings
Routine Operation	Identify employee hazards associated with the operating procedures Identify ways an overpressure transient might occur Identify hazards associated with out-of-service equipment
Process Modification or Plant Expansion	Identify whether changing the feedstock composition will create any new hazards or worsen any existing ones Identify hazards associated with new equipment
Decommissioning	Identify how demolition work might affect adjacent units Identify any fire, explosion, or toxic hazards associated with the residues left in the unit after shutdown

[a] CCPS 1992a

detailed guidelines for implementing hazard evaluation techniques are provided in *Guidelines for Hazard Evaluation Procedures, Second Edition with Worked Examples* (CCPS 1992a), *Chemical Process Quantitative Risk Analysis* (CCPS 1989), and in recent publications by Greenberg and Cramer (1991), Hendershot (1992) and others.

3.2 PROCESS DESIGN

Process flow diagrams are developed to show major equipment items including sizes, duties, selected operating pressures and temperatures, major control loops and the process flow arrangement. The material and energy balances are also included on the process flow diagrams. Some of the safety elements that can be included on the flow sheets are:

- Process materials properties
- Process conditions (pressure, temperature, composition)
- Inventory
- Emergency and waste releases
- Process control philosophy

3.2.1 Dangerous Properties of Process Materials

Safe handling of materials in both process and storage begins with understanding their physical and chemical properties. This concept applies to all chemical substances used by a process, including reactants, intermediates, products, and nonreacted substances such as catalysts, solvents, and adsorbents. Some of the important characteristics are listed in Table 3-2 and discussed in the following pages.

3.2.1.1 General Properties

Data describing the general properties of substances comprise some of the most useful and easily located information about most chemical substances. These data are typically located in handbooks, such as the *CRC Handbook of Chemistry and Physics* or Perry's *Chemical Engineers' Handbook*, and are usually found on the Material Safety Data Sheets (MSDSs) that are provided by manufacturers. The Design Institute for Physical Property Data (DIPPR) is developing critically evaluated thermophysical property data for pure components and mixtures (Danner and Daubert 1983; Daubert and Danner 1989).

Boiling point and freezing point data establish whether a substance is a solid, liquid or gas at atmospheric pressure. Comparison of boiling points, hence, relative volatilities, provides insight into a number of significant issues such as flammability or ease of separation by distillation. Vapor pressure data

Table 3-2 Typical Material Characteristics

PROPERTY	CHARACTERISTIC
General Properties	Boiling point Vapor pressure Freezing point Molecular weight Critical pressure and temperature Electrical conductivity Fluid density and viscosity Thermal properties enthalpy, specific heat, heat of mixing
Reactivity	Reactivity with water or air Potential for sudden violent reaction Sensitivity to mechanical or thermal shock Polymerization Compatibility with materials of construction and other process materials
Flammability	Flash point Autoignition temperature Flammability limits Self-heating Minimum ignition energy
Toxicity	Threshold limit values Emergency exposure limits Lethal concentration LC_{50} Lethal dose LD_{50} Exposure Effects
Stability	Thermal stability Chemical stability Shelf life Products of decomposition

are more difficult to obtain but are more useful in predicting volatility-related behavior. Freezing point data reveal that some relatively common substances may require special handling for cool weather. For instance, commercially available sources of sulfuric acid (90% H_2SO_4) and sodium hydroxide (approximately 50% NaOH) freeze at temperatures between –1 and 10°C (30 and 50°F). A study of phase diagrams of these compounds in aqueous solution is instructive and will aid in the selection of a more suitable storage concentration.

Molecular weight provides a quick comparison of gas densities, which indicate whether a vapor released to the atmosphere will rise and disperse or travel along the ground in search of sources of ignition or potential asphyxiation victims. Critical pressure and temperature are useful for corresponding-states thermodynamic expressions. Since vapors cannot be compressed into liquids at temperatures above their critical regions, substances that can exist only as vapor are indicated by critical temperatures.

Fluid density and viscosity determine the difficulty of transporting substances inside piping, but this information is also useful in other transportation-related issues, such as overloading tank trailers with high-density liquids and design of relief systems. In the event of spills, density and solubility relative to water are important issues. Electrical conductivity often indicates concentration of conductive or easily ionized solutions. Thermal properties are required for analysis of these problems. Enthalpy or specific heat data predict temperature rises for heated substances, critical information when vessels containing volatile flammable liquids are subjected to fire. Heat of mixing data indicate pronounced thermal effects that might occur when mixing substances, such as two different concentrations of sulfuric acid.

3.2.1.2 *Reactivity*

The reactivity of a chemical substance not only influences process reactions but influences hazard potential in accidental releases (Figure 3-3). Exothermic reactions pose hazards because the heat evolved raises the temperature of the

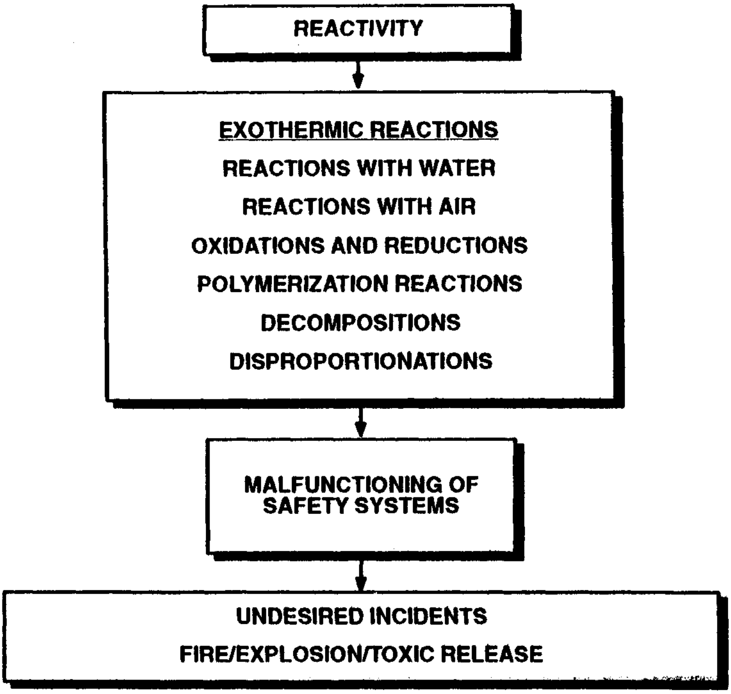


Figure 3-3. Some reactivity hazards of chemical materials.

reactants leading to increased reaction rate or vaporization of materials. In an open system, when high temperature is reached, the materials may ignite or explode. In a closed system, high temperature can lead to vessel rupture from overpressurization caused by accelerated reaction.

Some materials react violently upon contact with water, generating considerable heat. For example, some strong acids may evolve large amounts of hazardous fumes when contacted with water or moisture in the air. It is important to recognize this aspect when preparing fire fighting contingencies.

Pyrophoric substances react violently with air, resulting in spontaneous ignition. Such substances are typically handled by methods that prevent contact with air, often by submerging the substance in water or a compatible oil.

Other chemicals react violently with oxidizing or reducing agents. Oxidants may generate heat, oxygen, and flammable or toxic gases. Reducing agents react with a variety of chemicals and may generate hydrogen, as well as heat, and flammable or toxic gases. Storage and usage of strong oxidizing and reducing agents requires special precautions that are unique to the particular substance in question. Generally each supplier provides complete packages of safety-related information to its customers.

Some chemicals polymerize or decompose at elevated temperature or if contaminated by polymerization initiators or catalysts. Common substances, such as water or dust, can initiate polymerization reactions. When polymerization is initiated, exothermic reaction may occur leading to high temperature and pressure, possibly resulting in explosion or release of flammable or toxic substances. Such decomposition and polymerization reactions may be prevented by incorporating safety systems, inhibitors and safe operating procedures.

Because chemical reactivity is extremely complex, hazardous materials should be examined on a specific case-by-case basis. Chemical reactivity data are available in NFPA 49 and 491M, *Handbook of Reactive Chemical Hazards* (Bretherick 1990), "A Method of Determining the Compatibility of Hazardous Wastes" (EPA 1980), and *Guidelines on Chemical Reactivity Evaluation and Applications to Process Design* (CCPS in press).

3.2.1.3 Flammability

Another important material characteristic requiring attention in early stages of process design is flammability. The most common measures of flammability potential for materials are:

- Flash point
- Lower flammable limit
- Upper flammable limit
- Autoignition temperature

Flammability data are available in various handbooks, hazardous material data bases, and Material Safety Data Sheets. The higher the flash point temperature is above ambient temperature, the more difficult it is to ignite the substance. Liquids with flash points below ambient temperatures are considered particularly hazardous because they generate fumes that can be ignited at room temperature. Extensive flash point data are available in the book by Stephenson (1987) and NFPA 325M.

Flammability limits are altered by pressure, temperature, direction of flame propagation, and surroundings. The general result of increasing temperature or pressure is to expand both the upper and lower limits. A decrease in pressure or temperature may tend to narrow the flammable range by raising the lower limit and reducing the upper limit. These aspects should be remembered since published flammable and explosive limits are based on measurements taken at room temperature and atmospheric pressure unless indicated otherwise. Refer to Chapter 11, Sources of Ignition, for further discussion of flammability.

3.2.1.4 Toxicity

Toxic release under unfavorable conditions is normally regarded as having a disaster potential greater than fire or explosion; therefore, recognizing the toxicity of materials is important in process design. There are three primary routes of entry of toxic chemicals into the body of a living creature: inhalation, ingestion, and dermal contact. The common types of physiological damage due to exposure to toxic chemicals are: irritation, narcosis, asphyxiation, and systemic damage. Hazards posed by materials are not functions of toxicity alone. Consideration should be given to the parameters of exposure spill potential, properties of the substance, and inventory. In considering effects of toxic exposure, both airborne concentration and duration of exposure are consequential. Toxic exposures are described as either acute or chronic. Acute exposures represent brief contacts with potentially lethal concentrations, typically experienced during sudden large discharges of toxic materials. Chronic exposures occur due to prolonged low concentration exposure, usually over a working lifetime.

Various sources of recognized exposure limits for airborne contaminants are presented in Table 3-3. Refer to these sources to determine exposure limits under a variety of different circumstances.

3.2.1.5 Effect of Impurities

Impurities in process streams may jeopardize desired reactions and possibly pose threats to plant safety. These impurities may be traces of compounds typically present in raw materials (e.g., pyrophoric iron sulfides in petroleum or catalyst poisoning agents). Sometimes impurities are the same substance but in a different physical form, such as solids in a liquid stream or liquid slugs

Table 3-3 Selected Primary Data Sources for Toxic Exposure Limits

Source	Acronym	Exposure Limit	Acronym
American Conference of Government Industrial Hygienists	ACGIH	Threshold Limit Value	TLV
Occupational Safety and Health Administration	OSHA	Permissible Exposure Limit	PEL
American Industrial Hygiene Association	AIHA	Workplace Environmental Exposure Limit	WEEL
		Emergency Response Planning Guideline	ERPG
National Institute of Occupational Safety and Health	NIOSH	Immediately Dangerous to Life or Health Level	IDLH
National Academy of Science/ National Research Council	NAS/ NRC	Short-Term Public Emergency Guidance Level	SPEGL
		Emergency Exposure Guidance Level	EEGL

in a gas stream. Effects of impurities should be critically analyzed before beginning process design. Most engineering solutions prevent impurities from entering the process. These range from filters and strainers to stop entry of heterogeneous mixtures (solid particles) and slug catchers (large disengagement vessels) to regenerable adsorbent beds to adsorb impurities for release later during regeneration, guard beds (large vessels full of inexpensive substances that react with impurities, thereby removing them from process streams), and guard reactors (reactors with catalysts specifically designed to convert impurities to nonharmful substances).

3.2.2 Process Conditions

Process conditions, such as pressure and temperature, have their own characteristic problems and hazards. High pressures and temperatures create stresses that must be accommodated by design. Extreme temperatures or pressures individually are usually not the problem, but rather their combination. A combination of extreme conditions results in increased plant cost due to the need for material with high mechanical strength and corrosion resistance.

High pressure increases the amount of potential energy available in the process plant. For these plants, in addition to the energy of compressed gases and of fluids kept under pressure in the liquid state, there may also be a concern of chemical reactivity under pressure, or an adverse reaction from rapid depressurization. Leakage is much more pronounced in high pressure operations. Because of the large pressure difference, the amount of fluid that can discharge through a given area is greater. This has a considerable impact on the consequences of a release, as the hazard zone extends to a larger area.

High temperature also poses material failure problems, most frequently due to metal creep and hydrogen embrittlement. The use of high temperature conditions usually increases plant cost, not only due to materials of construction but also due to the requirement for special supports to handle the stresses generated. Process design should take these stresses into account. The design should aim at minimizing such stresses, especially during startup and shutdown.

High temperatures are often obtained with the use of fired heaters, which have additional hazards like tube rupture and explosions. It is a good idea to consider using steam heaters, where possible, instead of fired heaters to prevent such hazards.

Low pressure operation usually does not pose much of a hazard in comparison with other operating conditions. However, in the case of vacuum applications where flammable materials are present, the potential for ingress of air does create a hazardous situation. This can result in the formation of a flammable mixture leading to fire and/or explosion. It is essential that this aspect is reviewed and adequate measures provided in the process design to prevent air ingress. For equipment not designed for vacuum, damage frequently occurs because of failure to vent while draining, allowing heated equipment to cool while blocked-in, or failure of a vacuum relief device due to pluggage.

The safety elements to be considered in designing low temperature process units are: low temperature embrittlement due to inadvertent flow of low temperature fluids into systems constructed of mild steel; thermal stresses; possibility of failure of refrigerant or coolant systems which are normally provided to maintain low temperature.

3.2.3 *Inventory*

A common factor in major disasters in the chemical industry is a large release of a hazardous material. One of the best ways to make a plant safer is to minimize the potential quantity of hazardous materials that could be released. The principal approach is to minimize inventory, so that even if there is a leak or explosion, the consequences are minimized. The concept of risk analysis, that is, consequence versus probability, is discussed fully in *Guidelines for Chemical Process Quantitative Risk Analysis* (CCPS 1989).

Low inventories result not only in a safer plant but in a cheaper one too. Lower inventories can be achieved by using smaller or fewer vessels. Other

Table 3-4 Methods to Limit Inventory

- Reduction of reactor volumes by improving mixing conditions or better understanding reaction kinetics.
- Storage tanks and day tanks usually contain large inventories. Reduction of inventory by integrating plant operation is desirable.
- Use of continuous reactors instead of batch reactors.
- Reduction of holdup in distillation columns by using low holdup internals. Packing has less holdup than conventional trays.
- Use of thermosiphon reboilers instead of kettle reboilers where possible.
- Location of peripheral equipment such as reboilers inside the column.
- Laying out equipment and pipe to reduce pipe rack holdup.
- Improving the performance of the reactor (reducing byproduct production) so that subsequent operations such as distillation become easier, further reducing holdup.
- For highly toxic materials (e.g., phosgene) make the material in the plant as a subprocess just prior to mixing the material into the main process. Inventory is then made up of less toxic precursor materials.

methods to limit inventory are listed in Chapter 2 and Table 3-4. If fewer vessels are used, fewer protective devices, such as alarms, valves, trips, and smaller flare systems may be required, further reducing plant cost.

If reduction of the inventory of hazardous material is not feasible, attempts should be made to use less hazardous conditions, such as low pressure and temperature storage; use of gaseous material instead of liquid; or use of a safer solvent. If neither limiting the inventory nor operating the plant under less hazardous conditions are viable options, other ways to make the plant safer should be considered, such as substituting less hazardous materials. For example, consider using steam as heat transfer medium instead of a flammable material.

3.3 SITE SELECTION AND EVALUATION

Plant siting plays an important role in process safety. Important factors in plant siting typically include the following items:

- Population density around the site
- Occurrence of natural disasters, such as earthquake, flood, hurricane
- Accessibility to raw materials
- Accessibility to markets
- Transportation
- Availability of land

- Availability of power and utilities
- Labor
- Interface required with other plants
- Government policies, such as siting permits and investment incentives
- Means of effluent disposal

Safety considerations may take precedence over other factors, possibly causing otherwise attractive sites to be eliminated for process or general safety concerns. A plant must be located near sources of workers, but not so close that neighbors can be injured by gas release, fire, or explosion. Only the safety considerations of site selection will be discussed in this section.

3.3.1 Site Selection

A process safety management program initiated during the development phases of a new project will identify and explain the nature of hazards associated with the proposed plant. Based on these discoveries, a site can be selected after considering many of the recognized hazards. Some important safety considerations are listed in Table 3-5 and discussed below.

Frequently, the most important consideration in plant siting is providing an adequate buffer zone between hazardous plant operations and nearby plants, communities and public facilities such as schools, hospitals, highways, waterways, and airways. Distance usually mitigates the consequences of loss-of-containment incidents and reduces casualties in case of undesired incidents; however, the importance of distance depends upon the nature of the hazard. Dispersion and other types of exposure studies for off-site areas

Table 3-5 Some Important Safety Considerations in Plant Siting

- Adequate buffer space between the plant site and vulnerable communities and public facilities
- Presence of other hazardous installation nearby
- For highly toxic materials (e.g., phosgene) make the material in the plant as a subprocess just prior to mixing the material into the main process. Inventory is then made up of less toxic precursor materials.
- Emergency response support
- Adequate water supply for fire fighting
- Stable power supply
- Weather extremes
- Presence of strategic installations in nearby area
- Presence of highways, waterways, airways
- Pollution and waste disposal

help determine the amount of open area needed between potentially hazardous process units and the general public. This should be continually analyzed for the life of the plant as communities grow. Bhopal was a "safe" site until a town was allowed to develop outside the plant fence.

One of the major hazards in process plants is fire. A flash fire or fireball from a boiling liquid expanding vapor explosion (BLEVE) can expose human populations to thermal hazards at greater distance than a pool fire. When considering fires, the effect of distance is to reduce the intensity of thermal radiation.

For explosions, especially unconfined vapor cloud explosions, the effect of distance is to reduce intensity of blast waves. Because explosions are sudden and violent releases of energy, effects are immediate and allow no time for evacuation or shelter.

When considering toxic releases, distance reduces gas concentration, due to dilution with the atmosphere. Even though toxic clouds can extend to greater distances than blast waves or thermal radiation, the time lag between release and potential public exposure can be utilized for warning and possible evacuation with effective emergency planning. Very large releases of highly toxic substances, such as phosgene, under unfavorable conditions are usually regarded as having disaster potential greater than fire or explosion. Nearby topographic features, such as hills or rivers, can influence the consequences of a chemical release and require examination during site selection.

Distance to nearby hazardous installations is also important. All of the considerations mentioned above apply in reverse when new facilities are sited near existing facilities. Consider the possibility that new facilities and their employees can be exposed to vapor releases, fires, or explosions from neighboring plants. If possible, try to anticipate and model problems at nearby facilities to determine consequences for proposed units. Hopefully, plant sites can be chosen where dangerous effects from neighboring facilities are minimal.

Safety should be considered when evaluating alternatives for transportation to proposed plant sites. Try to choose sites that minimize exposure to the public from potential transportation accidents. If possible, locate plant sites so that hazardous materials are transported through open country rather than through populated areas. Also choose plant sites that allow use of the safest possible mode of transportation. Some modes of transportation, such as pipelines, are safer than others, such as tank trailers.

Suitable emergency response support, such as medical resources in nearby communities, is vitally important in emergency situations. Other considerations are adequate fire fighting water supply and availability of fire fighting equipment in nearby plants which can be relied upon in large-scale emergencies.

Finally, consider susceptibility of the location to weather extremes and potential natural disasters, such as floods, earthquake and hurricane, which cause or contribute to other hazards. For example, locations on the U. S. Gulf Coast, while being near feedstocks and markets, are subject to hurricanes. Plants located in earthquake zones may require more flexibility in piping to prevent rupture during tremors.

3.3.2 *Site Evaluation*

Sites must be evaluated for potential risks to human populations. Factors to be evaluated include:

- Credible "worst case" scenarios
- Reasonable definition of local meteorological conditions and possible extremes
- Population density and the numbers of people likely to be involved
- The general planning and development guidelines for the region
- The ability to control movement of people in an emergency

Determining consequences of the "credible worst case" scenario is the first step in evaluation of sites. The process safety management program should ensure that the analysis is based on reasonable and consistent assumptions. This is vital when alternate sites are compared.

In certain situations, the distance between the plant site and the nearest inhabited area may be inadequate so that potential offsite impacts involving the general public cannot be avoided. Possible alternatives such as changing process routes, changing process conditions or reducing the inventory of hazardous materials should be examined to minimize potential impact on the public, i.e., to mitigate the "worst case" scenario.

It is impossible to completely eliminate the risk to the public from hazardous plants. It is often not cost effective to keep a large buffer area or sterile zone surrounding a plant where land value is at a premium. Therefore, in some selected situations, the use of quantitative risk analysis techniques in site selection may be appropriate. Risk assessment is a technique used to quantify the total risk by evaluating the consequences and probabilities. These methods are described elsewhere (CCPS 1989).

3.4 PLANT LAYOUT AND PLOT PLAN

The arrangement of process units and buildings are crucial factors in the safety and economics of a chemical plant. The plant layout (plot plan) should incorporate safety while providing access for operations and maintenance. Some of the safety benefits of a good layout are:

- Minimal explosion damage, since explosion overpressure falls off rapidly with distance from the center of the explosion.
- Minimal thermal radiation damage, as the intensity of thermal radiation also falls off with the distance.
- Less property damage caused by a given incident.
- Easier access for emergency services such as fire fighting.
- Easier access to equipment for maintenance and inspection.
- Efficient and safe construction.
- Optimum balance among loss control, maintenance, and operation requirements.

As mentioned earlier, plant layout can have a large impact on plant economics. Additional space increases the investment due to high capital costs (more land, piping, cabling, etc.) and operating costs. On the other hand, additional space tends to enhance safety. It is important, therefore, to carefully weigh these issues to optimize the plant layout.

3.4.1 Overall Layout Development

A preliminary identification of various hazards during early planning stages of the project will help establish proper layout at the beginning of the project and prevent design rework later. The selected layout should minimize the personal injuries, overall property damage, and related business interruption from an accident. Hazard evaluation will also aid in establishing the relative orientation of blocks or units within the plant, location of the control room, and firefighting facilities.

Good layout can reduce the effects of some of the controllable factors, such as liquid spills, and uncontrollable factors, such as exposure to natural hazards, site slope, wind direction and force, that contribute to losses. Some important factors in plant layout development are listed in Table 3-6. Proper

Table 3-6 Important Safety Factors in Plant Layout

- Containment of accidents
- High hazard operations
- Segregation of different risks
- Exposure to possible explosion overpressure
- Exposure to fire radiation
- Minimization of vulnerable piping
- Drainage and grade sloping
- Prevailing wind direction
- Future expansions

drainage and separation will control spills and fire spread. Locating ignition sources such as fired heaters, incinerators, and flares upwind of potential vapor leaks will reduce the likelihood of an unconfined vapor cloud explosion or fire. Locating tank farms downwind of process units and utilities will also reduce the chance of ignition of vapors released from the tank farm.

It is not unusual for separation distances to be compromised as the result of subsequent plant expansions, process changes or other modifications. For this reason, it is essential that minimum separation distances be clearly defined and maintained if at all possible. If future plant modifications are anticipated which might impact separation distances, consideration should be given to employing larger initial separation distances and/or other protective means.

3.4.2 Site Layout

A preliminary layout is developed without regard for the site. As a general guideline, the layout of the units is based on the flow principle so that the material flow follows the process flow diagram. The goal is to minimize the transfer of materials both for economic and safety reasons, and allow a release to be contained at its source. Plant layout is largely constrained by the need to observe minimum safe separation distances. Examples of facilities that should be separated from each other are:

- Process units
- Tank farms
- Outdoor drum storage yards
- Loading and unloading stations
- Heat transfer fluid heaters and other fired equipment
- Flares
- Power and boiler houses
- Electrical and instrument rooms
- Utilities (e.g., substations, gas metering stations, nitrogen plants, cooling towers)
- Control rooms
- Warehouses
- Fixed fire protection facilities, such as fire pump houses and reservoirs and sprinkler riser buildings
- Other support facilities, such as waste treatment areas, maintenance areas, administrative buildings, and laboratories

Adequate separation is often achieved by dividing up a plant into process blocks of similar hazards (e.g., process units, tank farms, loading/unloading operations, utilities, waste treatment, support areas), and then separating individual operations or hazards within each block. The block approach also serves to reduce the loss potential from catastrophic events, such as unconfined vapor cloud explosions, and to improve accessibility for emergency operations. The traditional approach is to use standards developed by the industry. Selected references for safe separation distances include:

- NFPA 30, Flammable and Combustible Liquids Code
- NFPA 59A, Liquified Natural Gas
- *Guidelines for Safe Storage and Handling of High Toxic Hazard Materials* (CCPS 1988a)
- Plant Layout and Spacing for Oil and Chemical Plants (IRI 1991a, 1992)
- *Loss Prevention in the Process Industries* (Lees 1980)
- *Process Plant Layout* (Mecklenburgh 1985)
- *Fire & Explosion Index, Hazard Classification Guide* (Dow 1987)

Once a site has been selected, the site layout is revised following the lines of the preliminary layout and considering the site constraints. Site constraints include topographical and geological features; weather; people, evacuation routes, activities and buildings in the vicinity; access to utilities; treatment of effluents; and laws and regulations. When the site layout is complete, it should be reviewed carefully for statutory requirements, consequences and mitigation measures, ease of fire fighting and emergency operations. For example, interunit spacing between units for oil and chemical plants may be as presented in Table 3-7.

A maximum block size of 300 feet (92 m) by 600 feet (183 m) (IRI 1991a) with adequate spacing between the blocks allows access for fire fighting. Each section of the plant should be accessible from at least two directions with at least two entrances to the plant for emergency vehicles in case one road is blocked during an incident. Adequate overhead and lateral clearance for pipeways, pipe racks and hydrants should be provided to prevent possible damage by large moving vehicles, cranes and trucks. Dead ends should be avoided. Slightly elevated roads may be required in areas subjected to local flooding. Main service utility lines should be designed to run alongside primary or secondary plant roadways in a clear corridor or right-of-way.

Two methods exist for determining minimum separation distances within chemical process plants. The first method is to use recommended separation distances for generic plant hazards, such as those shown in Tables 3-7, 3-8, and 3-9. These distances are generally conservative and will cover most situations. Recommended separation distances are available in several references, such as those listed above. Standards and codes of practice dealing with spacing specify only minimum spacing guidelines. These should not be used where hazard analysis or critical hazardous operation requires larger separation distances.

The second method for determining minimum separation distances is calculating the amount of heat received by an object from a fire involving the

Table 3-7 Inter-unit Spacing Requirements for Oil and Chemical Plants

	SERVICE BUILDINGS	MOTOR CONTROL CENTERS AND ELECTRICAL SUBSTATIONS	UTILITIES AREAS	COOLING TOWERS	CONTROL ROOMS	COMPRESSOR BUILDINGS	LARGE PUMP HOUSES	PROCESS UNITS MODERATE HAZARD	PROCESS UNITS INTERMEDIATE HAZARD	PROCESS UNITS HIGH HAZARD	ATMOSPHERIC STORAGE TANKS	PRESSURE STORAGE TANKS	REFRIGERATED STORAGE TANKS DOME ROOF	FLARES	UNLOADING AND LOADING RACKS	FIRE WATER PUMPS	FIRE STATIONS
SERVICE BUILDINGS	/																
MOTOR CONTROL CENTERS AND ELECTRICAL SUBSTATIONS	/	/															
UTILITIES AREAS	50	50	/														
COOLING TOWERS	50	50	100	50													
CONTROL ROOMS	/	/	100	100	/												
COMPRESSOR BUILDINGS	100	100	100	100	100	30											
LARGE PUMP HOUSES	100	100	100	100	100	30	30										
PROCESS UNITS MODERATE HAZARD	100	100	100	100	100	30	30	50									
PROCESS UNITS INTERMEDIATE HAZARD	200	100	100	100	200	50	50	100	100								
PROCESS UNITS HIGH HAZARD	400	200	200	200	300	100	100	200	200	200							
ATMOSPHERIC STORAGE TANKS	250	250	250	250	250	250	250	250	300	350	•						
PRESSURE STORAGE TANKS	350	350	350	350	350	350	350	350	350	350	•	•					
REFRIGERATED STORAGE TANKS DOME ROOF	350	350	350	350	350	350	350	350	350	350	•	•	•				
FLARES	300	300	300	300	300	300	300	300	300	300	300	400	400	/			
UNLOADING AND LOADING RACKS	200	200	200	200	200	200	200	200	200	300	250	350	350	300	50		
FIRE WATER PUMPS	50	50	50	50	50	200	200	200	300	300	350	350	350	300	200	/	
FIRE STATIONS	50	50	50	50	50	200	200	200	300	300	350	350	350	300	200	/	/

NOTES:

open, horizontal distances between adjacent edges of units are given in feet (1 ft = 0.305 m)

/ = no spacing requirements

- spacing given in Table 3–9

(Source: IRI 1991a)

actual hazards in question. While this method generally results in more realistic separation distances, the calculations are often complex and should only be performed by persons familiar with the concepts involved. In addition, the calculations should consider all possible scenarios. Space does not permit complete discussion of this subject here; however, additional information can be found in the Society of Fire Protection Engineering technical manuals (SFPE 1988) and commercially available computer programs. NFPA

30 should also be consulted for minimum necessary separation distances, particularly with respect to storage tanks.

In addition to radiant heat exposure, other factors that should be considered in determining separation distances and plant layout include topography, prevailing winds for normal and accidental vapor/gas releases, liquid drainage paths for accidental liquid spills, location of fire protection equipment and accessibility for emergency vehicles.

The important factors in siting central services, such as the boiler house, cooling towers, power station, are listed below:

- Central services should not be put out of action by fire or explosion or flood.
- Central services should not constitute a source of ignition.
- Cooling towers should be located to minimize water drift to avoid corrosion of other units.
- Flare stacks should be located upwind to minimize the ignition of vapor cloud releases and should be analyzed for intensity of thermal radiation and noise.

3.4.3 Unit Layout

Unit layout is the arrangement of equipment within a particular block on the site. The processing units are usually grouped because they are generally more hazardous than central services. The unit layout also depends on whether the unit uses single or multistream operation. Space for future expansion of plant equipment or pipe work, as well as access for installation is another factor to consider. Large vessels and equipment needing frequent maintenance or cleaning should be located close to unit boundaries for ease of access by cranes. Plant items such as heat exchangers and reactors that need removal of internals should be provided with necessary space and lifting arrangements. Guidelines for spacing within process units are presented in Table 3-8. The recommended distances are the clear, horizontal distances between adjacent edges of equipment.

Some further considerations in unit layout are:

- Location of fired heaters in relation to units that could leak flammable materials.
- Separation of equipment that is a potential source of explosions, such as chemical reactors, by blast resistant walls, if increased spacing is not practical.
- Location of pumps and compressors handling flammable material. These items are frequent sources of releases and should not be grouped in one single area. They should not be located under vessels, air-cooled heat exchangers or pipe racks.

Table 3-8 Inter-unit [Equipment] Spacing Requirements for Oil and Chemical Plants

	COMPRESSORS	INTERMEDIATE HAZARD PUMPS	HIGH HAZARD PUMPS	HIGH HAZARD REACTORS	INTERMEDIATE HAZARD REACTORS	MODERATE HAZARD REACTORS	COLUMNS, ACCUMULATORS, DRUMS	RUNDOWN TANKS	FIRED HEATERS	AIR COOLED HEAT EXCHANGER	HEAT EXCHANGERS	PIPE RACKS	EMERGENCY CONTROLS	UNIT BLOCK VALVES	ANALYZER ROOMS
COMPRESSORS	30														
INTERMEDIATE HAZARD PUMPS	30	5													
HIGH HAZARD PUMPS	50	5	5												
HIGH HAZARD REACTORS	50	10	15	25											
INTERMEDIATE HAZARD REACTORS	50	10	15	25	15										
MODERATE HAZARD REACTORS	50	10	15	25	15	15									
COLUMNS, ACCUMULATORS, DRUMS	50	10	15	50	25	25	15								
RUNDOWN TANKS	100	100	100	100	100	100	100	100							
FIRED HEATERS	50	50	50	50	50	50	50	100	25						
AIR COOLED HEAT EXCHANGER	30	15	15	25	15	15	15	100	50	/					
HEAT EXCHANGERS	30	10	15	25	15	10	10	100	50	15	5				
PIPE RACKS	30	10	15	25	15	10	10	100	50	/	10	/			
EMERGENCY CONTROLS	50	50	50	100	50	50	50	100	50	50	50	50	/		
UNIT BLOCK VALVES	50	50	50	100	50	50	50	100	50	50	50	50	/	/	
ANALYZER ROOMS	50	50	50	50	50	50	50	100	50	50	50	50	/	/	/

NOTES:

open, horizontal distances between adjacent edges of units are given in feet (1 ft = 0.305 m)

1 ft = 0.305 m
/ = no spacing requirements

(Source: IRI 1992)

3.4.4 *Storage Layout*

Layout of hazardous materials storage areas requires careful attention. Typically a far larger quantity of material is held in storage than in process. Siting, design, fabrication, and operation of storage facilities are thoroughly addressed in *Safe Handling and Storage of High Toxic Hazard Materials* (CCPS 1988a). Some of the important aspects of storage layout are:

- Storage tanks should be arranged in groups so that common dike and fire fighting equipment can be used for each group.
- Tanks should be located downwind of other areas to prevent flammable materials reaching ignition sources, should a leak develop in a tank.
- It is essential to keep storage tanks away from process areas since a fire or explosion in a process unit may endanger the large inventory of the storage tank.
- Storage tanks should be diked in accordance with NFPA 30. Piping, valves and flanges should be kept to a minimum when located within dikes. Valves, manifolds, and piping should be installed outside dikes or impounding areas.
- The effect of intensity of thermal radiation from an adjacent tank on fire should be considered in spacing the tanks. Tolerance of tanks to thermal radiation can be increased by insulating or fireproofing the tank shell, and providing water cooling arrangements.

Guidelines for spacing above-ground storage tanks are presented in Table 3-9. The spacing is given as a tank shell-to-shell separation distance and is a function of the largest tank diameter. Additional spacing may be required depending upon accessibility, fire water supply, fire fighting facilities, and drainage.

Spacing requirements will vary depending on whether storage tanks are classified as pressurized, refrigerated or atmospheric. Separation distances depend on the shape of the tank, the size of the tank, the distance between tanks and groups of tanks, the number of tanks in a group, the type of roof (dome or floating), insulation on the tank, and the tank contents. Consult the codes for specifics because many exceptions and limitations exist.

Many aspects of storage and piping system design require special attention to reduce seismic risks. Tanks can tip over or slide due to inadequate bracing or anchorage. Tank movement can cause attached piping to fail, resulting in release of toxic or flammable liquids. Unanchored tanks may be anchored and flexibility provided in attached piping to ensure it moves independently of the tank during an earthquake. "Proper design and location of pipe supports will ensure that severe stresses at nozzles do not occur during seismic shake" (Dow 1990). Tank foundation problems may be reduced by designing for asymmetric pressures from sloshing of vessel contents and the sliding and overturning loads at the vessel anchorage.

3.4.5 Control Room Location

The control room is the nerve center of a process plant. Its design and location should receive careful analysis. The safety of the personnel inside the control room will allow control to be maintained in the early stages of an incident and

Table 3-9 Storage Tank Spacing Requirements for Oil and Chemical Plants

FLOATING & CONE ROOF TANKS <3000 BARRELS	FLOATING & CONE ROOF TANKS >3000 <10,000 BARRELS	FLOATING ROOF TANKS >10,000 <300,000BARRELS	JUMBO FLOATING ROOF TANKS <300,000 BARRELS	CONE ROOF TANKS CLASS II, III PRODUCT >10,000 <300,000 BARRELS	CONE ROOF TANKS INERT CLASS I PRODUCTS** >10,000 <150,000 BARRELS	PRESSURE STORAGE VESSELS SPHERES AND SPHEROIDS	PRESSURE STORAGE VESSELS DRUMS AND BULLETS	REFRIGERATED DOME ROOF STORAGE TANKS
0.5 D*								
0.5 D	0.5 D							
1 X D	1 X D	1 X D						
1 X D	1 X D	1 X D	1 X D					
0.5 D	0.5 D	1 X D	1 X D	0.5 D				
1 X D	1 X D	1 X D	1 X D	1 X D	1 X D			
1.5 D 00' MIN	1.5 D 100' MIN	1.5 D 100' MIN	2 X D	1.5 D 100' MIN	1.5 D 100' MIN	1 X D 50' MIN		
1.5 D 00' MIN	1.5 D 100' MIN	1.5 D 100' MIN	2 X D	1.5 D 100' MIN	1.5 D 100' MIN	1 X D 100' MIN	1 X D	
2 X D 00' MIN	2 X D 200' MIN	2 X D 200' MIN	2 X D	2 X D 200' MIN	2 X D 200' MIN	1 X D 100' MIN	1 X D 100' MIN	1 X D 100' MIN

NOTES:

spacing is given as tank shell to tank shell separation distance in feet (1 ft = 0.305 m)

D = Largest Tank Diameter
1 barrel = 42 gallons = 159 liters

(Source: IRI 1991a)

* FOR CLASS II, III PRODUCTS, 5 FT SPACING IS ACCEPTABLE
** OR FOR CLASS II OR III OPERATING AT TEMPERATURES T > 93 °C (200 °F)
CLASSES I, II AND III ARE DEFINED IN NFPA 30.

so reduce the probability of escalation into a disaster. Traditionally, control rooms have been part of a complex of facilities including analytical laboratories, instrument workshops, electrical switchgear rooms and plant offices. As a result some plant personnel were unnecessarily exposed to hazard. This hazard has to be balanced against the possible management advantages (safety and quality) of having supervision and support personnel located close to and involved in day-to-day operation of the process. A control room should contain only the facilities required to perform process control. Other facilities, such as analytical laboratories, supervisor's offices, etc., should be housed away from the operating unit. It should be recognized that the control room should not be designed to serve as the emergency control center during an accident since operations must continue and should not compete with emergency response functions. There are two principal approaches to making control rooms safe. One is to locate the control room so that it is not exposed to fire or explosion; the other is to design the control room to withstand potential explosion overpressures (see Section 3.7.1, Control Room Design, page 86).

From an operations viewpoint, the ideal location for the control building may be the most unsafe location for people and equipment. To minimize the time for operators to respond to emergencies, the control building should be near the center of operations, the most hazardous location.

Since the advent of electronic controls, the use of centralized control rooms that control a number of plants has proven more efficient and less costly than individual control rooms or stations located in each plant. The disadvantage of a central building is that a single incident could damage the central control building, causing shutdown of a number of processes.

A basic consideration in selecting the location for the control building is distance to a potential explosion. A compromise must be made so that a location can be found which is practical with minimal risk. NFPA and Industrial Risk Insurers (IRI) criteria govern the distance from the control building to potential sources of flammable gases. Wind data are required to provide probability of direction and speed. For behavior of toxic clouds, refer to *Guidelines for Use of Vapor Cloud Dispersion Models* (CCPS 1987) and *Guidelines for Vapor Release Mitigation* (CCPS 1988b).

3.5 CIVIL ENGINEERING DESIGN

The safety of the plant can depend on the civil, structural, and architectural design. Failures of foundations, walls or supporting structures can rupture piping and vessels and lead to release of hazardous materials. As long as the structural loads are below or at design limits, failures are usually not a problem, because "structural failure probabilities under such conditions are usually one to three orders of magnitude smaller than mechanical, electrical and equipment failure probabilities" (Sundararajan 1991). In rare situations, like natural hazards and explosions, these structural failure probabilities must be incorporated into the risk assessment (Sundararajan 1992).

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3.5 CIVIL ENGINEERING DESIGN

The safety of the plant can depend on the civil, structural, and architectural design. Failures of foundations, walls or supporting structures can rupture piping and vessels and lead to release of hazardous materials. As long as the structural loads are below or at design limits, failures are usually not a problem, because "structural failure probabilities under such conditions are usually one to three orders of magnitude smaller than mechanical, electrical and equipment failure probabilities" (Sundararajan 1991). In rare situations, like natural hazards and explosions, these structural failure probabilities must be incorporated into the risk assessment (Sundararajan 1992).

3.5.1 Site Preparation and Analysis

Preparation of the site, governed by plot plans and grading and paving drawings, will establish the safe placement of the plant, provide for drainage and runoff containment, and define environmental considerations to be addressed.

Geotechnical Studies. Geotechnical investigations will establish excavation requirements, types of foundations required, and site drainage requirements. Any existing hazardous conditions discovered during site selection, such as contaminated soil, buried waste pits, etc., must be addressed in accordance with environmental regulations.

Man-Made Underground Obstacles. Two explosions and fires within one week in the Houston, Texas area in early 1992 involving underground pipelines point out the necessity of being absolutely sure, before the start of excavation or piling, that a seemingly clear site is free of hazardous obstacles. Many heavily industrialized areas rely upon underground pipelines as a vital part of the product transportation infrastructure. Where products are potentially hazardous, it is wise to consider protected above ground, rather than underground, transfer. Protected above ground transport makes leak detection and correction more likely and will generally result in a safer operation. In many areas pipeline "easements" have been granted by individual real estate owners to allow this type of product transport. Where major easements exist, real estate title documents are generally amended to assure that a purchaser is aware of these restrictions on use. Therefore a scan of title documents may reveal nearby underground pipelines.

Pipeline easements generally restrict above-ground use in the easement. Process plant erection will not be allowed, and possibly more important, site access will be severely restricted. Vehicular crossings will be prohibited, except on established roads that usually have limited bearing loads. New crossings will have to be carefully constructed and supported, in effect being "bridges" across the easement though constructed at grade. Other crossings, such as pipe bridges and power lines, will similarly require careful consideration and design. Underground crossings may require special permission and documentation.

Along the sides of the easement branch take-offs may run through the proposed site. These may be more insidious than larger lines as they may not have the documentation that the easement does. An abandoned branch could be the most dangerous, as it may be capped or sealed at only the user's end and could be live from the supply underground end. An undocumented line also could exist within the boundaries of a single site where development occurred at distant locations. It is likely that "isolated" units were once connected to other units or to a central utilities center. Though most interconnections are above ground, there is a high probability of underground lines as well.

The most likely existence of underground lines, but fortunately the most easily anticipated, is in the reuse of an old site where a unit was demolished. It may have been razed *to* the ground but not *below* the ground. Foundations, tanks, sumps and diversion boxes, some of which may be connected to process lines containing toxic or explosive chemicals, may be encountered. Therefore, it is as important, if not more important, to conduct an underground survey as well as an above-ground survey for any proposed site.

3.5.2 *Surface Drainage*

Normally, the process engineer does not consider surface drainage, but there are a few topics that may need to be examined. One is the potential for hazardous flammable (or explosive or toxic) vapors to enter the normal surface water drainage and collection system; another is adequate collection, treatment, and disposal of firefighting water.

Each facility must have a well-drained working surface and a drainage system to carry off storm water and/or spills to a holding area or treatment facility. Local, state, and federal regulations should be consulted to determine drainage or treatment required. Drain lines for these systems must be adequately sized not only for the chemicals involved but also for runoff fire water that might be introduced. Drains should be sized to carry firewater flows as required by local regulations or NFPA guidelines.

3.5.3 *Foundations*

Foundations must be designed to transmit all loads and forces from the equipment or structures to the soils or rock beneath the foundations. Loads should be calculated using actual density of liquids and solids used in the process if heavier than water. Seismic and explosion or blast loads also must be considered. Foundation design of facilities related to the containment of hazardous material must address internal and external pressures, equipment loads, dynamic forces from vibrating equipment and hydraulic uplift pressure from groundwater.

The geotechnical report will specify flood design considerations, such as reduced lateral pressure factor or lower shear resistance for foundation designs. For any large volume underground chambers, such as buried drainage lines, below grade storage tanks, or "basement" levels used for maintenance or storage, flotation must be considered in the design to assure anchorage. Similarly, open concrete pits or reservoirs have to be designed with this problem in mind. An American Petroleum Institute (API) separator or other concrete chamber, even a manhole, must be investigated to insure that the weight of the item, plus its normally expected contents, will not float out of the ground, or otherwise be dislodged from its designed location due to hydrostatic buoyancy forces.

Foundation design is determined by bearing pressure geotechnical investigation and testing. The designer may also need to evaluate spread footings versus surcharge versus piling pile testing–bearing and uplift. *In situ* pile testing (test piles) should include not only bearing tests but uplift resistance tests as well.

Good engineering practice or regulatory criteria may require that foundation designs for vessels containing hazardous materials also provide for containment and detection of leaks. For example, a ring foundation may not be appropriate for a tank storing hazardous material because it provides an undetected path for leaks to migrate to groundwater. For corrosive fluids, the design should include protection against seepage of the fluid into soil areas around the foundation.

3.5.4 Underground Piping

Underground piping in process plants is generally water piping, including services such as sewers and drains, city and service water, fire protection, cooling water supply and return. Utility lines and pressure piping also may be underground. Special elements of design should be considered for safety, such as anchoring and thrust blocks to prevent movement of pressured lines, use of cathodic protection to prevent corrosion, and avoidance of process water tie-ins to fire water supply or sanitary water.

Headers or mains for these services are normally located in open corridors outside plant operational areas for maintenance and modification accessibility. Elevations of lines containing liquids must be below any nearby underground electrical conduits. Underground process drains should be evaluated for creation or transportation of hazardous or flammable vapors. In normal operation, an open area above the fluid in the drains allows vapors to migrate beyond the areas where they are generated. Such vapors could enter an area where an open flame or electrical sparks could cause combustion. Therefore, oily water sewer systems must be designed with P-traps, submerged outlets, vent tubes, and vapor sealed manholes to prevent flammable vapors from migrating to sources of combustion. Monitoring of the concentration of flammable materials may be necessary.

In transporting hazardous liquids, particularly hazardous wastes, double-walled piping has become the preferred or required method of transport, to prevent the release of the transported materials to the environment. Double-walled piping is also used for transporting highly toxic gases. Double-walled piping normally consists of an inner pipe, an outer pipe, a spacer system that suspends the inner pipe within the outer, and a leak detection system. This type of system is normally used where any release of the material would create a major health hazard. In designing this system, certain elements need to be addressed:

- Both pipe walls and the piping supports should be compatible with the material being transported.
- The supports should be spaced so that the inner pipe will not sag, and potentially rupture, between supports.
- For long pipe runs it may be desirable to zone the leak detection system to pinpoint the location of the leak.

3.5.5 Below Grade Structures

Process or support structures below grade include items such as API separators, pump pits, spill ponds, water treatment facilities and sumps. Structural failure of pump pits may damage the pumps and associated piping causing uncontrolled release of process fluids.

There may occasionally be a requirement for a hot or cold liquid "dump" system to an isolated underground tank to conserve or isolate expensive or hazardous liquids. The dump piping will be installed and stay at ambient temperature until actually used. Introduction of the process fluid will cause the underground lines) to expand or contract. As with above-ground lines, this movement must be considered in the design. The lines generally run in trenches, with solid or open grating covers, with expansion room at turns. If for some reason (generally, the depth of the lines) it is not practical to trench, the lines must be sleeved, usually with larger bore piping, to allow free movement during growth or shrinkage.

3.5.6 Grade Level Structures

The primary plant layout determines the location of roads and other structures that affect excavations and underground piping. For example, roadbases can produce heavy loading on underground piping; ruptured piping could lead to process spills or washouts involving dislocation of other plant piping or equipment. An envelope is normally established to insure proper clearance between piperacks and any plant roads. Small piping lines can deliver flammable, toxic or corrosive products as well as large pipes; small piping and electrical lines, only shown diagrammatically, must be kept out of the roadway envelope. Encroachment could lead to an electrical fire or explosion or a power outage. Sometimes this potential hazard is identified only during review of a request for changes to structural steel or revisions to the radius of a road curve.

The plant layout also defines separation requirements for storage facilities. A good source of spacing requirements is the book *Guidelines for Safe Storage and Handling of High Toxic Hazard Materials* (CCPS 1988a). Storage requirements should be reevaluated if there is a change or addition to plant production that may involve different raw materials, catalysts, etc., requiring changes in storage capacities or patterns. Design and utilization of these facilities should be monitored to insure they provide adequate protection for different storage requirements: outdoor storage may be acceptable for a well-drained area, but standing water may change or weaken (by oxidation, for example) the stored items over time. Enclosed storage with atmospheric control and monitoring is a necessity for some process materials.

3.6 STRUCTURAL ENGINEERING DESIGN

3.6.1 Natural Events

To ensure the integrity of structures and equipment, design engineers must consider potential natural events. "Engineering design and construction effort should be devoted to hazardous materials containment systems as well as earthquake resistant construction. Relatively minor damage in structural terms can become responsible for a large release. [The goal] is the prevention of leaks rather than just prevention of collapse." (Dow 1990). This statement also would apply to other "natural" events with the potential to cause disaster, such as hurricanes or other high velocity winds, floods, heavy snows, and Arctic freezes.

Seismic Considerations. ANSI A58.1, Minimum Loads for Buildings and Other Structures, defines seismic considerations in design. The most commonly used building code is the Uniform Building Code (UBC) produced by the International Conference of Building Officials. This code may be strengthened by local building code requirements. The hazardous nature of process chemicals may call for design to go beyond the codes, particularly if the loss of integrity of the plant structures would release hazardous materials or affect the safety of plant personnel. Seismic hazards should be evaluated, and not just in areas of known seismic activity. Figure 3-4 shows the areas of relative seismic risks in the United States.

Seismic damage is likely to occur in many plant components including supported systems, process towers, piping, conduit and cable trays, buildings and other structures, and tank foundations. Designing flexibility in the systems and including lateral loads and overturning loads induced by horizontal ground motion will minimize support problems.

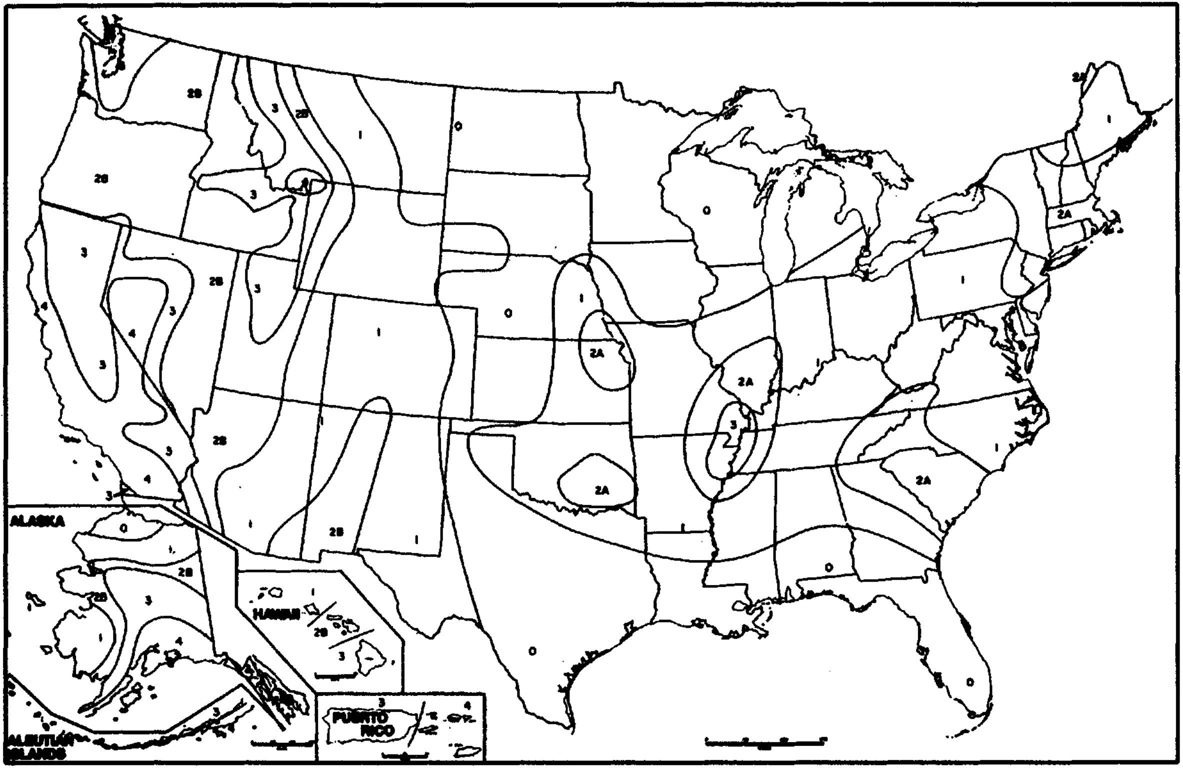


Figure 3-4. Seismic zone map of the United States, used to assign Seismic zone factor Z (Reproduced from the 1991 edition of the Uniform Building Code, ©1991, with permission of the International Conference of Building Officials

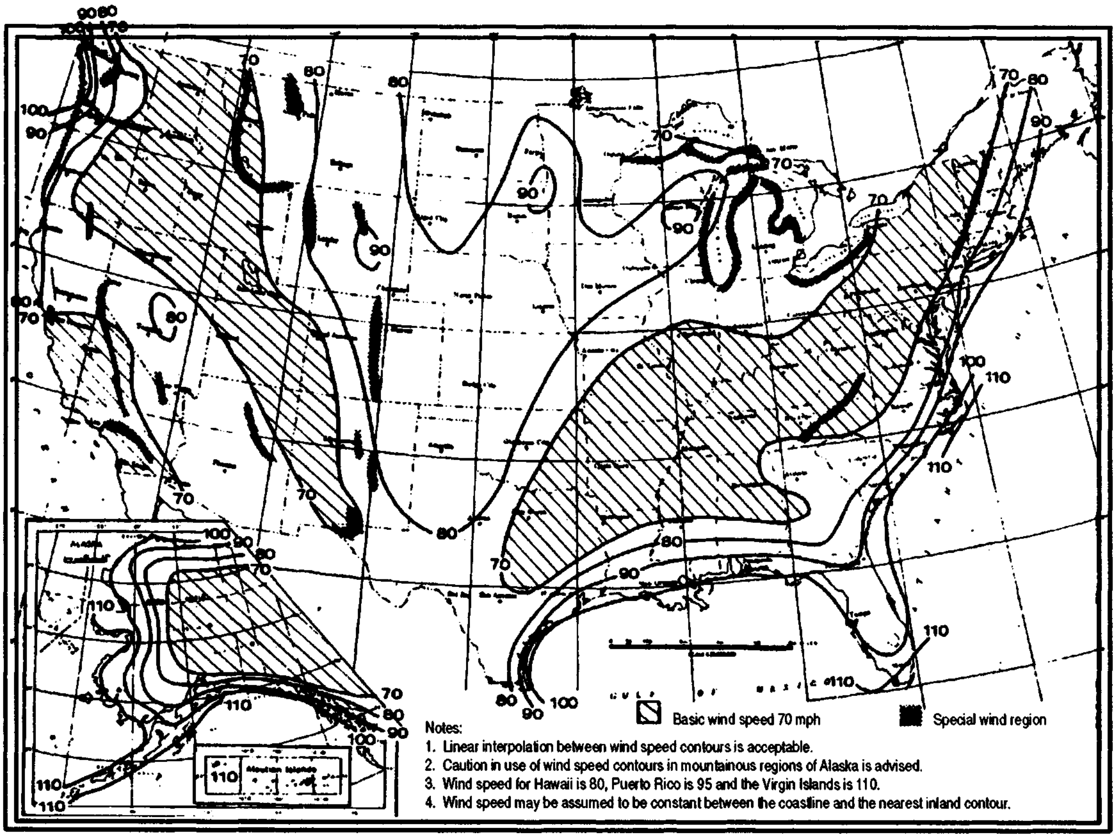
Cold Weather Protection. Adequate structural design must include design for anticipated snow loads as well as runoff, drainage and retention designs to cope with ruptured process and utility lines. Even along the U.S. Gulf Coast, freezing weather can interrupt plant operations. Underground lines, if buried with adequate cover should cause no problems, but they must be protected where they emerge to become above-ground piping. Table 3-10 lists causes of losses for 1990 and the three year dollar average of these losses. These failures may interfere with process operations or cause a rupture of process facilities. "The difference-in-conditions losses were largely the result of a string of weather-related catastrophes. Chief among them was a severe arctic freeze that affected 21 states and resulted in 374 freeze losses" (IRI 1991b). Arctic freezes accounted for more than 50% of the sprinkler failure losses in 1990 (IRI 1991b).

Winds. Winds are another factor addressed in the design (see Figure 3-5). Table 3-10 shows basic maximum wind speeds (not tornados), thermal upsets (wind shear) or larger (hurricanes). High winds may destroy buildings or damage weather protection elements and hinder process operations. The lower number of windstorm-related losses in 1990 (Table 3-10) reflects the absence of a hurricane (IRI 1991). Wind spoilers may be used to reduce the effects of strong winds.

Table 3-10 1990 Loss Report

Peril	3-Year Average		1990	
	%	Avg. $	%	Avg. $
Fire	36.6	171,857	36.5	138,026
Difference-in-Conditions	18.4	110,979	22.5	157,413
Boiler/Machinery	8.9	49,692	11.6	67,549
Sprinkler Leakage	8.0	24,911	10.3	29,201
Windstorm	11.4	142,060	6.7	76,882
Explosion	4.5	1,816,255	4.3	503,886
Lightning	4.1	32,978	3.6	39,898
Water Damage	0.6	271,169	0.5	514,022

(Source: IRI 1991b, p.11)



Notes:

1. Linear interpolation between wind speed contours is acceptable.
2. Caution in use of wind speed contours in mountainous regions of Alaska is advised.
3. Wind speed for Hawaii is 80, Puerto Rico is 95 and the Virgin Islands is 110.
4. Wind speed may be assumed to be constant between the coastline and the nearest inland contour.

Figure 3-5. Minimum basic wind speeds in miles per hour, used to determine design wind pressure. (Reproduced from the 1991 edition of the Uniform Building Code, ©1991, with permission of the International Conference of Building Officials

3.6.2 Open versus Closed-In Structures

As mentioned in Chapter 2, the designer must consider safety issues in determining whether to use an open or closed-in structure. Open structures allow the escape of leaked vapors at the facility. This will reduce any concentration of combustible, nauseous or toxic fumes, spills or leaks from the process unit, but may result in environmental contamination. Open structures also allow the escape of excess heat generated in the process area. Both these benefits decline when the weather is calm and hazardous concentrations of gases may accumulate.

Kiosk type ("telephone booth") shelters are sometimes used to provide protection for personnel within an open structure. If the process is sensitive to low temperatures, heat tracing can be used instead of enclosing the unit. Often a closed-in structure may be required because of factors such as humidity, temperature, toxicity of material, or an inclement environment.

3.6.3 Access and Egress

Access and egress considerations are of primary importance in regard to safety of operators and access to process controls when upset conditions occur. Operators should have a minimum of two widely separated routes from each area, either as a means of escape from a hazardous condition or access to the source of a problem. Within buildings, or on above-grade structures, the general rule is to provide "at least two" exits, whether it is doors, stairs, or ladders, in case one of them is blocked by fire, structural damage, etc. Determination of when two exits are needed is sometimes based on whether the area is a normal "operation level" or strictly a "maintenance level." Codes sometimes dictate the number of exits (e.g., UBC, Section 3303).

3.6.4 Pipe Racks

Maintaining the integrity of process lines to avoid loss of containment requires adequate support of piping and process units. Pipe racks are designed to carry the heavy weight of pipes and their contents. In many cases, codes [or the owner] stipulate that the rack be capable of carrying 20% more weight than the original piping design calls for, in addition to snow, ice, wind and other loads. Process changes or additions may mandate additional piping on, or through, existing racks. Prior to installation of additional rack levels or bay extensions, rack design must be checked to confirm the structural safety of such additions.

In many plants the pipe racks support not only process piping but also elements critical to process control and emergency shutdown, such as instrument air and wiring and electrical cabling. These elements are usually relegated to the top rack level (along with the flare header) to reduce the possibility of damage, should piping or support beams in the rack fail. Many times plant access roads run under the pipe racks, so locating this vital network on the top level also protects against inadvertent damage during plant maintenance.

If the pipe rack also supports process equipment (usually air coolers and boiler feedwater deaerators), these items must be located above the top piping level and the design should ensure that incidents (e.g., fire) involving this equipment will not jeopardize the instrument/electrical system located in the same rack.

The hydrostatic test weight is another pipe rack load that must be addressed. For a large line, where the process fluid is normally vapor, the hydrotest weight may be twice (or more) the normal operating weight of the line. It is feasible to design pipe racks for all lines filled with water, but in many cases it is not practical to do so, due to increased foundation loadings or, more practically, increased beam depth that could possibly result in increased spacing between the different tier levels. Cost-effective ways to address the problem of hydrotest loads are: (1) Specifying that no more than *X*% of the lines on a given level and *Y*% of all the lines in the rack can be hydrotested simultaneously, (2) requiring specific lines to be separately (temporarily) supported from grade during hydrotest, (3) allowing "service" tests for nonhazardous fluids, or (4) specifying pneumatic tests for excessively large vapor lines. If any of these measures are used, these restrictions/specifications must be included in all documentation, construction testing requirements, yard steel calculations, foundation loadings, etc., to assure that any future testing conforms to these restrictions. Additionally, if pneumatic testing is specified for very large or very long lines, there may be owner or construction restrictions on the amount of stored energy allowed in the pneumatic test, without supplemental nondestructive testing before the test or a requirement to subdivide the line into "acceptable" volumes.

3.6.5 Elevated Structures

Location of equipment is generally determined by its sequence in the process and may be at ground level or in an elevated structure. The location should be checked against necessity for frequent access, process maintenance requirements (e.g., fouling of heat exchanger tubes), sampling requirements, etc.

Many drums and exchangers are installed in above grade structures fabricated from steel or reinforced concrete. If steel is used, the structure should be analyzed for fireproofing requirements (see Chapter 16).

Flooring for the above grade levels will normally be of steel grating or checkered plate. If the atmosphere is chemically active, the use of alternate materials should be considered (see Chapter 5). If these upper levels are subject to spills, concrete floorslabs may be used. These may be given additional protective coating. Checkered plate, concrete, or other solid floors should be designed to avoid the pooling of liquids that might be flammable or the extent of fireproofing should be reconsidered.

3.7 ARCHITECTURAL DESIGN

The structural integrity of buildings, equipment, piping and supports, and instrumentation and control systems is essential in preventing loss-of-containment.

3.7.1 Control Room Design

Modern control buildings are designed for optimum protection of control and monitoring equipment and operating personnel (FMEC 1980). Examples of design criteria addressed in building codes are building orientation and location, type, and size of doors and windows. These features protect the operators in the event of a fire, explosion, or toxic release so that they may respond to the hazard and minimize its consequences.

Plant management may prohibit handheld radios and electronic devices to prevent radio frequency intrusion into unshielded control systems.

3.7.2 Explosion-Resistant Buildings

An important distinction must be made between explosion resistant and explosion proof. An explosion-resistant building is designed to withstand a blast effect without collapse, thereby protecting operators from injury and controls from damage. However, the building may require significant refurbishing before being returned to service. Explosion-proof means there will be no significant damage to the building due to the anticipated explosion case. Explosion-proof design cost is significantly more expensive, so much so that it is generally not considered.

Explosion-resistant construction can add from 50% to 80% to the cost of a building because of heavier foundations, heavier walls and roof, expensive explosion-resistant doors and more expensive outdoor mechanical equipment. Design criteria for explosion resistance may use static or dynamic bases; the dynamic approach allows engineers to develop the ultimate strength of the structural steel frame and as a result, smaller members are required. The Chemical Industries Association has recently issued a report on control building design to withstand deflagrations (CIA 1990).

3.7.3 *Safe Havens*

Instead of constructing the entire control building for maximum safety, safe havens can be constructed to provide islands of safety in the process area. A safe haven is designed to be sealed off during a toxic vapor release; it contains emergency air supplies. A safe haven also has a higher degree of fire protection.

Explosion-resistant buildings can be equipped for use as a safe havens in the event of a serious incident. If designed to be explosion resistant, the building will likely have some inherent fire resistance, but other fire protection measures, such as construction of fire barriers, should be implemented (see Chapter 16).

3.7.4 *Ventilation Systems*

Ventilation is one of the most important engineering controls available for mitigating potential atmospheric hazards within a facility handling chemicals. By controlling airborne chemicals, ventilation controls the spread of toxic materials and can prevent fire and explosion. In general, ventilation is a means to control the environment in a defined area within the facility. Heating, air conditioning, contaminant removal, contaminant dilution, and supplying make-up air are functions of a ventilation system.

General Ventilation. General ventilation is the introduction of a large quantity of "clean" air (no toxic or flammable materials) to dilute the concentration of a contaminant. General ventilation reduces the concentration of the contaminant to an acceptable level, i.e., its lower flammable limit or toxic exposure limit.

In most cases it is not an acceptable practice to recirculate the exhausted air because air filters do not always effectively collect the toxic or flammable contaminants. If recirculation is considered, a complete understanding of the hazards of the contaminant, information on the performance and efficiency of the air cleaner, and general ventilation scheme must be obtained. Recirculation can be considered if design includes vapor detectors with shutdown and full exhaust when vapor is 25% LEL.

Local Ventilation of Hazardous Areas. "Local" or "specific" exhaust ventilation removes the contaminant at or near its source. Local exhaust ventilation captures the contaminant and exhausts it to the atmosphere or to purification systems, thus preventing the release of the contaminant into the controlled environment. Local exhaust ventilation is useful in laboratories and shop areas, in loading and unloading areas, and in plant areas where contaminants, such as volatile or highly toxic substances and irritants, are present either as a process material or by-product of the process.

Local exhaust ventilation systems usually complement, rather than replace, general ventilation systems. However, in chemical plants the control of flammable and toxic vapors, dusts, and fumes is mainly accomplished by local exhaust systems of varying sizes and complexities. The design of local ventilation systems for process plants is covered in the books by ACGIH (1986) and Constance (1983).

The advantages of using local exhaust ventilation for hazardous locations are:

- The volume rates of both exhaust and make-up air are less than with general ventilation.
- Auxiliary plant equipment is better protected from airborne contaminants and corrosive atmospheres.
- If the system is adequately designed, the capture and control of the contaminant can be complete.

Vemtilation of Control Room. Control rooms housing a large number of computers and other electronic equipment have very specific air conditioning requirements. A separate system is usually provided. The air intake stack must be high enough to prevent the intake of low-lying gases; chemical filters are usually required to preclude entry of corrosive gases or other contaminants. The air stack will have a sensing device that measures the amount of contaminant entering the building and trips or alarms when the level is unacceptable.

Ventilation following Purge with an Inert Gas or Purge after Halon Release or Building Shutdown. In case of a complete shutdown caused by an accident, periodic plant maintenance or release of a Halon fire suppression system, contaminants will enter the building and will contaminate the equipment. A system must be devised to purge the equipment and the building of all contaminants before restarting the air conditioning system.

Ventilation of Motor Control Centers. Provide cooling of motor control centers (MCC) to prevent overheating. Provide positive pressure to prevent intrusion of flammable or toxic materials.

3.8 PLANT UTILITIES

Design of plant utility systems is covered in standard references. This section will highlight scenarios in which loss or malfunction of a utility service results in a loss of containment. Table 3-11 lists various utility system failures and equipment that is affected.

3.8.1 Electricity

Electricity is supplied for various purposes: to drive equipment and machinery, to operate instrumentation and control systems, to provide heating of process operations and as tracing of piping runs, etc.

Table 3-11. Possible Utility Failures and Equipment Affected

Utility Failure	Equipment Affected
Electric	Pumps for circulating cooling water, boiler feed, quench, or reflux Fans for air-cooled exchangers, cooling towers, or combustion air Compressors for process vapor, instrument air, vacuum or refrigeration Instrumentation Motor-operatied valves Agitators
Cooling Water	Condensers for process or utility service Coolers for process fluids, lubricating oil, or seal oil Jackets on rotating or reciprocating equipment Quench water
Instrument Air	Transmitters and controllers Process-regulating valves Alarm and shutdown systems Pumps
Steam	Turbine drivers for pumps, compressors, blowers, combustion air fans, or electric generators Reboilers Reciprocating pumps Equipment that uses direct steam injection Eductors Snuffers
Fuel oil, gas, etc.	Boilers Reheaters reboilers Engine drivers for pumps or electric generators Compressors Gas turbines
Inert gas	Seals Catalytic reactors Purge of instruments and equipment

(Source: API RP 521. Reprinted courtesy of the American Petroleum Institute.)

Loss of motive power on process equipment may be quite hazardous. Other serious hazards would result from failure of cooling fans or heating loops required to control temperature and pressure or loss of ventilation to prevent build-up of flammable gases. Provision of back-up electrical power is routinely addressed in plant design. (See Section 3.8.1.2.) Electrical system hazards derive from their potential to serve as ignition sources. Electrical area classification is a way to separate flammable materials from ignition sources; see Chapter 12 for further discussion of classification of areas and materials.

The biggest hazards include:

1. A common cause failure (i.e., loss of electrical power, loss of cooling water, loss of the plant utilities, etc.)
2. Loss of pumps and compressors.
3. Loss of key instruments, emergency lighting, computer controls, lube oil pumps and the like can be catastrophic and should be addressed through use of uninterruptible power supplies and emergency generators.

It is necessary to have an emergency or standby power system to protect personnel and plant integrity. Such systems need to be maintained and checked at regular intervals. A chemical or process plant may have several types of emergency power systems that may be used for different purposes.

3.8.1.1 Emergency Power Supply

The Emergency Power Supply is required for process equipment to allow safe shutdown of the unit or plant; however, it can be interrupted. The application and design of emergency power systems is extensively covered in the IEEE Standard 447-1980 Orange Book "Emergency and Standby Power Systems for Industrial and Commercial Applications." Diesel generators should be on a timing circuit to be turned on at least once a week, allowed to come up to full heat (i.e., run for about a half an hour), and alarm if not successful.

3.8.1.2 Uninterruptible Power Supply

The uninterruptible power supply (UPS) is used for controls and other systems that must have a continuous supply of power. The UPS is designed to be the prime source of power to a critical load. A UPS not only provides continuous power to the critical load, but also isolation from the main AC line (by means of the battery charger) and a regulated source of synthesized AC power from the inverter. The UPS differs from a standby power system in that it is truly uninterruptible since it provides "on-line" continuous power supply. Standby and backup power systems involve transfers with switching intervals ranging from several cycles to several seconds or more. Therefore,

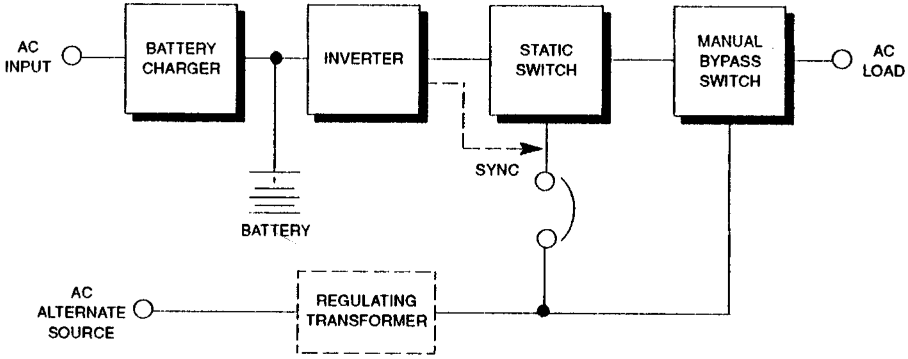


Figure 3-6. Single module UPS with bypass. *Note:* On the single module UPS with bypass as shown, the system takes ac power and converts it to dc through the battery charger. Here, the battery charger acts as a rectifier to supply dc to the inverter under normal conditions. It also "floats" a charge on the battery. The inverter converts the dc back into ac and feeds it to a static switch. The switch, under normal conditions, passes this ac power through to a manual bypass switch and on to the load. If ac power to the battery charger is lost, or the battery charger fails, then the batteries automatically begin supplying the required dc power to the inverter for some predetermined time (usually 15–30 minutes); there is no switching involved at this point. If a failure in the inverter should occur, or the inverter has to be serviced, the static switch will automatically transfer to the alternate position and supply the alternate source of power, via an optional regulating transformer, through the manual bypass switch and on to the load. The manual bypass switch is a mechanical make-before-break switch that is used to bypass the UPS for maintenance purposes. The regulating transformer may not be necessary if the ac alternate source voltage meets the same specification as the UPS ac output voltage.

UPS supplies are the recommended power source for critical process and safety shutdown systems in a chemical plant.

Types of UPS Systems. There are three basic types of UPS hardware configurations: the single module with bypass ("float") type, the rectifier input type, and the parallel redundant type, shown in Figures 3-6, 3-7, and 3-8. Improved reliability is provided by the rectifier input type UPS. Even greater reliability is provided by the parallel redundant hot-tie type, shown in Figure 3-8. The float type single module with bypass UPS configuration is the most widely used in chemical plants because of its simpler arrangement and lower cost. The advantage of a partial or fully redundant system is increased system reliability.

Selection of Critical Loads. An important aspect related to the application of a UPS is the selection of critical loads that need to be supplied from it. Safety and security systems, as well as operating systems, that need to be connected to a UPS supply may include:

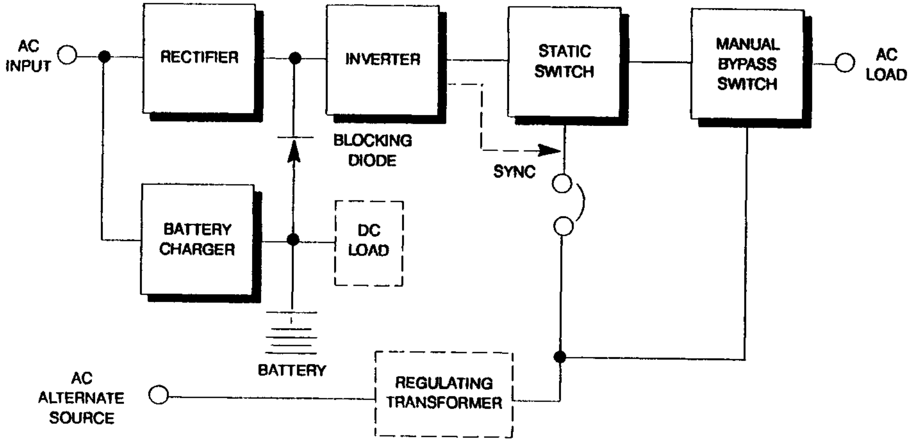


Figure 3–7. Rectifier input type UPS.

Note: A regulated rectifier performs in the same manner as a battery charger in converting ac to dc. The rectifier differs in that it does not have current limiting capabilities or a selectable output voltage. The output may be variable, however, with internal adjustments. Once set, it should not require changing. In this configuration, the normal ac line feeds a rectifier panel in the inverter cabinet, which supplies dc to the inverter. The dc from the battery is connected to the rectifier output through a blocking diode. This diode prevents charging of the batteries by the rectifier without inhibiting the normal flow of current to the inverter during an ac power failure. The switches perform the same functions as in the float system. The rectifier may be unregulated or regulated and the blocking arrangement may be diode or SCR logic, depending on the steady-state variation of ac input line and the method of charging batteries. The configuration is often used where there is an existing system supplying other loads, such as battery and charger, where the battery is large enough for short-term inverter powering but the charger is too small to carry the steady-state inverter requirements. The regulating transformer is required when the bypass source voltage does not match the output of the UPS.

- Distributed control system (DCS) process computers, with associated video display units, printers, etc.
- Process package units computer systems
- Plant shutdown DCS and PLC systems
- Safety related instrumentation (gas analyzers, chromatographs)
- Critical controls and interlocks
- Fire alarm and detecting systems
- Large rotating equipment local control panels

If a power failure occurs, electric pumps and compressors will stop, and process operations will begin deviating from normal operating values. At this point it may be necessary to implement a safety emergency shutdown sequence in the plant (see Chapter 9). While shutdown is being implemented, a reliable and continuous power supply is required to bring the process to a stable condition where it is safe and does not jeopardize the integrity of equipment. All the instrumentation and control devices that would be called upon to operate under an emergency situation should be identified and

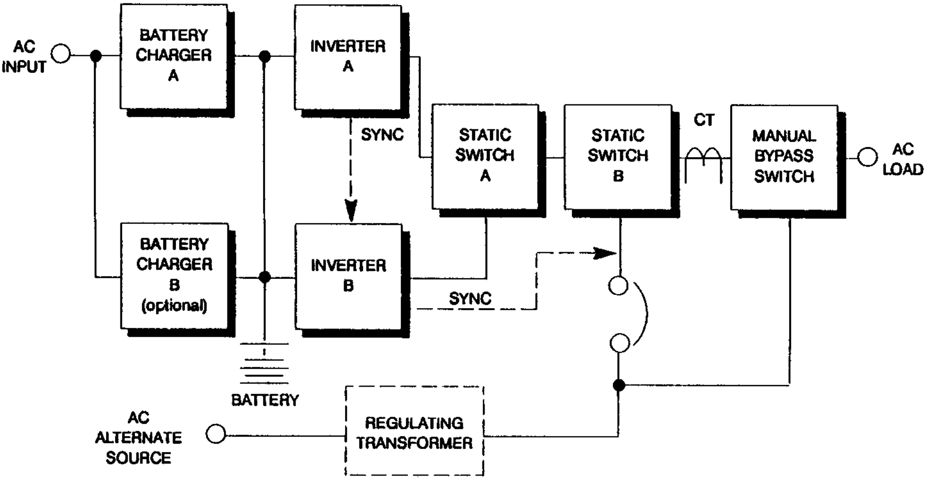


Figure 3-8. Parallel redundant hot-tie type UPS.

Note: Each inverter is sized to supply the entire load. Inverter A will supply the load through Static Switch A and Static Switch B in normal operation. In the hot standby mode, with both inverters runing, the failure of Inverter A will initiate the transfer of Static Switch A to the output of Inverter B. In the cold standby mode with Inverter B off, the failure of Inverter A will initiate the transfer of Static Switch B to the alternate source-to-load position. As an option, a second battery charger as well as a second set of batteries could be specified for extra reliability. The transfer between inverters is accomplished with absolutely no loss of power to the load. It is superior in reliability to paralleled redundant inverters because Inverters A and B are not hard-tied to each other. This system is often used where load frequency and commercial power source frequencies differ, and where the increased system reliability can be economically justified.

supplied power from a UPS in order to perform an orderly plant shutdown, or maintain the plant in a safe standby condition.

It is widely justified to power devices that monitor both personnel safety and plant integrity from a UPS bus. Fire alarm and detecting systems also fall within this category. Modern process package units, such as the Pressure Swing Adsorption (PSA) unit for hydrogen recovery, are furnished with a separate process computer to control valve settings, yield parameters and safety sequences; feeding this load from the UPS is recommended.

Sizing of the UPS and its application should be performed carefully to select the critical process and safety related systems that must remain operational without overburdening the UPS with less critical loads that could be served equally well from other standby power systems.

3.8.2 Steam

Steam is frequently used as part of the chemical process as well as to drive machinery, provide heating to the process or heat tracing, and as a safety measure to control a process reaction by snuffing and purging operations. Loss of heating steam may need to be addressed (e.g., if cooling of reactants would cause condensation or solidification and thus create unsafe conditions). Often, steam is considered a secure backup to electric drivers. If this is not assured through a highly reliable design, plant-wide emergency shutdown can occur upon power loss. Consideration for operating steam systems during power outages is a common design philosophy. For steam piping and tracing, design should address adequate flexibility and avoiding condensate pockets.

Static electricity may build up where steam leaks occur. This potential hazard should be considered where flammable gases exist see (Chapter 12).

The problems that should be addressed due to steam loss in the plant will include:

- Loss of heat in endothermic reactors
- Loss of heat in tanks where steam coils are used to keep material liquid
- Loss of process motive power because of steam driven pumps and eductors
- Freezing of steam traced piping
- Loss of steam for purging
- Loss of mixing steam to the flare units

3.8.3 Cooling Water

Loss of cooling water is a serious hazard. Alternate power supplies or pumping arrangements (both steam and motor drivers) are usually provided to allow for only partial loss.

Corrosion of cooling water systems is commonly prevented by the addition of corrosion inhibitors or oxygen scavengers or by pH adjustment. Unusual ambient conditions in the plant or process may require special considerations. Since cooling water systems are the primary service for equipment cooling to remove process heat, clean, unfouled conditions are a must to avoid failures of the equipment or the cooling water system itself. One must also address the potential for process leaks into the cooling water causing possible flammable or explosive conditions at the cooling tower. Water leaking from a heating coil in a hot storage tank can cause froth-over.

3.8.4 Inert Gas

Explosion hazards can be reduced by preventing the formation of flammable mixtures; this is done by replacing air with an inert gas. Atmosphere control is used in reactors, storage tanks, flare headers, centrifuges, driers, and pneumatic conveyors. The inert gas system should be designed so that all potential deviations from design conditions are outside combustible limits. To ensure safe operation of the system, the oxygen content should be monitored and provided with interlocks to shut down the system if the oxygen level rises. It is preferable to use duplicate analyzers of different types to monitor quality of the purge system gases. Maintain reliable operation of the oxygen sensor by filtering out particulates, condensing out vapors and remaining corrosive gases (Halpern 1986).

A list of safety design concerns for inerting systems (CCPS 1992b) which might be carried forward through the life of the facility include:

- Pressure indication on equipment being inerted
- Check valves to prevent back-flow and contamination
- Flow indication to verify inerting is adequate during pump out
- Capability to test the system regularly
- Nitrogen vacuum break and block valve in line to vacuum source on systems
- Purge gas or steam used in flare systems to prevent flashback
- Furnace purge timer set for 4 to 6 changes of furnace volume

Gases such as nitrogen and carbon dioxide are frequently used to replace oxygen and allow process pressures to be maintained. Non-reactive atmospheres are frequently required for process reasons, for example, polymerization reactions. In some cases, nitrogen may react and argon is used. A minimum oxygen level may be required to activate a polymerization inhibitor, for example, in reactive monomer systems.

Air is removed prior to start-up by replacing it with nitrogen, carbon dioxide, or gas from an inert gas generator. The process of bringing the equipment online is complex and requires integrating many systems, to avoid reintroducing air or water.

3.8.5 Instrument Air

High quality instrument air is required for proper operation of instrumentation and control systems. In particular, moisture must be extremely low to avoid corrosion and freeze up problems. Compressed air systems must also be free of oil.

It is often considered prudent to "back up" the instrument air supply with another compatible fluid. The backup fluid is often nitrogen. From an instrumentation standpoint, this poses no significant problems. However, from a personnel safety standpoint, a little recognized but significant hazard is introduced to closed buildings or vessels: the possibility of lowering the oxygen content in the enclosure to dangerous and possibly lethal levels. At an oxygen concentration of 16% or less humans will exhibit symptoms of respiratory distress (ACGIH 1986).

With the trend to electronic instrumentation and distributed control systems instruments, the central control room is less vulnerable to this hazard than when instrumentation was pneumatic. The main problem in new plant construction is in small buildings, such as analyzer houses, that are not normally occupied. These buildings, though "climate controlled" for the instrumentation, do not usually have elaborate HVAC systems; they use smaller units not usually designed to "change" as well as condition the internal air. Rather than adding a backup system, more care should be taken in designing an adequate secure instrument air supply.

Sometimes during maintenance, plant air is used to ensure air movement through vessels or other enclosures, either by a blower or eductor. In cold climates where the plant air must be low in moisture, the instrument air and plant air system are the same. A backup system for instrument air consists of air cylinders. If high capacity is required, nitrogen may be used; however, provisions for safe breathing atmosphere must be addressed.

3.8.6 Fuel

Failure of fuel systems (oil, gas, etc.) can affect many processes requiring temperature and pressure control. Affected systems may include:

- Boilers
- Reheaters
- Engine drivers
- Compressors
- Gas turbines
- Fired reboilers

The flammability hazards of these fuels are usually addressed in routine design, but often ignored in temporary or emergency operations. For that reason, multiple interlocks, precise air-freeing operations, and other controls are used to make operating fuel systems as fail-safe as possible. Also, combustible gas or oxygen analyzers are commonly used to provide necessary information to plant operators.

3.8.7 Redundant Sources of Power

Redundancy (providing a backup system) is often used to increase safety. Typically alternative means of motivation and sources of supply are provided. For example, a mix of motive means may be provided by:

- Pumps and spares on different motor control centers
- Cooling water systems with a mixture of drivers (turbine and motor)
- Instrument air/plant air systems with mixed drivers
- Boiler feed water system with two sources of supply
- Air: two sources of instrument air

3.9 PLANT MODIFICATIONS

The safety and integrity of a well-designed plant can be jeopardized by even a minor modification to the process or equipment. It is critical that safety reviews consider the effects on all interfacing systems and processes. Many of the familiar examples of plant explosions illustrate this point (e.g., the Flixborough incident). In addition, modifications to the process, such as changes in feedstock or operating conditions, must be analyzed for consequences. A formal set of procedures is used to control both process and plant modifications (see Chapter 10).

Not only the design of plant modifications, but their implementation is a source of hazards. For example, "inadequate isolation of equipment on which maintenance is to be carried out" (Lees 1980; Kilby 1968) frequently leads to formation of flammable mixtures.

Modifications often require emptying, purging, and cleaning, and these operations are frequently not properly analyzed for safety issues (e.g., removal of flammables prior to welding). Welding and hot tapping are inherently hazardous operations in plants where flammable and toxic materials are used. Hazard review of a modification should address "temporary" modifications and isolation procedures, as well as the obvious hazard of welding. The new lines, recently isolated lines, and lines in active service all need consideration.

3.10 REFERENCES

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4.3.3 Safety Considerations for Bin Storage

The safety considerations for the bin storage of powdered or pelleted materials is similar to that for fixed roof tanks. The primary danger in the bins comes from dust in the vapor space above the material creating an explosive or ignitable condition. Ignition sources should be minimized and dust conditions reduced by the use of filters or baghouses. A safety vent or rupture disk should be included to prevent overpressurization in case the filter bags clog during operations. Care should be taken during the design of the bin to reduce horizontal surfaces inside the bin where material can remain and create a hazard when the bin is opened for maintenance; the air above such areas has been known to explode while work inside the bins was being performed during normal repairs. Additionally, the bin can be inerted in a manner similar to that used for atmospheric storage tanks (NFPA 68 and 69). The pneumatic transfer of solids can also be preformed using an inert or a low-oxygen gas with a closed loop return to the sending tank.

4.4 PROCESS EQUIPMENT

Unit operations may include physical operations and further processing or preparation for further reactions or for shipment. These operations include mixing or separating, size reduction or enlargement, and heat transfer. General hazards in physical operations are:

- vaporization and diffusion of flammable liquids and gases
- spraying or misting of flammable liquids
- dispersion of combustible dusts
- mixing highly reactive chemicals
- increase in the temperature of unstable chemicals
- friction or shock of unstable chemicals
- pressure increase in vessels
- loss of inertants or diluents

Both design and operations are important in maintaining the integrity of the process and equipment. The high pressures and temperatures frequently used in the process accelerate the dispersion (release) of hazardous materials after loss of containment; therefore, maintaining the integrity of the system is critically important.

Failure of a column, associated piping or equipment may release substantial quantities of vapors or liquids above their boiling points, resulting in a flammable vapor cloud explosion or flash fire (FMEC 1974a,b). Failures of liquid/solids and solids handling equipment may release hazardous liquids and dust, creating a fire, explosion, or health hazard.

Deviations in operating conditions are responsible for most service failures (Lees 1980). Excursions in temperature and pressure can apply stresses that the equipment was not designed to handle. Obviously, then, the designer must provide means to relieve the extremes (low as well as high) in temperature and pressure, as well as to monitor and alarm for these conditions. The creativity of the designer should be focused on innovative ways to avoid these conditions, using the methods of intensification, substitution, attenuation, and error tolerance, as discussed in Chapter 2, Inherently Safer Plants. Protective measures, such as spill containment, vessel isolation, fire protection, and explosion protection, are applicable to all types of equipment.

This section highlights the major safety concerns for several types of equipment and provide references for detailed design. Table 4-1 is a list of common causes of loss of containment for different kinds of process equipment. Applicable causes are listed by letter under each category of equipment. This list does not include the causes of overpressure for which equipment is analyzed during relief protection studies. The list does not presume to be an exhaustive tabulation of causes. It shows that diverse kinds of equipment can have common problems in addition to some unique ones.

4.4.1 Reactors

4.4.1.1 Overpressure Relief

All reactors should be provided with overpressure relief protection. Review all reaction systems for the possibility of a "runaway" reaction, which often results in the need for an appreciably larger relief device than other relief scenarios may require. (See Chapter 14, Pressure Relief Systems.)

4.4.1.2 Relief Device Discharge Piping and Effluent Disposal

Where "runaway" reactions are known to occur, the piping from the relief device may be handling a multiphase stream (vapor–liquid or vapor–liquid–solid) and should be routed first to a knockout drum/catch tank containment system to separate the vapors from the liquid. The vapor line from the knockout drum/catchtank should then be routed directly to the atmosphere or to a scrubber or flare stack if environmental considerations require this. See Chapter 15 for discussion of knockout drums/catch tanks and effluent disposal systems.

4.4.1.3 Design Pressure

For reactors fabricated of metal only (not glass-lined), it is recommended that a minimum design pressure of 50 psig be specified, even if the operating pressure is essentially atmospheric. This provides inherent safety for unexpected pressure swing events (pressure spikes). If an explosive mixture might

Table 4-1 Common Causes of Loss of Containment for Different Process Equipment

COMMON BASIC CAUSES Applicable causes are listed by letter under each type of equipment	COLUMNS	HEAT EXCHANGERS	FURNACES	BOILERS	FILTERS
1. Rupture of vessel due to overpressurization	a	a	a	a	a
a. Inadequate relief due to:					
—Absence of relief					
—Incorrect sizing or setting of Relief Device (RD)					
—Incorrect installation of RD					
—Incorrect material of construction of RD					
—Isolation of RD by operator mistake					
—Excessive back pressure limiting full flow of RD					
—Plugging of RD by foreign materials					
b. Boiling liquid expansion vapor explosion (BLEVE)	b			b	
2. Rupture of vessel due to brittle fracture					
a. Incorrect material specification	a	a			a
b. Vessel not designed for sudden depressurization resulting in low temperature	b	b	b		b
3. Flange/gasket failure/seals/plugs					
a. Incorrect gasket (size, material) installed	a	a	a	a	a
b. Incorrect installation (e.g. incorrect size or incorrectly tightened)	b	b	b	b	b
c. Gasket omitted	c	c	c	c	c
4. Weld failures/casting failure					
a. Incorrect welding/casting procedures	a	a	a	a	a
b. Incorrect specification of design codes	b	b	b	b	b
c. Failure to stress relieve, if needed	c	c	c	c	c
d. Improper inspection and testing procedure	d	d	d	d	d
5. Overstressing of containment shell					
a. Incorrect specification of design code	a	a		a	a
b. Incorrect setting of spring hangers and pipe support or they are not set free	b	b		b	b
c. Error in stress analysis calculations	c	c		c	c
d. Omission in testing	d	d		d	d
6. Vibration					
a. Inadequate support	a	a	a	a	a
b. Failure to correctly align connected rotating equipment	b	b	b	b	b
c. Failure to test for vibration of rotating equipment prior to start-up after installation/ maintenance	c	c	c	c	c
d. Failure to check for tube vibration during design (exchangers)		d			
e. Failure to stop operating when vibration exceeds limits	e	e	e	e	e
7. Corrosion/erosion					
a. Corrosion due to abnormal process conditions	a	a	a	a	a
b. External corrosion from atmosphere	b	b	b	b	b
c. Erosion due to high velocities, dust and debris, liquid droplets	c	c	c	c	c
d. Lack of periodic inspection and correction	d	d	d	d	d
e. Due to local concentration in crevices and pockets	e	e	e	e	e
8. Failure due to external loadings/impact					
a. Error in foundation designs (e.g., hydraulic head not considered)	a	a	a	a	a
b. Foundation collapse	b	b	b	b	b
c. Excessive ground movement, earthquake	c	c	c	c	c
d. Collapse of fan/motor onto air fans		d			
e. External impact during maintenance	e	e	e	e	e
f. Vacuum (i.e., not designed for vacuum)	f	f		f	f
9. Internal explosion					
a. Improper purging of air from the system prior to admitting combustible.	a	a		a	a
b. Failure to isolate system during maintenance	b	b		b	b
c. Ingress of flammables from loss of containment elsewhere	c	c	c	c	c
—into equipment skirt, with local ignition					
—into fire box					
d. Human error when operating manually			d	d	
e. Liquid carryover to gas burners			e	e	

Table 4-1 *Continued*

COMMON BASIC CAUSES Applicable causes are listed by letter under each type of equipment	CENTRIFUGE	PRESSURE VESSELS, SEPARATORS	DRYER	SIZE REDUCER
1. Rupture of vessel due to overpressurization	a	a	a	a
a. Inadequate relief due to:				
—Absence of relief				
—Incorrect sizing or setting of Relief Device (RD)				
—Incorrect installation of RD				
—Incorrect material of construction of RD				
—Isolation of RD by operator mistake				
—Excessive back pressure limiting full flow of RD				
—Plugging of RD by foreign materials				
b. Boiling liquid expansion vapor explosion (BLEVE)		b		
2. Rupture of vessel due to brittle fracture				
a. Incorrect material specification	a	a	a	
b. Vessel not designed for sudden depressurization resulting in low temperature	b	b	b	
3. Flange/gasket failure/seals/plugs				
a. Incorrect gasket (size, material) installed	a	a	a	a
b. Incorrect installation (e.g. incorrect size or incorrectly tightened)	b	b	b	b
c. Gasket omitted	c	c	c	c
4. Weld failures/casting failure				
a. Incorrect welding/casting procedures	a	a	a	a
b. Incorrect specification of design codes	b	b	b	b
c. Failure to stress relieve, if needed	c	c	c	c
d. Improper inspection and testing procedure	d	d	d	d
5. Overstressing of containment shell				
a. Incorrect specification of design code	a	a	a	a
b. Incorrect setting of spring hangers and pipe support or they are not set free	b	b	b	b
c. Error in stress analysis calculations	c	c	c	c
d. Omission in testing	d	d	d	d
6. Vibration				
a. Inadequate support	a	a	a	a
b. Failure to correctly align connected rotating equipment	b	b	b	b
c. Failure to test for vibration of rotating equipment prior to start-up after installation/ maintenance	c	c	c	c
d. Failure to check for tube vibration during design (exchangers)		d		
e. Failure to stop operating when vibration exceeds limits	e	e	e	e
7. Corrosion/erosion				
a. Corrosion due to abnormal process conditions	a	a	a	a
b. External corrosion from atmosphere	b	b	b	b
c. Erosion due to high velocities, dust and debris,liquid droplets	c	c	c	c
d. Lack of periodic inspection and correction	d	d	d	d
e. Due to local concentration in crevices and pockets	e	e	e	e
8. Failure due to external loadings/impact				
a. Error in foundation designs (e.g., hydraulic head not considered)	a	a	a	a
b. Foundation collapse	b	b	b	b
c. Excessive ground movement, earthquake	c	c	c	c
d. Collapse of fan/motor onto air fans		d		
e. External impact during maintenance	e	e	e	e
f. Vacuum (i.e., not designed for vacuum)	f	f	f	f
9. Internal explosion				
a. Improper purging of air from the system prior to admitting combustible.	a	a	a	a
b. Failure to isolate system during maintenance	b	b	b	b
c. Ingress of flammables from loss of containment elsewhere	c	c	c	c
—into equipment skirt, with local ignition				
—into fire box				
d. Human error when operating manually			d	
e. Liquid carryover to gas burners			e	

Table 4-1 *Continued*

COMMON BASIC CAUSES Applicable causes are listed by letter under each type of equipment	SIEVES, SCALPERS, CLASSIFIERS	MIXERS, BLENDERSS	PUMPS, COMPRESSOR	VACUUM EQUIPMENT
1. Rupture of vessel due to overpressurization	a	a	a	a
a. Inadequate relief due to:				
—Absence of relief				
—Incorrect sizing or setting of Relief Device (RD)				
—Incorrect installation of RD				
—Incorrect material of construction of RD				
—Isolation of RD by operator mistake				
—Excessive back pressure limiting full flow of RD				
—Plugging of RD by foreign materials				
b. Boiling liquid expansion vapor explosion (BLEVE)				
2. Rupture of vessel due to brittle fracture				
a. Incorrect material specification			a	a
b. Vessel not designed for sudden depressurization resulting in low temperature			b	b
3. Flange/gasket failure/seals/plugs				
a. Incorrect gasket (size, material) installed	a	a	a	a
b. Incorrect installation (e.g. incorrect size or incorrectly tightened)	b	b	b	b
c. Gasket omitted	c	c	c	c
4. Weld failures/casting failure				
a. Incorrect welding/casting procedures	a	a	a	a
b. Incorrect specification of design codes	b	b	b	b
c. Failure to stress relieve, if needed	c	c	c	c
d. Improper inspection and testing procedure	d	d	d	d
5. Overstressing of containment shell				
a. Incorrect specification of design code	a	a	a	a
b. Incorrect setting of spring hangers and pipe support or they are not set free	b	b	b	b
c. Error in stress analysis calculations	c	c	c	c
d. Omission in testing	d	d	d	d
6. Vibration				
a. Inadequate support	a	a	a	a
b. Failure to correctly align connected rotating equipment	b	b	b	b
c. Failure to test for vibration of rotating equipment prior to start-up after installation/ maintenance	c	c	c	c
d. Failure to check for tube vibration during design (exchangers)				
e. Failure to stop operating when vibration exceeds limits	e	e	e	e
7. Corrosion/erosion				
a. Corrosion due to abnormal process conditions	a	a	a	a
b. External corrosion from atmosphere	b	b	b	b
c. Erosion due to high velocities, dust and debris,liquid droplets	c	c	c	c
d. Lack of periodic inspection and correction	d	d	d	d
e. Due to local concentration in crevices and pockets	e	e	e	e
8. Failure due to external loadings/impact				
a. Error in foundation designs (e.g., hydraulic head not considered)	a	a	a	a
b. Foundation collapse	b	b	b	b
c. Excessive ground movement, earthquake	c	c	c	c
d. Collapse of fan/motor onto air fans		d		
e. External impact during maintenance	e	e	e	e
f. Vacuum (i.e., not designed for vacuum)	f	f	f	
9. Internal explosion				
a. Improper purging of air from the system prior to admitting combustible.	a	a	a	a
b. Failure to isolate system during maintenance	b	b	b	b
c. Ingress of flammables from loss of containment elsewhere	c	c	c	c
—into equipment skirt, with local ignition				
—into fire box				
d. Human error when operating manually				
e. Liquid carryover to gas burners				

be encountered, a deflagration test is recommended to determine by testing what internal blast pressure might occur and what the design pressure should be. For deflagration design pressure requirements see NFPA 69.

4.4.1.4 *Reactants and Liquid Catalyst Addition*

All flammable liquids should be charged into a reactor via dip legs or elbows which cause the liquid to run down the reactor wall to prevent static electricity generation. Where the addition rate of a reactant or catalyst could result in a "runaway" reaction if added too quickly, a restriction orifice should be installed in the feed line to limit the flow rate. Where overcharging (adding too great a quantity) of a reactant or catalyst can cause a runaway reaction, the use of a gravity flow head tank, sized to hold only the quantity needed, should be considered.

4.4.1.5 *Solids Addition*

Where solids have to be added to a batch reactor containing flammable or toxic liquids, they should be charged by means of a rotary valve, lock-hopper, or screw feeder so that the operator will not have to open the reactor and be exposed to hazardous conditions or chemicals. There should be instruments or procedures to assure that the solids are being fed. In addition, special attention should be given to methods of safely unplugging valves and lines.

4.4.1.6 *Agitation*

Where a "runaway" reaction could result due to unrecognized cessation of agitation (the shaft is still rotating although the impeller has fallen off or corroded out), the malfunction detector shall be installed in the reactor in the vicinity of the impeller. (An ammeter is not adequate to detect agitation stoppage.) For details of a detector used successfully in industry, see the article by Wilmot and Leong (1976). The detector should have an alarm and be interlocked to cut off feed of reactants or catalysts and to ensure an appropriate restart sequence. Back-up power supply should be supplied for critical reactions, such as polymerization reactions. A good reference on mixing was published by IChemE (1982).

4.4.1.7 *Process Measures for Preventing Runaway Reactions*

Where runaway reactions are known to occur, and an excessively large relief device is needed, consideration should also be given to providing means to inhibit (kill or "short stop") the reaction or drown (quench) the batch. It is recommended that independent and redundant temperature instrument in the reactor be interlocked to actuate any of the following remedial actions at a specified high temperature reading:

- Add a considerable amount of coolant or diluent to reduce the reaction rate. This measure requires that process design and detailed design provide for:
  - —choice of an appropriate fluid which does not react too exothermically with the reaction mixture
  - —sufficient free volume in the reactor
  - —piping, instrumentation, etc. to add the fluid in the time required
- Rapidly depressure the vessel if the reactor is under pressure.
- Add an inhibitor to stop the reaction. This measure requires intimate knowledge of how the reaction rate can be influenced and whether effective mixing/inhibition is possible
- Dump the reactor contents into a vessel that contains cold diluent. This option also requires particular care that the dumping line is not blocked or does not become blocked during the dumping procedure.

4.4.1.8 Inerting

For reactors containing flammable liquids, where the reactor design pressure is insufficient to contain a deflagration, consideration should be given to providing an inert gas blanket (usually nitrogen). Among the principal reasons for providing inerting on reactors is the desirability of eliminating flammable vapor–air mixtures which can be caused by:

- Addition of solids through the manhole (there are not enough nozzles for an air lock valve, etc. through which to add the solid).
- Materials having low minimum spark ignition energies, or autoignition temperatures
- Potential ignition sources that cannot be controlled adequately, such as:
  - —spontaneous combustion
  - —reactive chemicals: pyrophoric materials, acetylides, peroxides and water-reactive materials
  - —static electricity: material transfer where lines and vessels are not grounded properly, agitation of liquids of high dielectric strength, addition of liquids of high dielectric strength to vessels, addition to or agitation of liquids in vessels having nonconductive liners

Another purpose of inerting is to control oxygen concentrations where process materials are subject to peroxide formation or oxidation to form active compounds (acetylides, etc.) or where materials in the process are degraded by atmospheric oxygen. An inert gas supply of sufficient capacity must be ensured. The supply pressure must be monitored continuously.

The designer should consider the need for additional measures to supply inert gas. Particular attention must be given to the following situation: In the case of locally high nitrogen consumption (e.g., when a large kettle is inerted), the pressure in the main line may drop so far that the mains could be contaminated by gases or vapors from other apparatus connected at the same time. Depending upon the application, the quality of inert gas can be important to process safety (e.g., water content, contaminants).

The required level of inerting must be ensured by technical and administrative measures, for example:

- control and monitoring of inert gas flow and inert gas pressure
- continuous or intermittent measurement of oxygen concentration
- explicit information in the standard operating procedures or in the process computer program for the correct procedure to achieve a sufficient level of inerting

4.4.1.9 Heating and Cooling Systems

Heat removal systems should be designed with abnormal operating conditions taken into account. For systems where runaway reactions are possible, the heat removal system should be capable of functioning at the temperatures achieved during the runaway reaction though it may not have the capacity to stop the runaway (e.g., water coolers should not become vapor bound).

Where both heating and low temperature cooling are required, a heat transfer fluid cooling/heating package system should be provided. Depending on the heat transfer fluid selected, appropriate safety and occupational health practices should be followed (see Chapter 7, Heat Transfer Fluid Systems). Do not use steam and calcium chloride brine in a steel reactor jacket as this results in stress corrosion cracking and subsequent vessel and/or jacket failure.

4.4.1.10 Precautions for Glass-Lined Reactors

Because of the "fragile" nature of glass, precautions should be taken to avoid causing damage to a glass-lined reactor by thermal shock and corrosion. When specifying a glass-lined reactor, the vessel manufacturer should be given complete details about the reactants, the reaction conditions, and the batch cycles so that the proper type of glass can be provided. Glass-lined reactors should be periodically inspected for the presence of holes.

Thermal Shock. Heating and cooling cycles in a glass-lined reactor can cause thermal shock damage if proper consideration is not given to the batch liquid and heat transfer media temperatures. Thermal shock failure occurs due to abrupt changes in temperature of the glass-lining and results in relatively small but thick pieces of glass spalling off in rigid fractures. Depending on the contour of the area and the manner in which thermal shock occurs, the failure may exhibit a shattered or elephant skin appearance. In most cases of thermal shock, the steel substrate will be exposed.

There are four operations in which sudden temperature variations can cause thermal shock:

- Sudden cooling of a glassed surface by subjecting a preheated surface to a cold liquid
- Sudden heating of the vessel wall by rapid circulation of a very hot fluid through the jacket of a cold vessel
- Sudden heating of the glassed surface by introducing a hot liquid into a cold vessel
- Sudden cooling of the vessel wall by rapid circulation of a cold fluid through the jacket of a preheated vessel

In the first two operations, the glass-lining tends to lose compressive stress causing the lining to weaken. In the second two operations, the glass lining is subjected to sudden overcompression causing the glass to fail. Reactor manufacturers can provide limits for rate of temperature change for glass-lined reactors.

Corrosion. When specifying a glass-lined reactor, careful thought must be given to what chemicals are in the reactor and what the temperatures are during the batch cycle. It must be understood that glass is not completely inert and is always undergoing local chemical reactions at the glass surface. What allows glass-lined steel to be used with corrosive materials is the low rate of reaction (kinetics): the slower the rate, obviously, the longer the glass lining will last.

Acids, alkalis, and even water can corrode glass in varying forms and degrees. Strange as it may seem, water can cause severe corrosion, and the rate increases with water purity. The corrosion rate also increases with increasing temperature and becomes greatest when the boiling point is exceeded. A small amount of acid added to water will greatly retard corrosion caused by water vapor condensation in the vapor area. This type of corrosion can also be reduced or eliminated by the introduction of an inert gas, insulating the vapor area, or both. These are important factors to consider in steam distillation processes.

The method of charging reactants into a vessel is particularly important. For example, caustic charged into a vessel should always be fed through a dip pipe directly into the liquid phase. If fed through a nozzle, the alkali will run down the side wall of the vessel in the vapor space and could cause severe alkaline attack, especially if the vessel is being heated. It is, therefore, important not only to monitor the reaction temperature, but also to consider the actual temperature of the glass lining and concentration of reactant charged to the vessel. Many reactors in the field have been lost prematurely because such conditions were not considered.

4.4.2 Columns

Columns, like other pieces of equipment, are available in a variety of mechanical designs. All of these various types are covered by the standard design codes, such as ASME Section VIII, Rules for Construction of Unfired Pressure Vessels.

The thermodynamics and other physical properties of the mixture to be processed help to define some of the choices, such as whether the separation technique should be:

- distillation
- absorption
- adsorption
- extraction
- pressure versus vacuum
- batch versus continuous

Other choices are concerned with the degree of flexibility that needs to be built into the system. The designer may need to determine whether the system will be fed at a steady rate or operate at varied rates and compositions. Different types of internal components do not have the same degree of flexibility. Choices for internal components include:

- bubble cap trays
- valve trays
- sieve trays
- packed beds
- reciprocating trays
- rotary trays

Distillation columns often contain a large inventory of flammable liquids at high pressure and temperature. Inventory reduction may be obtained by prudent reduction of operating flexibility to obtain minimum holdup. Various tray designs and packing options can affect holdup volumes and, of course, column efficiency. Improved feed distribution, preheat, column pressure or multiple columns may be used to improve efficiency.

A reduction in the bottom inventory to reduce hazardous inventories may make a column more sensitive to upsets if the response time of the control instrumentation is not capable of making quick adjustment. The same is true with the reflux inventory. For example, if a level controller fails open, is there adequate time for response before the reflux pump runs dry, which can create another serious problem? Consideration must be given to maintaining safe, stable operation as well as inventory controls.

Operational problems include flooding, fouling, excessive pressure drop or inefficient liquid/vapor contact (Harrison and France 1989; Kister 1992). There is a need to provide pressure relief caused by loss of coolant, excessive heating in a reboiler, or fire (IRI 1990a). Design of pressure relief systems must account for many factors (Bradford & Durrett 1984; Walker 1969). Chapter 14 discusses pressure relief systems.

Internal supports should be designed to withstand deviations such as flooding or pressure surge, a sudden collapse of packing, or tray failure. Process conditions may be particularly severe in distillation columns. The materials of construction should be thoroughly reviewed to understand any corrosion mechanisms that could occur in the vapor or liquid phases and with the vaporization and condensation processes.

Adequate instrumentation must be provided for monitoring and controlling pressure, temperature, level. The location of sensing elements in relation to column internals must be considered so that they can each function properly. Actuation of emergency shutdown systems can be made just as reliable as a relief valve (Lawley and Kletz 1975) while reducing relief loads (Zheman and Early 1992); alternative designs must be supported by company procedures for instrument maintenance.

A loss of vacuum in a distillation column due to a failure of the vacuum producing equipment may result in air leaking into the column. Consideration should be given to installation of emergency block valves in the vacuum line that would close at selected column pressure and the purging of the column with nitrogen to break vacuum. Another hazard associated with loss of vacuum is a rapid increase in the column bottoms temperature which could lead to undesirable decomposition reactions depending on the chemical species involved in the distillation. The column pressure relief system should be designed for this potentially worst case scenario.

Opening packed columns for maintenance when not sufficiently cooled can result in fires when the high surface area, which may be coated with organics or pyrophoric materials, is exposed to air.

4.4.3 Heat Exchangers

Heat transfer is one of the most widely used operations in the chemical process industries; not only is it used in physical operations (distillation, drying) but it is a required component of most reactions. This category of equipment includes heat exchangers, vaporizers, reboilers, process heat recovery boilers, condensers, coolers and chillers.

Standard design is addressed by the ASME Code, API RP 520, API Standard 660, Tubular Exchanger Manufacturers Association (TEMA) and Heat Exchanger Institute standards.

Control of temperature is critically important in maintaining control of the process. Loss of temperature control has many adverse effects, including increase in pressure, increase in reaction rate, increase in corrosion rate, change in equilibrium conditions, destruction of products, and instability of products (FMEC 1974a). Temperature excursions beyond normal operating limits may put excessive stress on either the shell side, tube side or both. Startup, shutdown or maintenance procedures may present a situation where one side has no fluid in it while the other side is at an extreme. The exchanger design should be provided with an expansion joint if required by differential temperature conditions.

Common problems of exchangers include tube rupture, leaking, fouling, tube vibration, and polymerization and solidification (Lees 1980). Failures in heat exchangers result in pressure changes (overpressure or underpressure) and contamination of the heat transfer fluid or process fluid. The primary hazard is failure to maintain separation of materials that might react violently upon contact. Therefore, methods to monitor for these conditions should be provided.

Double tube sheets should be used for heat exchangers handling toxic chemicals (Yokell 1973). All areas must be drainable to reduce corrosion (avoid baffles, which allow water to be trapped). A sometimes overlooked potential operating problem is that of gas blinding or inert blanketing. Many exchangers in condensing service need a tube sheet vent nozzle and/or a means to vent noncondensable gases from the process system.

4.4.3.1 *Material of Construction*

Materials must be carefully selected to resist corrosion and fouling on both sides. The use of bimetallic tubes may create a new set of potential problems as each tube may respond in a different manner.

The bending of exchanger tubes to form U-bends introduces residual stresses in the tube material which may make it more susceptible to stress corrosion cracking. Stress relief of U-bend exchanger tubes depends on the alloy and service conditions (temperature and constituents); in fact, stress relief may introduce undesirable metallurgical effects.

External stress corrosion cracking from chlorides in cooling water must be addressed; for example, the designer may consider using alloys more resistant to chloride pitting. Risk can be minimized in some instances by using several smaller exchangers rather than one large one. Besides the reduction in hazardous material retained, more corrosion resistant materials can be used in the first exchanger, which experiences the greatest temperature differential. This first exchanger could either be a sacrificial type under continuous corrosion monitoring or be fabricated from a more corrosion resistant alloy. Attention should be given to selection, installation, and maintenance of insulation to avoid corrosion under thermal insulation (see Chapter 8). Design baffles so that water is not trapped.

4.4.3.2 *Contamination*

Leaking exchanger tubes usually contaminate the cooling water. Gas detectors or gas separators should be provided for the cooling water return. "At one refinery, an entire cooling tower was destroyed when light hydrocarbon vapor was ignited after it had leaked into the cooling-water system" (Amoco 1984). In addition to analyzing the compounds exchanging heat, the designer should consider the potential effects of inhibitors (or other water treatment chemicals) in the cooling water or heat transfer fluid.

To improve the inherent safety of an exchanger, consider potential interaction between the materials exchanging heat in the event of a leak. The decision as to which is the high pressure side may depend on the potential reactions between process chemicals and the heating medium. If a small amount of chemical A is introduced through a tube leak into large amounts of chemical B without a considerable reaction, then try to design the process so that A is slightly higher in pressure than B. In case corrosion or tube failure were to occur, then the only hazard would be poor product quality and heat exchange. Other hazardous conditions exist if water can poison the catalyst or reacts with an acid.

Different types of heat exchangers are available. Some provide higher surface area to volume ratios than others. When dealing with hazardous materials, minimizing the volume of material is important and can be accomplished by selecting the right equipment (Kletz 1991b). When auto-refrigeration is a possibility (such as in light ends distillation) minimum design metal temperatures during startup and depressurizing should be considered in the early design phase.

4.4.3.3 *Overpressure Relief*

Consideration must be given to possible tube rupture and an adequately sized relief device must be provided. Refer to Chapter 14 for more details.

4.4.4 *Furnaces and Boilers*

The two main problems with furnaces and fired boilers are explosion in the fire box, which occurs during "lighting up" or as a result of flame failure (Lees 1980) or rupture of process tubes. Tube rupture may be detected by monitoring flow or monitoring the temperature as the tubes overheat. In boilers, loss of the boiler water level supply is detrimental to safe operation. Reliable level monitoring and control is paramount. Reliable level and control includes the design of a continuous supply of boiler feed water.

Corrosion is a major source of tube rupture problems in fired heaters. External corrosion of furnace tubes and other equipment in fireboxes is due to:

- temperature
- deposits
- flue gas composition
- physical conditions existing beneath and in any overlying deposit of ash

Oxygen and contaminants in the fuel gas and oils, rather than the fuel itself, cause most of the corrosion in fireboxes. The harmful contaminants are alkali metals (Na, K), sulfur, and vanadium. Although heater tubes usually operate at much lower metal temperatures, consideration must be given to the corrosivity of the process fluid, typical metal temperature, and the fuel used in firing the heater when tube materials are selected.

Corrosion occurs in the convection section when the temperature is lower than the dew point of the flue gases. Proper operation/shutdown procedures are the most effective methods to avoid convection section corrosion.

4.4.4.1 Process Control Instrumentation

Direct-fired heaters are widely used in the process industries. Typical furnace applications include distillation–fractionator preheaters and reboilers; steam generators; reactor preheaters; and pyrolysis reactors. A comprehensive discussion of direct-fired process furnaces can be found in *Perry's Chemical Engineers' Handbook* (Perry and Green 1984). Frequently the process fluids that are being heated in a direct-fired process heater are flammable. Furnace tube failure in the radiant or convective section of the heater could result in serious fire and/or explosion hazard and damage to heater internals. Incomplete combustion of fuel in the fire box will cause a build up of combustible gases (unburned fuel or carbon monoxide) which may ignite when sufficient oxygen is present resulting in an explosion within the fire box.

Process variables and parameters that determine safe furnace operation are coil outlet temperature (COT), coil inlet temperature, pass outlet temperature (POT), excess oxygen in the flue gas, combustible gases in the flue gas, flue gas opacity, fire box pressure, firing rate (furnace tube heat flux), coking, stack and bridgewall temperatures and combustion efficiency. A sound control scheme must supply sufficient air to promote complete combustion, ensure safe operation and maintenance, maintain COT at specified target, balance burner firing, maintain equal POTs, constrain the furnace firing rate to avoid maximum allowable stack temperature, furnace tube temperature, or convection section temperature, and monitor indications of coking over long term operation. In the design of safe control systems, constraints imposed on process variables must ensure plant safety and efficient operation. Excessive temperatures lower the strength of carbon steel and alloy materials used in the furnace and may lead to premature failure. Thermocouples can be located in critical areas of the furnace to indicate when temperatures are above safe operating conditions. Constraint controls should be used to override furnace duty or COT controls and maintain the furnace within metallurgical constraints.

Some specific control considerations include an upper bound of COT and POT which prevents excessive furnace tube temperatures, excessive fouling on the inside of the furnace tubes due to coke deposit, and product degradation. Other control considerations are designed to maintain combustion efficiency.

4.4.4.2 *Combustion Control Instrumentation*

In process plants, fired equipment such as furnaces and boilers are a vital necessity. The combustion process must be controlled to maintain the desired rate of heat transfer, to maintain efficient fuel combustion, and to maintain safe conditions in all phases of operation. These combustion controls are normally a part of the basic process control system and typically consist of some or all of the following control functions:

- Firing Rate Demand Control
- Combustion Air Flow Control
- Fuel Flow Control
- Fuel/Air Ratio (Excess Air) Control
- Draft Control
- Feedwater Flow Control (Steam Boilers only)
- Steam Temperature Control (Steam Boilers only)

For further details on the implementation of fired equipment combustion controls and their safety considerations, refer to the *Instrument Engineers' Handbook* edited by B. G. Liptak (1985) and *Steam, Its Generation and Use* published by Babcock & Wilcox. A checklist of basic considerations is presented in Table 4-2. Industry and local governmental agencies have developed the following codes and standards to define minimum requirements for safe operation, startup, and shutdown of fired equipment:

National Fire Protection Association (NFPA): 85A, B, D, & G

Factory Mutual (FM): Approval Standards for Combustion Controls

Industrial Risk Insurers (IRI): Loss Prevention and Recommended Practices

4.4.4.3 *"Lighting-Up," Flame Failure*

Furnaces and heaters should be designed and located to minimize the potential fire hazards associated with open flames in a process environment. Design considerations for these hazards beyond those already discussed in Section 4.4.3.2 may include (Amoco 1984):

- providing steam snuffing for control of possible tube rupture events

Table 4-2 Basic Considerations for All Fired Equipment

- One flame sensor and one safety shutoff valve should be provided for each gas-fired burner. For oil burners, consideration should be given to providing two flame sensors per burner.
- Interlock the fuel supply and combustion air so that (a) failure or dangerous reduction of either the fuel pressure or combustion air pressure and (b) dangerously excessive fuel pressure will immediately shut off and lock out the fuel supply to the burners.
- The system shall have a timed purge prior to light-off with an interlock to ensure that all dampers are adequately open and that the fuel supply valves are closed.
- Provide interlocked low-fire lighting-off controls so that on a call for heat and subsequent completion of the pre-ignition purge, the fuel and combustion-air controls to the burner are in the proper lighting-off positions before the ignition cycle can proceed.
- Provide air flow and temperature sensors for the process material to monitor process operations and determine heater efficiency.
- If the unit is designed to operate during a power failure, provision must be made for continued operation of the flame safety system.
- Provide a permanent and ready means for periodic tightness tests of the main burner safety shutoff valves.
- Provide a means for calibration and check-testing of combustion control and associated safeguard equipment.
- Total shutdown interlocks should be provided.
- Fired equipment using gaseous fuel requires high and low gas pressure interlocks to cut off the fuel. High pressure interlock is only required when high gas pressure can cause incomplete combustion. The maximum time for ignition when using gaseous fuel is 10 seconds so that the amount of gas released can be limited.
- Fired equipment using liquid fuels requires cut off of fuel on low pressure (to assure atomization of the liquid), and on loss of atomizing steam or compressed air. A maximum time for ignition when using liquid fuel is 15 seconds to prevent accumulation of the fuel.
- A combustibles-oxygen analyzer should be provided on the exhaust stack of large boilers to determine when unsafe firing conditions are occurring.
- There are types of multiburner units where the combustion safeguard can be safely eliminated. For these units, such as reformers or cracking furnaces, the FM safety cock system should be provided.
- A total fuel shutoff valve should be provided 50 feet from the furnace.

(Grossel 1992)

- providing pilot burners with a separate fuel line system in case of failure of main fuel supply
- providing flashback protection for burners, including all potential ranges of temperature pressure, gas composition
- providing means to prevent liquid slugs from entering burners (e.g., providing enough condensation drums; providing means to heat trace

and insulate the line from the knockout drum; adhering to proper startup, operation and shutdown procedures)
- preventing flame impingement on tubes, supports or refractory
- providing safe firebox purging sequences
- providing fuel shutoff and startup checking sequence

Fired heaters should be designed to transfer to natural draft in an emergency and operate on loss of air-preheater or fan. A furnace air preheater must be designed to allow the fired heater to operate on natural draft if the fan fails (consider the fail-safe position of dampers, emergency air doors, etc.); for example, dampers should fail to natural-draft. Instrumentation enabling the fired heater to switch to natural draft should be very reliable; consider installing separate sensor taps and independent actuating systems.

4.4.4.4 *Tube Rupture*

A "hot spot" (localized excessive metal temperature) is a major cause of process heater tube failure. Hot spots are generally caused by flame impingement due to incorrect burner adjustment, excessive heater firing rates and/or excessive coking or scaling on the internal tube surfaces, or loss of (or minimal) flow of process fluid in the tubes. Overheating results in heater tube failure from one or more of the following effects:

- stress rupture at higher than design metal temperature
- accelerated internal (process side) corrosion
- accelerated oxidation (fire side) corrosion
- microstructural effects on strength properties

Heater instrumentation should provide for detection of failure and automatic shutdown to minimize secondary damage. Such items as stack temperature increase, heater tube pressure and/or flow loss and loss of outlet temperature can be used to detect a tube failure.

4.4.5 *Filters*

Separation of a gas–solid or liquid–solid mixture by means of a filter medium such as a screen or porous medium which permits the flow of gas or liquid and retains the solid particles may be done utilizing a variety of filters. There are high pressure in-line filters utilizing a bag to retain the particles removed in liquid or gas service and there are bag houses for removing dust particles from gas streams.

For the pressure filtration services, the primary concerns are loss of containment of flammable and toxic materials and operator safety during the frequent opening and closing of the process system. As with every process step, we must look for ways to change the process to eliminate or lessen the need for filtration, such as, for example:

- high purity feeds
- make filtration continuous, not batch
- make filters self-cleaning
- use disposable filters

Filters are often pressure vessels. In addition to what is true for pressure vessels with regard to overpressure protection and corrosion of the shell, the designer should be concerned for the materials of construction of the filter media and the mechanical ability to withstand pressure differential. Reliable instrumentation, particularly pressure differential and temperature monitoring, must be maintained to prevent mechanical damage and the resulting possible downstream contamination. Utility connections should also be reviewed to ensure they are in or out of service as required. Self-cleaning or sluicing filters are recommended for pyrophoric or toxic materials as they do not have to be opened or disassembled to remove the filter cake. Filters for liquid service should be provided with fire-relief valves and / or safe operation procedures for out-of-service conditions.

Bag house filters are normally low pressure units. They can vary in operating conditions from hot and chemically aggressive to cool and inert. As with all filters, not exceeding the design pressure differential is important to both the process stability and safety. As the solid is removed from the gas stream and is subsequently handled for recovery or disposal, all of the conventions and concerns for handling dust, powders and other solids apply. The system should be protected from the potential of dust deflagration by the use of pressure relief or suppression devices. A discussion of safety considerations is found in *Dust Collectors* (FMEC 1991) and (IChemE 1992).

4.4.6 Centrifuges

Because centrifuges incorporate the hazards inherent in all rotating equipment, the designer should first consider whether other, safer methods of separation (such as decanters or static filters) can be used. If it is determined that a centrifuge must be used, the design should be reviewed to ensure that it is as safe and reliable as possible.

There is no group in the U. S. issuing standards or codes for centrifuges. In Europe and the Far East there are some agreements among principal centrifuge manufacturers, but at the time of writing these have not been formalized to a set of standards. A good discussion of centrifuge safety design features and operating practices is found in an IChemE publication (1987).

Potential problems of centrifuges include:

- Mechanical friction from bearings
- Vibration
- Leaking seals
- Static electricity
- Overspeed

Redundant monitoring of critical components along with reliable maintenance procedures for both the mechanical equipment and the monitoring instruments is imperative. In an incident reported by Lees (1980), the loaded basket of a 48-inch suspended-type centrifuge suddenly became unbalanced and in consequence the shaft flew out and broke the outlet pipe of an adjacent centrifuge. The investigation indicated that the imbalance had been caused by a sudden escape of cake from one side of the basket due to a "hole in the cloth."

Vibration is both a cause of problems and an effect of problems. The potential destructive force of an out-of-balance load has led to setting lower shutdown limits on the magnitude of vibration than other rotating equipment. In the case history above, the unbalance was the effect of the "hole in the cloth." It is not clear whether it was wire cloth or some other fabric. And it is not clear whether the hole was caused by a physical tear or the result of corrosion.

Selection of "appropriate" materials of construction may be complicated by the additional stress put on the materials from the centrifugal forces.

Flexible connections for process and utility lines becomes a must so that vibration problems are not transmitted to connected equipment. Flexible hoses with liners having concentric convolutions (bellows type) avoid the sharp points inherent with spiral metallic liners. By avoiding the sharp point the liner is less likely to cut the exterior covering.

Grounding via some type of brush or other direct contract is inherently safer than grounding via the bearing system through the lubricating medium. A proof test at the vendor shop as an item of the inspection test run is prudent.

For flammable and/or toxic materials all of the cautions for a pressurized system should be considered. For example, when a centrifuge is pressurized, overpressure protection is required, even if the pressurization is an inert gas. Relieving of the pressure to a closed system or safe location must be considered.

Batch centrifuges should not be used for toxic slurries, as even bottom-unloading types require an operator to dig out the "heel." Various types of continuous centrifuges can be used for toxic slurries to avoid operator exposure.

4.4.7 Process Vessels

The process conditions of a vessel will influence all activities that contribute to the safe operation of the vessel. The reliability and integrity of process vessels begins with the definition of the process requirements, followed by mechanical design activities including material selection and continues with the fabrication techniques and quality assurance practices. After the vessel is in operation, the service requirements, maintenance practices, and inspection techniques will determine the length of time that the vessel can remain in service.

Special attention during the design phase is required to properly define parameters to which the vessel must be designed. Codes and standard practices are available to address design pressures and temperatures but attention to less obvious design factors must also be made. Of special concern is the allowance for corrosion, the vessel contents, discontinuity stresses, thermal and fatigue loads. The use of appropriate materials of construction, generous fillet welds, heat treatment, qualified weld procedures, radiused intersections, and unrestrained construction should be considered.

Process conditions must be accurately defined before the mechanical design efforts are started. Agents in the vessel environment which react with carbon must be identified because decarburization of ferrous alloys can result. Sulfur- and hydrogen-containing environments are significant and measures must be employed to prevent hydrogen embrittlement, laminations, and stress cracking in the metal of the vessel. Nelson curves (API Publ 941) are used to select steel material to be used for vessels in hydrogen service. An accurate definition of the vessel operating conditions, maximum and minimum excursions as well as normal, is required. Rapid cyclic heating of vessels is not desirable since this can cause local cracking of material. Minimum design metal temperatures dictate impact test requirements for materials in cold service and autorefrigeration upon depressurizing should be addressed. Table 4-3 identifies some selected material problems which must be addressed when identified as a design condition.

The fabrication techniques and inspections conducted during fabrication will greatly influence the quality of the finished vessel. Faulty fabrication, for

Table 4-3 Process Vessels: Special Material Concerns

Material Problem	Preventive Measure	Typical Inspection
Sulfide stress cracking	Heat treatment Control of weld procedures	Hardness testing Tension tests
Hydrogen Induced Cracking (HIC)	Post weld heat treatment Use HIC resistant steels	Wet fluorescent magnetic particle testing Ultrasonic testing
Carbon and alloy steel at low temperature	Heat treatment	Impact testing

example, poor welding, improper heat treatment, dimensions outside tolerances allowed, or improper assembly may cause problems to develop in pressure vessels.

The most common nondestructive techniques include x-ray examination, ultrasonic testing, liquid penetrant examination, and pressure testing (see Chapter 5). Other methods of inspection can include hardness and impact testing. Pressure testing requirements for new equipment are described by the applicable codes; testing of vessels following repairs and alterations may be modified. ANSI, API RP 510 and NBIC may be used to assist in determination of testing requirements.

Mechanical forces can cause a vessel to fail or to operate inefficiently, unless adequate provision has been made for such forces, for example, thermal shock, cyclic temperature changes, vibration, excessive pressure surges, thrust from relief devices and other external loads.

The process engineer can sometimes influence the inherent mechanical design integrity of a vessel as in the case of a two diameter trayed tower. By providing sufficient spacing between the internals at the conical transition between the large and small cylinders of the vessel, a more gradual transition between diameters is achieved (a cone apex angle less than 60 degrees is preferred) and the discontinuity at the cone to cylinder junctions will be less severe resulting in a better design. Alternatively, the process engineer may question whether the two diameter design is absolutely required.

Internal components such as baffles, agitators, trays, etc. must be installed in such a manner that liquid and vapors are not trapped from being drained or vented from the vessel. Although intermittent tack welding may provide sufficient mechanical strength for baffles or tray support rings, complete fillet welds are preferred so that crevices and pockets are not created that aid in providing hidden locations for corrosion. A useful book dealing with corrosion control in the design of pressure vessels has been written by Lansdrum (1989).

Agitators present a different set of challenges for pressure vessels. They not only bring with them the usual hazards of leaking seals, vibration and alignment, but additional loads beyond static and torque may be applied to the vessel head. Normal torque loads are in the same plane as the nozzle face and determined from the horse power required for the agitator motor. In some situations, such as polymerization, there is the potential for agglomerations to occur, creating a load perpendicular to the nozzle face (Figure 4-4). This load can cause the vessel head to flex, requiring additional head reinforcement to counter the force. This force may also require that heavier bearings be used for the agitator shaft. FRP pressure vessels require special attention, such as gusseting of agitation nozzles (ASME Code, Section X).

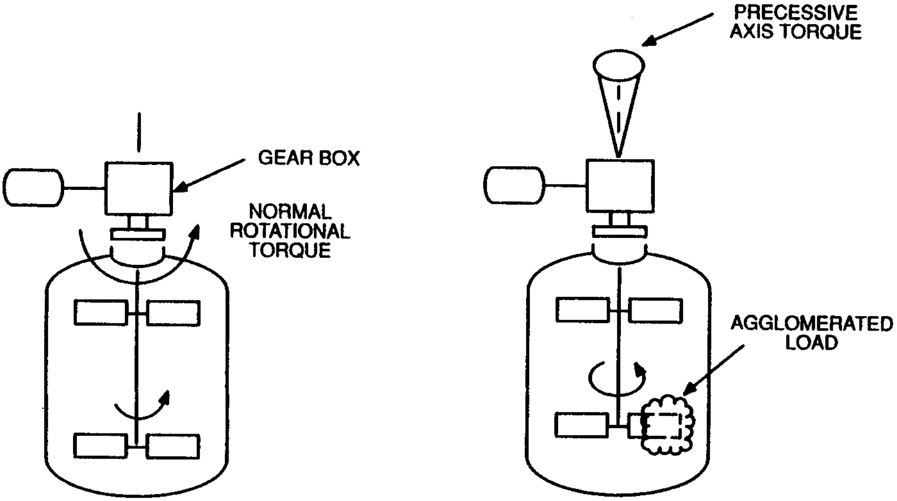

Figure 4-4. Uneven load on agitator.

4.4.8 Gas/Liquid Separators

Gas–liquid separators are commonly used to disengage liquid from a two-phase mixture of gas and liquid by gravity or centrifugal force. Typical applications for gas–liquid separators include: natural gas–crude oil separators, compressor suction liquid knockout drums, and distillation tower reflux drums, which should have the same design basis and concerns as process vessels. Gas–liquid separators are frequently equipped with a demisting pad to prevent the carryover of liquids into the exiting vapor and a vortex breaker located above the bottom outlet nozzle of the separator to prevent vapor entrainment in the liquid (gas blowby). Gas entrainment in the liquid stream can damage control valves, overpressure downstream vessels, and lead to product contamination. Low level switches can be used to alert the operator and shut down critical downstream equipment if necessary. Despite these design considerations, improper control of gas–liquid separators can result in liquid carryover or gas blowby.

Process variables and parameters to be considered include vapor velocity, liquid level, vapor density, and liquid velocity. Liquid carryover may occur when vapor velocities are far in excess of design velocities. Liquid carryover may also occur when the liquid level in the separator rises past the elevation at which the gas–liquid stream enters the vessel. If the separator is used as a compressor suction drum, liquid carryover can cause serious damage to the compressor. Liquid carryover can be prevented by maintaining good level control of liquid in the vessel. High level switches can be used to alert the operator and shutdown critical equipment (compressors) if necessary.

Gas blowby may occur when liquid level in the separator is too low. Gas entrainment in the liquid steam can damage control valves, overpressure downstream vessels, and lead to product contamination. Low level switches can be used to alert the operator and shut down critical downstream equipment if necessary.

4.4.9 Dryers

The choice between different dryers is guided by the chemicals involved and their physical properties, particularly heat sensitivity. As when selecting other equipment, the designer should ask whether this step is necessary; if so, whether this is the correct or safest process step. Does the material being processed have to have all of the liquid removed? Can the downstream step or customer use the material in a liquid, slurry or paste form?

The primary hazards in drying operations are:

- fires and explosions
- vaporization of flammable liquids
- diffusion of flammable gases
- overheating, leading to decomposition
- asphyxiation hazard after inerting for maintenance

These hazards may be encountered in many drying operations. The hazard may result in a loss of containment of a flammable or the formation of an explosive mixture within the equipment. The explosion of a poultry feed additive left in a dryer at a plant in King's Lynn, Norfolk, England, is an example of an accident in a "simple" dryer (Lees 1980).

If the dryer is fuel fired, all of the hazards described in the furnace and boiler section apply here. Even if the liquid to be removed is water, there may be hazards if the dried material is flammable or reactive or is heat sensitive (and it is not removed quickly enough while the heat is on). Perhaps this is oversimplification, but when several processing steps are combined, the hazards are a combination of those steps. If the drying takes place in a pressurized vessel, the design basis for the dryer is the same as the pressure vessel. When the material is moved through the heated space, beware of the additional hazards associated with the solids handling equipment. Lastly, once the material is dry, we must avoid the hazards associated with dust.

For heat sensitive material, limiting the temperature of the heating medium and residence time of the material are used to prevent decomposition. Inventories of hazardous materials should be minimized. Preventive measures include adequate ventilation and explosion venting, explosion containment, explosion suppression, inerting, elimination of ignition sources, vapor recovery. Instrumentation may include oxygen analyzers and sensors for temperature, humidity, etc. Effluent gases should be monitored for flammability limits.

The IChemE book (1990) should be consulted for a thorough review of fires and explosions in dryers.

4.4.10 Solids Handling Equipment (Size Reducers, Sieves, Scalpers, Classifiers, Mixers, Blenders and Conveyors)

There are various solids handling unit operations; crushing, grinding, mixing, classifying and conveying; many of these operations generate combustible dust. All mechanical size reducing or conveying methods carry the risk of overheating due to mechanical failure. Many of these methods also generate static electricity.

The two major hazards of combustible dusts are fire and explosion. Combustible dusts are often easy to ignite and may be difficult to extinguish. An explosion can destroy both process equipment and fire protection equipment. Methods to prevent fire and explosion (FMEC 1976) are: prevent accumulation of combustible dusts by collecting and removing them safely, that is, below the lower explosive limit; control ignition sources, and provide an inert gas atmosphere. Fire protection and explosion protection are discussed in Chapters 16 and 17.

Many chemicals are handled as a powder or dust; explosions of dust suspensions and fires of dust suspension or layers of dust are not uncommon. The designer may be able to change the process to avoid generating combustible dust; for example, by using a wet process. "The hazards of a dust explosion should be a factor in selecting a suitable method" of operation (Lees 1980). The shock sensitivity of the material should be established by testing before selecting size reduction equipment. Grossel (1988) discusses safety considerations in conveying bulk solids and powers.

Several general principles may be applied to equipment handling combustible dusts:

- design equipment to withstand a dust explosion
- minimize space filled by dust suspension
- minimize (monitor) mechanical failure and overheating (bearing, rollers, mills)
- minimize static electricity
- minimize passage of burning dust
- provide explosion prevention (e.g., by inerting) and protection (e.g., suppression, isolation)
- provide fire protection
- maintain design operating conditions
- eliminate sources of ignition.

Explosion prevention is preferable to suppression and venting; these topics are addressed in Chapter 17.

4.4.11 Pumps and Compressors

Various types of pumps are used to transfer toxic and flammable materials.

4.4.11.1 Pumps

The two main safety concerns when pumping highly toxic fluids are leaks and fugitive emissions. With proper precautions, a wide variety of equipment is available: centrifugal pumps, positive displacement pumps, liquid- or gas-driven jet pumps, and gas-pressurization or vacuum-suction transfer systems. Other important criteria to be considered are materials of construction, instrumentation to detect pump-component failure, methods to contain toxic materials within the pump, and methods to control leaks and emissions (Grossel 1990). The pumping system should be designed to operate in a manner that prevents the pump from a deadhead operation for more than a very short period of time. "Deadheading" a pump can result in excessive temperatures that can lead to high vapor pressure or decomposition reactions that will blow the pump apart. Methods to maintain and detect a minimum flow through the pump or a temperature rise in the pump may be required along with a shutdown interlock for heat sensitive materials. A number of pump explosions have occurred where the material in the pump overheated [even water]. Deadheading the pump can cause pump overheating with bearing burnout and flashing of the liquid in the pump, and the rupture of downstream piping if the piping is not specified to meet the pump's deadhead pressure. For flammables or hazardous service, cast iron pumps should not be used because they are brittle and may crack. Minimum metallurgy that should be considered is cast ductile iron (ASTM A395).

Operating centrifugal pumps at severely reduced flows can cause excessive vibration and damage to drivers, piping and adjacent equipment; a minimum-flow recirculating line should be installed to avoid the instability conditions caused by low flow rates. Minimum flow control is usually required for large centrifugal pumps to prevent cavitation in the pump impeller and subsequent damage to the pump. The minimum flow liquid should not pass directly from the pump discharge to suction without consideration of cooling. Excessive heat buildup defeats the purpose of the minimum flow which is intended to prevent the liquid being pumped from vaporizing and/or cavitating which causes mechanical damage to the pump. Normally the minimum flow stream passes from the discharge line back to the suction vessel. A temperature sensor in the pump casing and vibration sensors in the bearings may be interlocked to shut off the pump motor at excessive temperature or vibration. Close attention to the pump seal design and configuration is important to reduce normal wear and leakage for flammable and toxic service. Proper alignment will minimize mechanical seal failure.

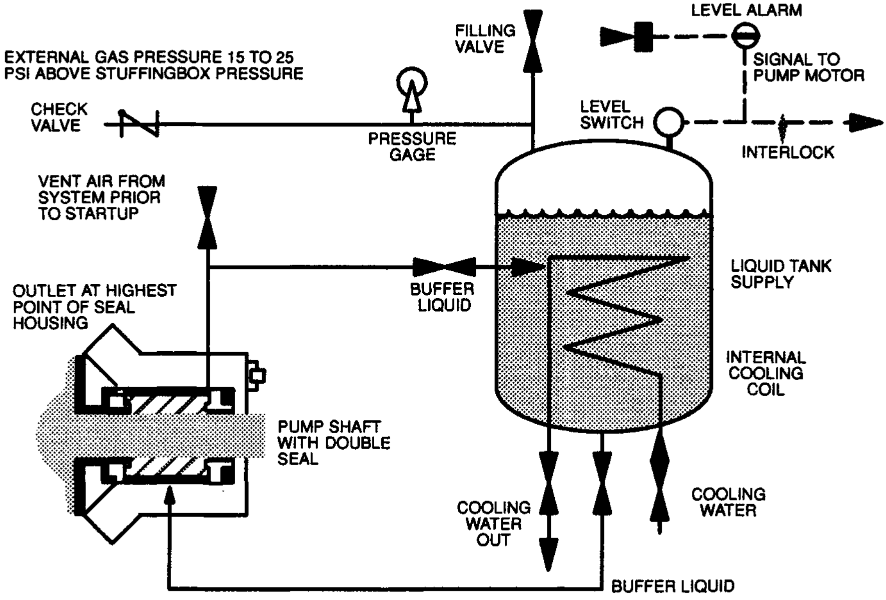

Figure 4-5. Buffer liquid circulates between double mechanical seal (left) and pressurized reservoir. Upon seal failure, the buffer liquid (rather than the toxic process liquid) leaks, the liquid in the reservoir drops, and the pump motor shuts off (Grossel 1990).

Conventional positive-displacement pumps can handle highly toxic liquids if provided with double or tandem seals. Positive displacement pumps which can be blocked in on the discharge side require a pressure relief device; use of an external relief device is recommended (Grossel 1990).

Diaphragm pumps, which do not have a sealing device which can leak, may be also considered. Air-driven diaphragm pumps can be operated at deadhead with no damage to the pump. For highly toxic fluids, pumps with double diaphragms should be specified, with the volume between the diaphragms monitored and alarmed.

To prevent loss of process fluids, centrifugal pumps should have a sealing system which consists of either double-inside or tandem mechanical seals with a barrier fluid between the seals plus a seal-failure alarm. If collecting the leaking seal is permissible, a secondary seal with a vent and drain gland fixture outside the primary seal is frequently effective in collecting leaked fluids. This secondary seal also offers a gland for inert gas blanketing, as well as providing protection if the primary seal fails.

Failures of mechanical seals still occur, though much improvement has occurred in recent years. Mechanical seal problems account for most of the pump repairs in a chemical plant with bearing failures being a distant second

(Reynolds 1989). Certain conditions increase the frequency of seal failure (e.g., heat, pressure, corrosion, cavitation, and product characteristics). Other conditions such as particle debris, shaft deflection, bearing wear, vibration, and poor installation can also affect seal life, but can usually be minimized by proper pump selection, careful installation, and proper maintenance (Monsanto Publ.9093). Particle debris, particularly during plant start-up, can be minimized by using a strainer in the pump suction piping; a T-type strainer is suggested due to the ease with which it can be removed and cleaned with the pump still on-line. Shaft alignment can be a major source of failure. The appropriate alignment techniques should be used to check the pumps prior to start-up, and the alignment should be rechecked if continuing bearing or mechanical seal problems occur on a pump.

High temperatures decrease lubricity, resulting in increased friction and heat buildup that can promote abnormal wear of the seal face. Temperatures can be decreased by providing a seal flush system which provides filtered and cooled fluid. The pump operating characteristics should be checked to make sure that the appropriate type of lubrication is being used.

Compatibility of the seal fluid with the process fluid should be established. Depending on the seal system used (tandem or double) leakage can occur into the seal fluid or into the process.

Excessive face pressure, either hydraulic or installation imposed, can reduce face lubrication, increase frictional heat buildup, and cause face distortion. Pressure surges and hydraulic shock created by automatic valving can also reduce seal life; therefore, carefully consider system hydraulics. Acid conditions can form acidic metal salts, which can be abrasive to seal faces. A seal flush system should be provided.

Cavitation can cause pressure variation, shaft deflection, vibration or mechanical shock that will damage seal components. Cavitation problems usually can be avoided by proper system design, especially net positive suction head (NPSH) and by avoiding entrained gases. Erosion by abrasive particles in the system contribute to seal failure, particularly particles under 200 mesh size, such as thermal decomposition products in heat transfer fluids (Monsanto Publ. 9093).

Canned-motor and magnetic drive pumps avoid the seal problem altogether. These types of pumps are driven by a magnetic coupling between the pump and an external rotating motor. The magnets are attached to the pump shaft and the motor shaft, with a nonmagnetic shield between them. Magnetic-drive pumps use permanent magnets; canned pumps use electromagnets. Virtually all pump manufacturers now supply magnetic drive pumps, both centrifugal and gear.

Canned motor and magnetic drive pumps have internal bearings which operate in the pumped fluid and support the internal rotor, shaft and impeller assembly. A magnetic drive pump can encounter problems like those of a standard centrifugal pump, such as conventional motor problems, coupling and alignment problems, and anti-friction bearing failure in the outer magnetic rotor bearing housing (Reynolds 1989). Magnetic coupling may be eddy-current-type or magnet-to-magnet synchronous drive type. Since non-leaking pumps are often sought for heat transfer fluid applications, temperature considerations should be examined carefully. Some magnetic drive pumps can handle heat transfer fluids at 370°C (700°F) without many special design features because they don't have temperature-sensitive electric motor winding insulation close to the outside of the can, as canned motor pumps have. If the fluid in the can cavity is isolated and cooled, canned motor pumps can be used.

Canned and magnetic drive pumps are not without their own safety considerations. Most failures of sealless pumps are caused by running them dry and damaging the bearings. A low-boiling liquid may flash and a reverse circulation system or bypass stream may be required (Reynolds 1989). If the temperature of the flush liquid increases, the vapor pressure may rise and liquid may flash and the sleeve bearings can run dry. Solids may abrade the bearings of magnetic drive pumps or may plug small ports in the can area.

Sealless pumps are equipped with a more complex hydraulic system involving sleeve bearings and other parts which must receive some attention if the pump is to be kept in good running condition (Hart 1990). The specific heat and the rate of change of vapor pressure are two critical physical factors which must be taken into account when designing the pump. A variety of monitoring devices are available to detect pump problems prior to pump failure:

- a thermocouple to monitor can temperature and prevent overheating and destruction of the magnetic field
- a vibration monitor to detect excessive wear of the inner liquid bearings
- installation of a secondary containment seal on the outer bearing housing cover with a leak detector
- a bearing-wear monitor to prevent serious pump failure including a rupture of the can

Monitoring may include motor monitoring devices to shut down the motor if the pump seizes or runs dry, and differential pressure or flow detectors can be provided at the suction and/or discharge.

4.4.11.2 *Compressors*

Compressors run the gamut from small, oilless fractional horsepower reciprocal units to massive turbine driven multistage fan compressors. Typical uses of compressors include: compression of process gas, supply of plant air, compression of air for furnace or fluidized bed combustion, exhaust, ventilation and aeration. A comprehensive discussion of reciprocating and centrifugal compressors can be found in *Perry's Chemical Engineers Handbook*. Several other references are available (Bloch et al. 1982; Faragallah 1985).

Compressors share several design problems that involve safety: potential overpressure and overheat of the gas, vibration, seal leakage, and liquid intake into the compression chamber. All of these can cause material failure in the compressors or its ancillary piping, causing a gas release to the atmosphere. For reciprocating compressors overpressure is a special problem. While centrifugal compressors will reach a maximum pressure when the compressor is deadheaded, the reciprocating compressor can continue to increase pressure until either material failure occurs or the motor stalls and overheats. For this reason reciprocating compressors are equipped with pressure relief valves, but these valves have been known to fail. To prevent these potential problems from occurring the following design features should be considered:

- the use of knockout drums, cyclones, or inlet heaters to prevent liquids from entering the compression chamber;
- the sizing and installation of the proper seals—for large units, this will include seals with a circulating lube oil system, degassing sealpots and piping of the sealpot gases to recovery or treatment;
- the proper design of compressor piping including the proper materials of construction, close set vent and drain lines, and the use of vibration isolation joints;
- the use of properly sized and located pressure relief devices; and
- the use of appropriate alarm and shutdown instrumentation including vibration switches, low/high discharge pressure, engine overspeed, high discharge temperature, and low oil pressure.

Process variables and parameters that determine safe compressor operation and maintenance include: throughput, suction and discharge pressure, rotary speed, gas molecular weight, heat capacity ratio(C_P/C_V), and suction and discharge temperature. In general, during stable operation with a constant rotary speed, the pressure differential across centrifugal and axial compressors decreases with increase in throughput. For a fixed pressure drop, throughput increases with increasing rotary speed. Likewise, for a constant throughput, pressure differential increases with increasing rotary speed.

Potential hazards of high throughput compressor operation, commonly referred to as the "stonewall region," include throughput limits caused by horsepower/torque constraints and insufficient pressure differential to meet the downstream process requirements. Low throughput operation is known as the "surge region." When the throughput falls below a critical value, known as the surge limit, self-sustained oscillations of pressure and flow are induced leading to flow reversal (or slippage inside the compressor) since the compressor wheel fails to impart sufficient kinetic energy to compress gas continuously. Under severe surge, a compressor can exhibit high frequency vibrations and high thrust bearing temperatures which can lead to permanent mechanical damage. A compressor under regulatory control and operating in close proximity to the surge limit can quickly move into surge.

Compressor controls are typically composed of basic process controls, antisurge controls and compressor optimization controls. The first control group is aimed at controlling discharge and suction pressures. The second application employs fast-acting controls to override regulatory controls as the compressor surge region is approached. Finally compressor optimization is typically computer based, high level, supervisory control which minimizes compressor energy utilization with respect to regulatory controls set points subject to process and equipment constraints.

Centrifugal compressors require minimum flow control in order to prevent them from going into a surge condition which might cause mechanical damage or destruction of the compressor. Flow measurement should be in the suction piping because there is a better correlation of suction flow with the surge line on the compressor curve than there is with discharge flow. Care should be taken that sufficient straight pipe run is available for the meter run. The use of low permanent head loss differential producing devices, such as venturi and low loss flow tubes, flow nozzles, or averaging pitot tubes should be considered for this application to minimize energy consumption. The *Instrument Engineers' Handbook* (Liptak 1985) provides a more in-depth discussion of surge control.

It is common practice to manipulate the throughput and pressure differential across the compressor in order to eliminate surge. Venting part of the compressor discharge upon the onset of surge will control surging. However, this is not practical if the discharge is valuable or a pollutant. Alternatively, a portion of the compressor discharge may be recycled back to the compressor suction in order to maintain a minimum compressor flow. Surge encountered during normal operation is most effectively controlled with feedforward (predictive) and override (detector) controls. Surge feedforward control uses a predictive model to anticipate the onset of surge and take corrective action by manipulating compressor recycle flow. Surge override control possesses a surge detector acting on time rate of change of pressure differential and throughput. Upon detecting surge, it must be equipped to open the compressor recycle valve quickly.

A typical feedforward/feedback surge controller calculates the compressor's proximity to surge using a multivariable function that is invariant to changes in conditions such as gas molecular weight, C_P/C_V, suction temperature, etc. Since the feedforward/feedback control loop must be very fast, it employs dedicated, fast response control hardware that eliminates response lag in determining this potentially hazardous surge instability.

4.4.12 Vacuum Equipment Considerations

Vacuum equipment, such as liquid ring pumps, mechanical pumps, and ejectors are used in many chemical process applications. Many of the design considerations used for pressurized equipment also apply to vacuum equipment, but certain specific design safety considerations need to be addressed:

- the system may need to be sealed against the infiltration of air into the vacuum system, which could create a potential flammable or reactive mixture;
- the equipment needs to be designed not only for vacuum but for the highest pressure that the equipment can experience when the vacuum pump fails. If the material in the system is toxic, this may require that the equipment and piping be specified for high pressure as well as vacuum; if less hazardous material is being processed, safety valves, rupture disks, or blowout panels may be used;
- the system should be designed to prevent equipment upstream of the vacuum section from experiencing vacuum if upstream pressure units fail, or the upstream units should also be designed for vacuum; and
- the exhaust of the vacuum system may require treatment to recover or destroy toxic or flammable vapors from the system prior to final release to the atmosphere.
- the liquid used in liquid ring vacuum pumps may also require treatment prior to release to atmosphere (for example, if it absorbs flammable process liquids).
- instrumentation should be provided to control and monitor pressure (vacuum).
- backup of motive steam could cause overpressure in ejectors
- loss of intercondenser cooling medium could lead to overpressure of the system.

Liquid recompressors (in pharmaceutical or chlorine service) may require an external cooler. If a liquid ring compressor absorbs flammable liquids, the vacuum performance may be affected as well as creating a disposal problem. A good discussion of vacuum equipment is presented in the book by Ryans and Roper (1986).

4.4.13 Activated Carbon Adsorbers

Several significant factors can lead to bed fires and explosions in actuated carbon adsorbers. These key factors include: (1) the type of adsorbent, (2) the moisture content of the carbon, (3) vapor flow distribution through the carbon bed, and (4) the type of solvents being adsorbed on the carbon. A brief discussion of these factors is presented below.

Adsorbent Selection. Adsorbents containing impurities which catalyze decomposition or polymerization of the adsorbate should not be used. As an example, metallic salts accelerate the decomposition of halogenated hydrocarbons and ketones. The resulting compounds are more corrosive than the undecomposed adsorbate, and the decomposition reactions can be exothermic, resulting in hot spots and fires. Petroleum-derived pelletized carbons have lower pressure drops, are subject to less attrition, and provide better gas distribution, thus minimizing the potential for hot spot formation.

Moisture Content. Keeping the activated carbon moist reduces the tendency of adsorbed oxygen to react with adsorbed solvent. Furthermore, the heat generated by the adsorption of the solvent will, at least in part, be given up in driving off water vapor rather than in raising the temperature of the carbon in the adsorber. The steaming operation leaves the carbon moist. The moist condition should be maintained during the adsorption portion of the cycle by pre-cooling the solvent-laden incoming air. This reduces the heat input by limiting the adsorption time so that excessive drying cannot occur, by adding humidity to the air–vapor mixture going to the adsorber or by combinations of these methods.

Vapor Flow Distribution. The vapor flow distribution through the carbon bed is another significant factor to consider in the cause of bed fires. To ensure proper vapor flow distribution, the design of the carbon bed including the manways and vapor flow distributor should be considered and checked out to avoid regions of low flow. An average vapor velocity through the bed of 60 to 100 fpm should be used to provide uniform distribution and minimize hot spot formation.

Solvent Type. The solvents being adsorbed on the carbon bed are critical in determining the potential for occurrence of bed fires. Oxidizable organic solvents such as ketones exhibit a self-heating phenomenon known as spontaneous combustion which can lead to bed fires. Ketones, aldehydes, and organic acids are more likely to oxidize in carbon beds than other organic compounds. Higher molecular weight compounds are more reactive. Esters and ethers, which also contain oxygen, however, do not oxidize as readily in carbon beds.

Design and operating practices recommendations are given in Table 4-4. A good discussion of safety aspects of activated carbon adsorption is presented by Akell (1981) and Naujokas (1979).

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Table 4-4 Checklist for Design and Operation of Activated Carbon Adsorbers

The following design and operating practices are recommended to eliminate or minimize carbon bed fires and explosions:

- The preferred location for activated carbon adsorbers is out-of-doors, a minimum of 25 feet (8 m) from important plant buildings or facilities. If they must be located indoors (usually because of weather conditions), they should be installed in detached buildings. If this is not feasible, then they should be located in walled-off rooms in process buildings.
- As a general rule, the inlet concentration of gas stream should be maintained at less than 25% of the Lower Flammable Limit (LFL). This is accomplished by adding dilution air to the process gas stream. It is recommended that the adsorber inlet air header, upstream of both units, contain a continuously operating flammable vapor indicator with audible signal and automatic shutdown and emergency venting interlocks.
- Dilution air is also required to reduce the concentration of the solvent in the solvent-laden air because high solvent concentrations produce a correspondingly large heat of adsorption. When handling reactive compounds such as aldehydes, ketones, and organic acids, solvent-laden concentrations should not exceed 2,500 ppm. For other compounds, such as chlorinated and unsubstituted hydrocarbons, 5,000 ppm is acceptable.
- Steam for desorption should be saturated and kept below 250°F. A steam desuperheater should therefore be provided in the steam line header. It is also very important to have good steam distribution in the adsorber vessel and a steam distributor pipe or sparger should be provided.
- Fixed water fire protection should be provided (FMEC 1986).
- CO monitoring systems should be provided to detect hot spot formation (FMEC 1986).
- Temperature sensing and recording devices with alarm function should be provided on the inlet and outlet of all adsorption vessels to monitor and maintain the process stream temperature below design limits.
- Units should be desorbed, *cooled down* and sealed prior to shutdowns for nights and weekends. The CO analyzers and automatic water spray system should be left operational during shutdowns.
- To minimize the possibility of spontaneous heating during extended shutdowns, one of the following should be done:
  —Remove the carbon
  —Maintain the vapor flow at a minimum of 75% of normal
  —Keep the bed wet (saturated) by periodically spraying it with water or steam.
  —Inert with nitrogen or carbon dioxide. The oxygen content inside the units, including the void spaces in the beds, should not exceed 1% by volume.
- Avoid the use of superheated steam for desorption because its temperature may approach the ignition temperature of adsorbed materials.

- Avoid the use of superheated steam for desorption because its temperature may approach the ignition temperature of adsorbed materials.

- Adsorbers should be designed to provide even distribution of vapor and steam through the carbon bed. Dead spots in the bed will increase the probability of spontaneous heating. Distributors and bed support screens should be fabricated of titanium when adsorbing chlorinated organics as hydrochloric acid can be formed when steam is used as the desorbing medium.
- It is recommended that all activated carbon adsorber vessels should be adequately grounded to avoid possible ignition or shock hazards (Calgon 1977).
- All analyzer sampling lines should be protected from malfunction due to adsorbate-caused fouling
- All valves should be tight-sealing to prevent air and/or steam leaks into the system which could cause reactions and hot spot formation.
- Adsorber vessels should be equipped with overpressure relief devices (rupture disks or safety valves). The basis of sizing should be to relieve the flow of solvent-laden air or steam assuming closed outlet valves
- Flame arresters should be installed at each interfacebetween ambient air and lines containing the solvent-laden air

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- Improvements in polyolefin manufacturing technology have resulted in lower operating pressures (Althaus and Mahalingam 1992; Dale 1987).
- Use of a higher boiling solvent may reduce the normal operating pressure of a process and will also reduce the maximum pressure resulting from an uncontrolled or runaway reaction (Wilday 1991).

2.5 LIMITATION OF EFFECTS

2.5.1 Isolation by Siting/Location

Proper siting of hazardous material processing facilities impacts inherent safety in two ways: by reducing the impact of a release of material and/or energy on surrounding people and equipment and by reducing the potential for one incident to initiate another incident in a nearby facility ("knock-on effects"). Adequate distances between hazardous material unloading, storage, and processing facilities must be maintained. Toxic and flammable materials should be stored as far as possible from the controlled site boundary or fence. Buffer zones between hazardous installations and on-site population concentrations or the surrounding community should be maintained. The size of the required buffer zones can be determined by estimating the consequences of potential credible accident scenarios (Crossthwaite and Crowther 1992). Relocation of manufacturing facilities can eliminate the need for storage and transport of hazardous materials (Wade 1987) or can provide greater separation of hazardous material handling facilities from surrounding population (Orrell and Cryan 1987).

Process siting decisions should include consideration of opportunities to eliminate the transport of hazardous materials and to minimize storage inventories. The three step process of Figure 2-9(A) requires shipment of a hazardous intermediate and also a large storage tank at two separate plant locations. The relocation of the second manufacturing step to Plant 1 eliminates the need for transport of the hazardous material and reduces total inventory. In general, an overall manufacturing process will be inherently safer if hazardous materials are manufactured as needed and immediately consumed at a single manufacturing location.

2.5.2 Batch Reactors

Semi-batch or gradual addition batch processes increase safety by limiting the supply of one or more reactants (Englund 1982, 1990, 1991a; Hendershot 1987; Wilday 1991). For an exothermic reaction, this limits the total energy of reaction available in the reactor at any time. Ideally, the limiting reactant will be consumed rapidly as it is fed, and there will be no buildup of unreacted

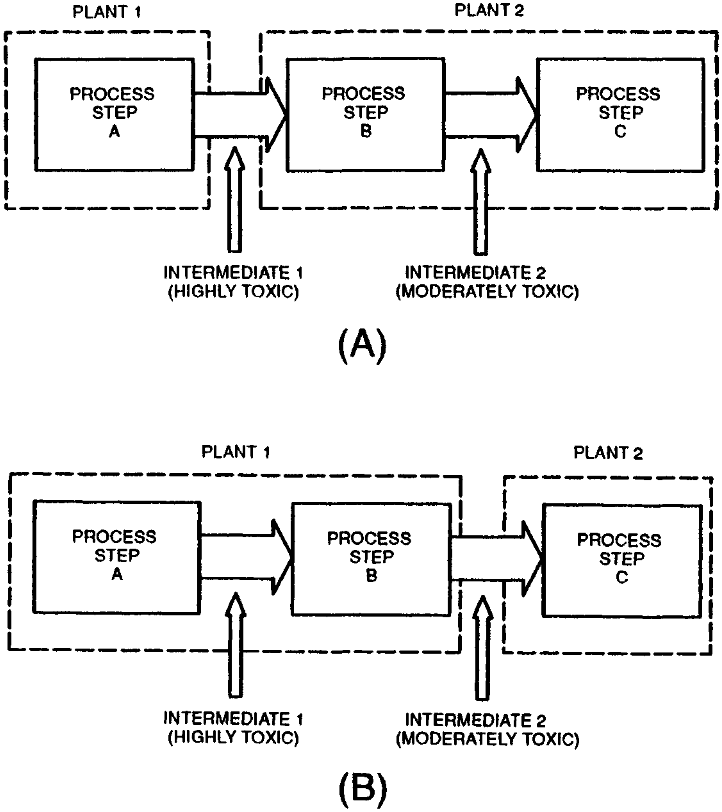

Figure 2-9. Manufacturing strategy options for a chemical. Strategy B is inherently safer because it eliminates the need to transport a hazardous material from Plant 1 to Plant 2.

material. If it is feasible to monitor the progress of the reaction, perhaps by monitoring some physical property of the batch, thus confirming that the limiting reactant is being consumed, process safety is further enhanced. Some suggested techniques include on-line heat balance (Wu 1985) and monitoring of the temperature gradient of the batch (the second derivative of temperature) (Regenass 1984).

A good understanding of the reaction kinetics and thermodynamics is required to establish safe conditions for operation of semi-batch exothermic reactions. A number of experimental methods have been developed for defining safe operating conditions for exothermic batch reactions, and guidelines based on theoretical consideration of reaction thermodynamics and kinetics and reactor heat transfer characteristics have been developed for both batch and semi-batch processes (CCPS in press; Comenges 1991; Grewer et al. 1989; Gygax 1988; Hugo and Steinbach 1986; Steensma and Westererp 1988, 1990).

2.5.3 Limiting the Possible Magnitude of Process Deviations

Processing equipment can be designed to limit the size of possible deviations from desired operating conditions. For example, the rate of addition of a material to a process vessel can be limited by selection of a pump with a maximum capacity lower than safe rate of addition for the process. For a material fed by gravity, maximum feed rate can be limited by sizing the feed pipe such that the maximum possible flow is within safe limits. Restriction orifices are sometimes used to limit flow rate, but pump or pipe sizing is a more reliable approach because a restriction orifice can corrode or be inadvertently left out of the line. It is essential that the design basis for any such mechanical constraints on material flow rate be well documented so that the facility's management of change processes can insure that future modifications do not compromise the design (for example, replacement of a pipe with a larger size, or installation of a different pump impeller).

The total charge to a batch reactor can be limited by using pre-charge or feed tanks of limited capacity. This will make it difficult to get a large overcharge into the reactor, although the potential for charging a material to the reactor twice should still be considered during a hazard evaluation of the process. Charge tanks can be designed using three way valves to make it nearly impossible to transfer material directly from storage to the reactor as shown in Figure 2-10. If a reactor has existing charge tanks which are larger than needed, the effective capacity of the tank can be reduced by providing an overflow at the appropriate level in the tank as shown in Figure 2-11.

Proper selection of heat transfer media can limit the maximum or minimum temperature attainable in a vessel (Gygax 1988; Wilday 1991). Hot water heating limits vessel skin temperature, as well as the maximum vessel contents temperature. If steam heating is used, maximum temperatures can be limited by controlling steam pressure and providing a high pressure relief valve on the steam supply to prevent overheating. For heat sensitive materials, a desuperheater may be needed to avoid excessive temperatures from superheated steam which may be produced by a steam pressure letdown station.

Heat transfer area should be optimized for the task at hand. In many cases this will mean maximizing available heat transfer area per unit of volume of the process equipment, for example, in a batch reactor conducting an exothermic reaction. However, in some cases it may be desirable to limit the amount of heat which can flow into the vessel. For example a material may require some heating to prevent freezing, but may become unstable if overheated. In this case a storage tank would need sufficient heat transfer capacity to prevent freezing, but the heating system should also be designed to minimize the potential for overheating in the event of failure of the tank temperature control system.

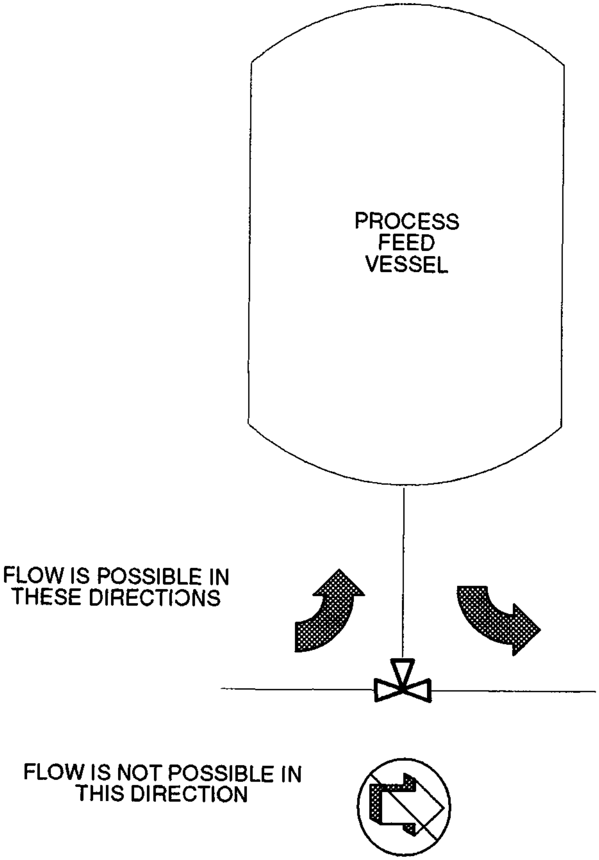

Figure 2-10. A feed tank designed to prevent simultaneously filling and emptying (Hendershot 1987).

2.5.4 Storage Tanks

Harris (1987) provides an excellent set of guidelines for designing a liquefied gas storage facility that minimizes potential vapor cloud hazards.

1. Minimize substrate surface wetted area
2. Minimize pool surface open to atmosphere
3. Reduce heat capacity and/or thermal conductivity of substrate
4. Prevent “slosh over” of containment walls and dikes
5. Avoid rainwater accumulation
6. Prevent passage of liquid spill into drainage system/sewer
7. Prevent free access of wind and air flow to pool surface

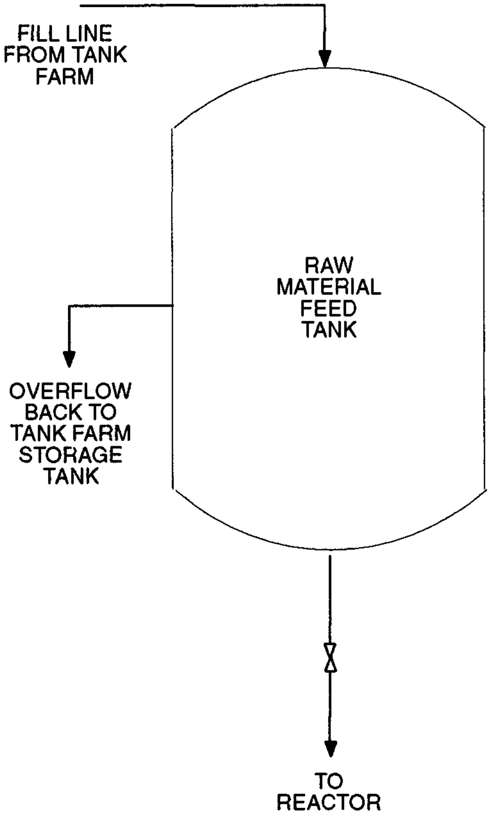

Figure 2-11. A feed tank modified to limit the amount of materials it can hold (Hendershot 1987).

8. Provide gas removal system to destruction or absorption
9. Provide liquid recovery system to storage where possible
10. Avoid direct sunshine on substrate surfaces in hot climates.
11. For flammable materials, direct spills away from the storage vessel to reduce the risk of a boiling liquid expanding vapor explosion (BLEVE) in case of fire (Brown et al. 1987)

Brown et al. (1987) also discuss many of these points and provide examples of how they can be implemented.

Dike design can have a large effect on the size of the hazard zone in case of a material spill. Figure 2-12 shows the flammable vapor cloud resulting from a refrigerated propane spill for three different dike configurations. Clearly the

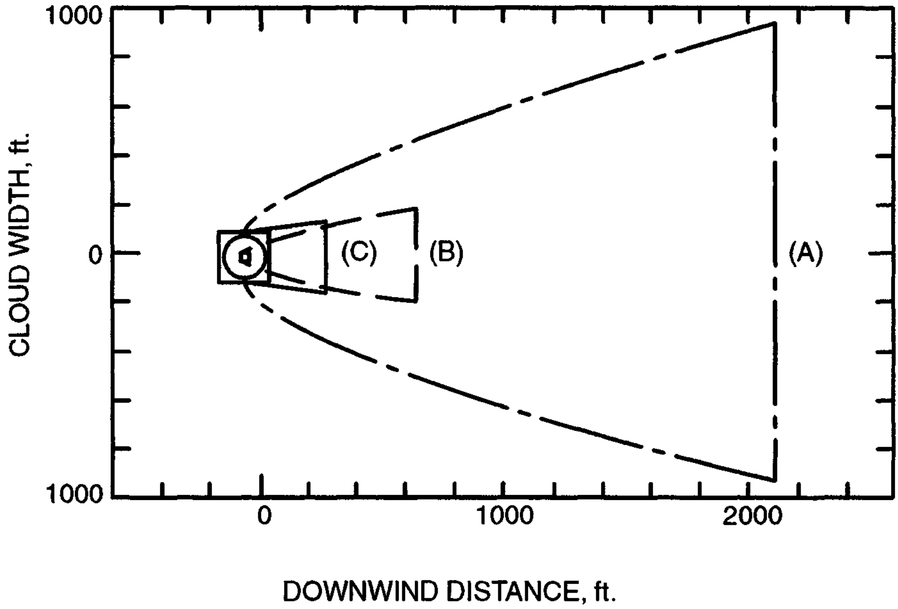

Figure 2-12. Effect of dike design on a flammable vapor cloud from a 250 lb/sec propane spill. (A) Unconfined, (B) confined to a 30 x 30 foot sump inside a 200 x 200 foot dike (Brown et al. 1987)

size of the hazard zone can be dramatically reduced by attention to the design of the dike.

Figure 2-13 is an example of the storage system design based on the above principles. The chlorine storage system in Figure 2-7 also illustrates many of the same principles. Figure 2-14 and Figure 2-15 are examples of storage system designs for flammable liquids and refrigerated flammable gases.

2.5.5 *Containment Buildings*

Containment buildings have been used to limit the impact of loss of containment incidents for many toxic materials, including chlorine (Hendershot 1991b; Puglionesi and Craig 1991, Somerville 1990) and phosgene (*Chemical Week Newswire* 1991; Englund 1991a). Englund (1990) describes the evolution in the design of a phosgene handling facility from an open air plant through various stages of increasing containment, culminating in the design of Figure 2-16. The process is totally enclosed in a large pressure vessel capable of withstanding the overpressure in case of a flammable vapor deflagration inside the containment vessel.

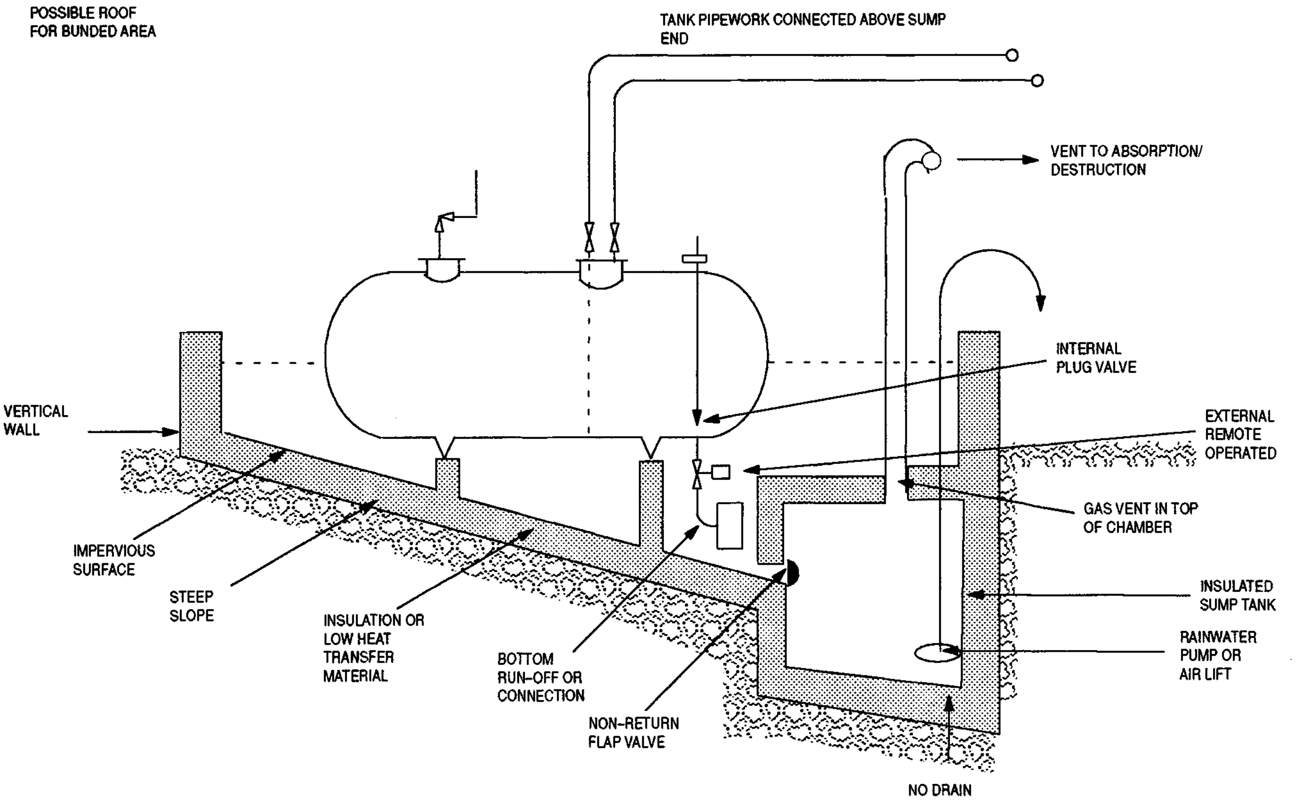

Figure 2-13. A liquefied gas storage facility (Harris 1987).

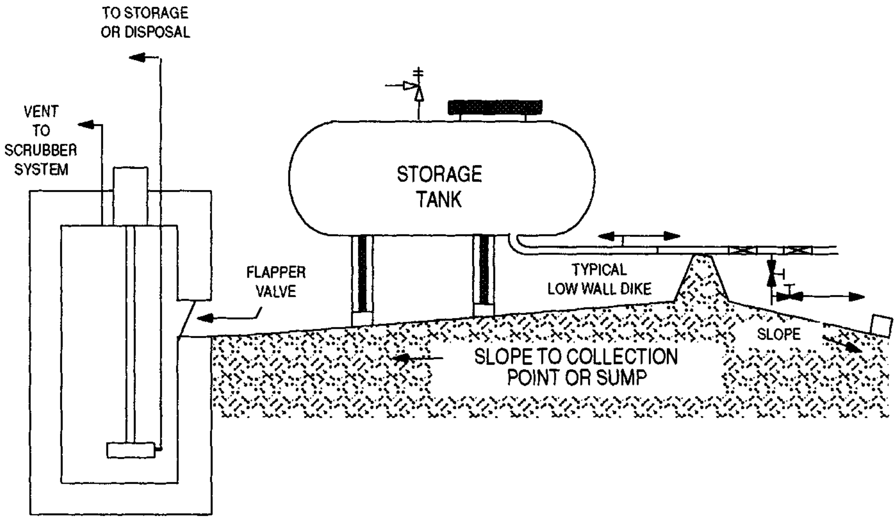

Figure 2-14. A chlorine storage system with collection sump with vapor containment (Puglionesi and Craig 1991)

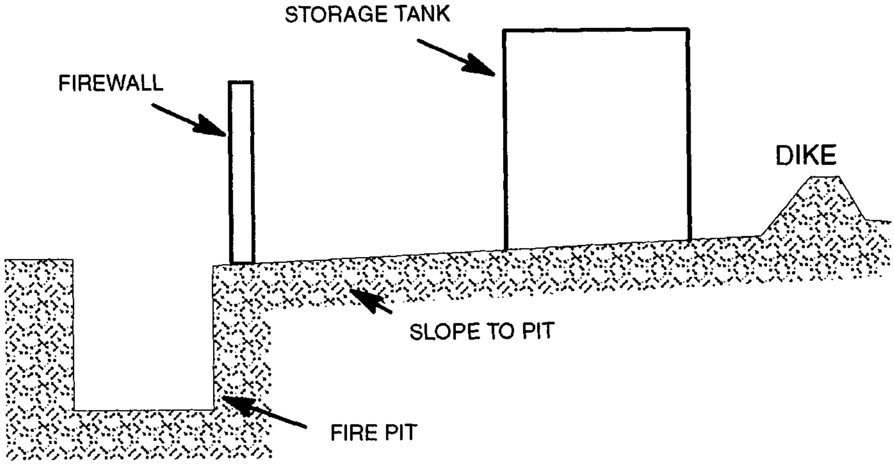

Figure 2-15. A diking design for a flammable liquid (Englund 1991a).

Special provisions must be made to insure worker protection for a process located in a containment building (CCPS 1988a, 1988b). For example, the atmosphere in the containment structure should be monitored for hazardous vapors, operations should be remotely controlled from outside the containment structures, access should be restricted and proper personal protective equipment used when entry into the containment structure becomes necessary.

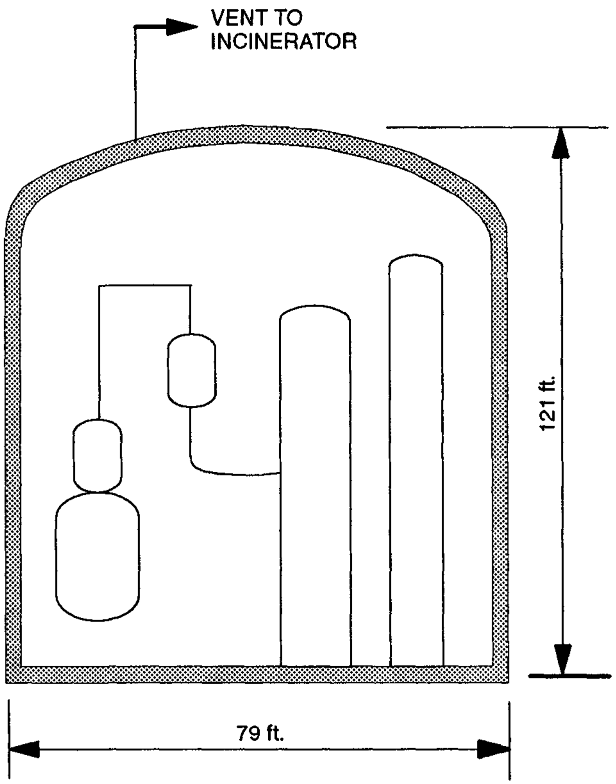

Figure 2-16. A chemical process totally contained in a large pressure vessel (Englund 1991a).

2.6 SIMPLIFICATION AND ERROR TOLERANCE

Plants should be designed to eliminate unnecessary complexity, thus reducing the opportunities for error and misoperation. A simpler plant is generally safer and more cost effective. For example, it is often cheaper to spend a relatively small amount of money to build a higher pressure reactor, rather than a large amount of money for an elaborate system to collect and treat the discharge from the emergency relief system of a reactor designed for a lower maximum pressure. A few examples of simplification and error tolerance are discussed in the following sections. Kletz (1991d) provides many additional examples.

2.6.1 Containment within Process Equipment

In many cases it is possible to design process equipment to be strong enough to contain the maximum or minimum pressure resulting from a process incident.

- *Combustion*—The maximum pressure resulting from a deflagration of a combustible organic dust or flammable organic vapor in air initially at atmospheric pressure is usually less than 120–150 psig. It is often feasible to build equipment strong enough to contain this type of event (Bartknecht 1981; Englund 1991a).
- *Vacuum*—Designing vessels for full vacuum eliminates the risk of vessel collapse due to vacuum. Many storage and transport vessels have been imploded by pumping material out with the vents closed.
- *Runaway Reactions*—Choosing a reactor design pressure sufficiently high to contain the maximum pressure resulting from a runaway reaction eliminates the need for a large emergency relief system. It is essential that the reaction mechanisms, thermodynamics and kinetics *under runaway conditions* are thoroughly understood for the designer to be confident that the design pressure is sufficiently high for all credible reaction scenarios. All causes of a runaway reaction must be understood, and any side reactions and shifts in reaction paths at the elevated temperatures and pressures experienced under runaway conditions must be evaluated. Many laboratory test devices and procedures are available for evaluating the consequences of runaway reactions (CCPS in press; Englund 1991b; Wilday 1991).
- *Containment Vessels*—In many cases, if it is not feasible to contain a runaway reaction within the reactor, it may be possible to pipe the emergency relief device effluent to a separate pressure vessel for containment and subsequent treatment (Speechly et al. 1979).
- *Heat Exchangers*—Design both shell and tube side of heat exchangers to contain the maximum attainable pressure, eliminating the need for pressure relief to protect the exchanger shell in case of tube rupture (Wilday 1991).

2.6.2 Piping

Piping systems should be designed to minimize the use of components that are prone to leak or fail. Sight glasses and flexible connectors such as hoses and bellows should be eliminated wherever possible. Where these devices must be used, they must be specified in detail so they are structurally robust and compatible with process fluids and installed such a way as to minimize the risk of external damage or impact. Proper piping design can often eliminate the need for flexible connections, which should never be used because the pipes don't fit together properly. All welded pipe is preferable to flanged piping, and threaded piping should be avoided for flammable and toxic materials (Englund 1991b; IChemE 1987).

Where flanges are necessary, spiral wound gaskets and flexible graphite type gaskets are preferred. The construction of these gaskets makes them less likely to fail catastrophically resulting in a large leak. Proper installation of spiral wound gaskets, particularly bolting of the flanges, is important in preventing leaks. Improper bolting has been identified as a cause of a significant leak resulting in a fire in an ammonia plant (Kharbanda and Stallworthy 1988; Sotebier and Rall 1986).

Proper design and construction of piping systems is essential to preventing leaks: the Flixborough explosion was caused by an improperly designed section of temporary piping (Marshall 1987). Proper support of piping can minimize stress on flanges, joints and process equipment, therefore reducing leaks. For example, one plant began a program to monitor flange leaks and found that most of the leaks were coming from a few flanges. Improvements to piping layout and support in these areas eliminated most of those leaks. Such a program to identify flanges and other equipment with chronic leakage problems can be useful in identifying areas for improvements in piping design and support.

2.6.3 Liquid Transfer

Liquid transfer systems can be designed to minimize leakage potential. For example, transfer systems that use gravity, pressure, or vacuum require no moving parts or seals. If a pump is needed, centrifugal pumps with double mechanical seals, diaphragm pumps, jet pumps, and various types of sealless pumps may be good choices (Grossel 1990). Sealless pumps greatly reduce the risk of a process fluid leak, but they also introduce some new hazards and concerns that must be considered in the design. These include the potential for overheating and for internal leakage ("Pump" 1987 and 1988; "Reliable" 1992; "Seal-less" 1991; Whalley 1987). Grossel (1990), Englund (1990, 1991b) and Newby and Forth (1991) provide excellent overviews of the advantages and disadvantages of various types of sealless pumps.

2.6.4 Reactor Geometry

Research on safer nuclear power reactors has identified systems that utilize natural convection to provide emergency core cooling rather than relying on pumped cooling water circulation. Other new approaches utilizing reactor geometry, *in situ* moderators, and novel materials of construction can prevent core overheating more reliably and are being researched (Forsberg 1989, 1990; Kletz 1991a).

Similar approaches are applicable in the chemical industry. For example, maleic anhydride is manufactured by partial oxidation of benzene in a fixed catalyst bed tubular reactor. There is a potential for extremely high temperatures due to thermal runaway if feed ratios are not maintained within safe limits. Catalyst geometry, heat capacity and partial catalyst deactivation have been used to create a self-regulatory mechanism to prevent excessive temperature (Raghaven 1992).

2.6.5 Fail Safe Valves

Processes should be reviewed to identify the safest failure position for all electric or pneumatic valves. In most cases process valves should fail closed. Often cooling water valves should fail open. In some cases a valve should fail its last position (in place), remaining open if it is already open and remaining closed if it is already closed. For example, the vent valve on a batch reactor that is vented to a scrubber in several steps, but must be closed for a pressurized reaction step, should probably fail its last position.

Remember that the failure position of a valve refers only to its failure mode in the event of utility failure. A valve can mechanically fail in any position. It is possible for a "fail closed" valve to get stuck in the open position. When doing a process hazard analysis it is important to consider all possible failure positions of a valve, and not only the failure position in the event of utility failure.

2.6.6 Distributed Control Systems

A distributed control system normally uses input and output modules which contain eight, sixteen, or more inputs or outputs. Failure of the module will simultaneously disable a large number of control loops. Attention to the assignment of input/output points to the modules can make the plant more tolerant of a failure of an input or output module. Figures 2–17 and 2–18 provide two examples of how a plant can be made more tolerant of a module failure by rearranging the assignment of inputs and or outputs.

2.6.7 Separation of Process Steps

A multistep batch process can be carried out in a single vessel, or in several vessels, each optimized for a single processing step. The complexity of the batch reactor in Figure 2-19, with many potential process fluid and utility interactions, can be greatly reduced by dividing the same process into three vessels as shown in Figure 2-20.

2.7 INHERENT SAFETY CHECKLIST

Appendix 2A at the end of this chapter provides a checklist for use in evaluating the inherent safety of a process. Kletz (1991d) provides a more extensive checklist. *Guidelines for Hazard Evaluation Procedures, Second Edition*

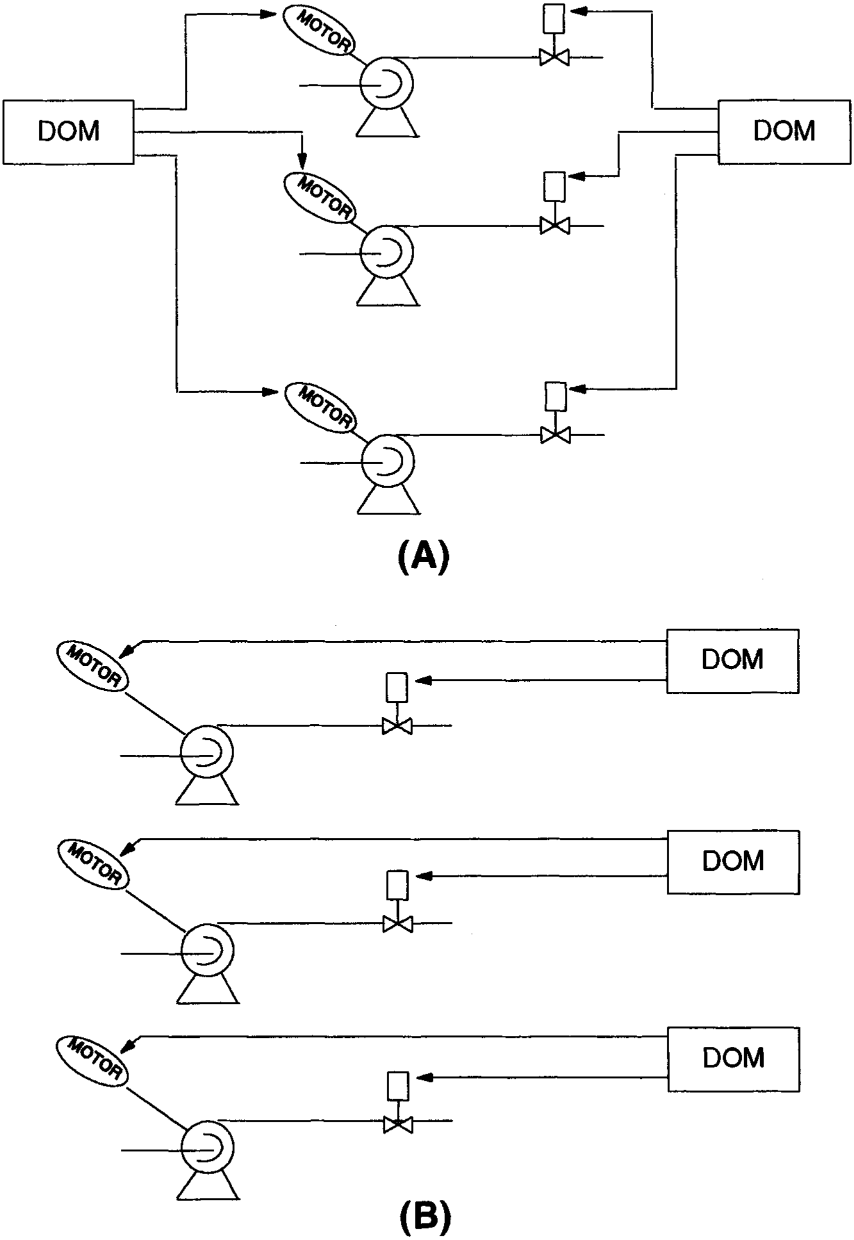

Figure 2-17. Alternate arrangements for digital output signals from a DCS Digital Output Mode (DOM) to a group of pumps. Arrangement (B) is more failure tolerant (Frank and Zodeh 1991).

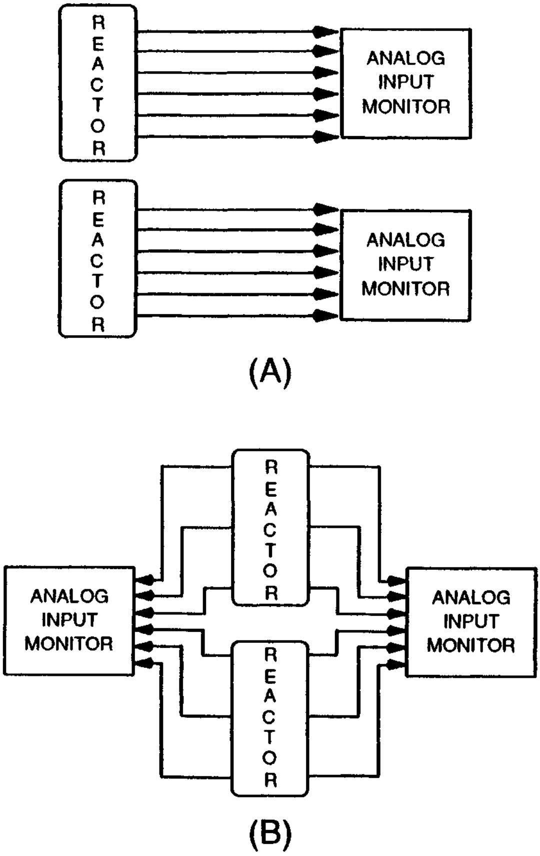

Figure 2-18. (A)Poor distribution of analog signals to a DCS analog input module (AIM). (B) An improved signal distribution, which is more failure tolerant (Frank and Zodeh 1991).

with Worked Examples (CCPS 1992) provides a very extensive general process safety checklist, and many items on the checklist address inherent safety issues.

2.8 SUMMARY—A FABLE

In Aesop's fable "The Crow and the Pitcher" (Avenel 1973), a crow, dying of thirst, comes upon a pitcher partly filled with water. Unfortunately the level of water in the pitcher is so low that the crow is unable to reach it despite strenuous efforts. The crow then attempts to overturn the pitcher so he might get a little water, but he is not strong enough. After pondering the situation

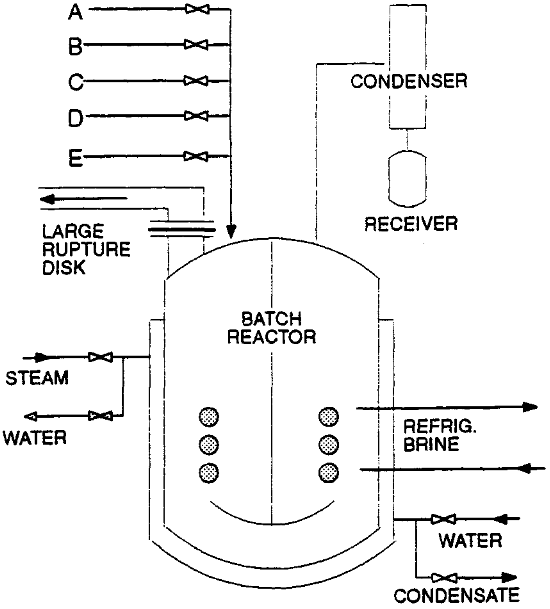

Figure 2-19. A complex batch reactor conducting a multistep process (Hendershot 1987).

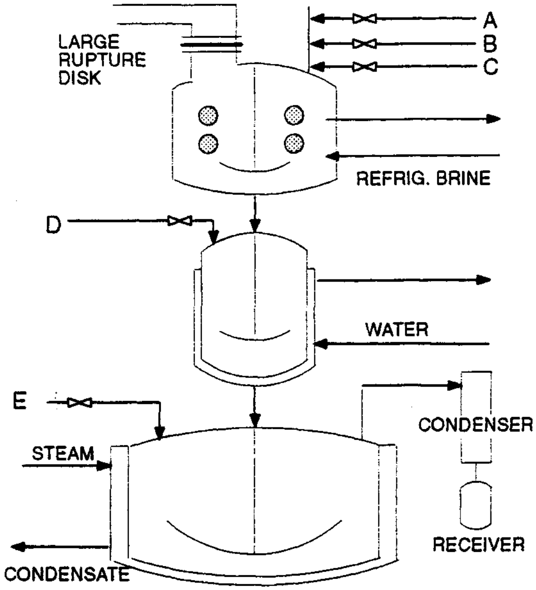

Figure 2-20. The same process as Figure 2-19, conducted in a series of simpler vessels (Hendershot 1987).

for a while, the crow began to drop small pebbles into the pitcher, and eventually was able to raise the water level to the brim and thus quench his thirst. The moral of the story is:

What we cannot compass by force, we may by invention and industry.

The process design engineer is often in the same position as the crow in Aesop's fable. Approaches to safe plant design that rely on force—safety interlocks, procedures, protective equipment and emergency plans for an inherently hazardous process—may not be able to satisfy the design engineer's desire for a reliable, low risk plant. Instead, a search for creative and innovative approaches to process design may identify ways of eliminating the hazard altogether, or of minimizing the potential impacts on people, property and the environment. A thought by Gygax (1988) with respect to reactor design expresses this approach (emphasis added): "It is the art of the Chemical Engineer that allows him to apply and combine *basic scientific and engineering principles* elegantly to realize an optimal process design."

APPENDIX 2A INHERENT PROCESS SAFETY CHECKLIST[1]

Elimination/Substitution

- Is it possible to completely eliminate hazardous raw materials, process intermediates, or by-products by using an alternative process or chemistry?
- Is it possible to completely eliminate in-process solvents by changing chemistry or processing conditions?
- Is it possible to substitute less hazardous raw materials?
  —Noncombustible rather than flammable solvents
  —Less volatile raw materials
  —Less toxic raw materials
  —Less reactive raw materials
  —More stable raw materials
- Is it possible to substitute less hazardous final product solvents?
- For equipment containing materials that become unstable at elevated temperature or freeze at low temperature, is it possible to use heating and cooling media that limit the maximum and minimum temperatures attainable?

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[1] From Hendershot 1991a

Safer Conditions

- Can the supply pressure of raw materials be limited to less than the working pressure of the vessels they are delivered to?
- Can reaction conditions (temperature, pressure) be made less severe by using a catalyst, or by using a better catalyst?
- Can the process be operated at less severe conditions? If this results in lower yield or conversion, can raw material recycle compensate for this loss?
- Is it possible to dilute hazardous raw materials to reduce the hazard potential? For example:
  —Aqueous ammonia instead of anhydrous
  —Aqueous HCl instead of anhydrous
  —Sulfuric acid instead of oleum
  —Dilute nitric acid instead of concentrated fuming nitric acid
  —Wet benzoyl peroxide instead of dry

Equipment Design

- Can equipment be designed with sufficient strength to totally contain the maximum pressure generated, even if the "worst credible event" occurs?
- Is all equipment designed to totally contain the materials that might be present inside at ambient temperature or the maximum attainable process temperature? (For example, don't rely on the proper functioning of external systems such as refrigeration systems to control temperature such that vapor pressure is less than equipment design pressure.)
- Can several process steps be carried out in separate processing vessels rather than a single multipurpose vessel? This reduces complexity and the number of raw materials, utilities, and auxiliary equipment connected to a specific vessel, thereby reducing the potential for hazardous interactions.
- Can equipment be designed such that it is difficult or impossible to create a potential hazardous situation due to an operating error (for example, by opening an improper combination of valves)?

Inventory Reduction

- Have all in-process inventories of hazardous materials in storage tanks been minimized?
- Are all of the proposed in-process storage tanks really needed?
- Has all processing equipment handling hazardous materials been designed to minimize inventory?

- Is process equipment located to minimize length of hazardous material piping?
- Can piping sizes be reduced to minimize inventory?
- Can other types of unit operations or equipment reduce material inventories? For example:
  —Wiped film stills in place of continuous still pots (distillation columns)
  —Centrifugal extractors in place of extraction columns
  —Flash dryers in place of tray dryers
  —Continuous reactors in place of batch
  —Plug flow reactors in place of continuous stirred tank reactors
  —Continuous in-line mixers in place of mixing vessels
- Is it possible to feed hazardous materials (for example, chlorine) as a gas instead of liquid, to reduce pipeline inventories?
- Is it possible to generate hazardous reactants *in situ* from less hazardous materials, minimizing the need to store or transport large quantities of hazardous materials?

Location/Siting

- Can process units be located to reduce or eliminate adverse impacts from other adjacent hazardous installations?
- Can process units be located to eliminate or minimize:
  —Off-site impacts?
  —Impacts to employees on-site?
  —Impacts on other process or plant facilities?
- Can the plant site be chosen to minimize the need for transportation of hazardous materials and to use safer transport methods and routes?
- Can a multistep process, where the steps are done at separate sites, be divided up differently to eliminate the need to transport hazardous materials?

Waste Minimization

- Is it possible to recycle waste streams to reduce the need for waste treatment?
- Have all solvents, diluents or other reactant "carriers" been reduced to minimum quantities? Can they be eliminated entirely?
- Have all washing operations been optimized to minimize the amount of wash water? Can countercurrent washing improve efficiently?
- Can valuable by-products be recovered from waste streams? Can the process be modified to increase the concentration of by-products making recovery more feasible?

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2.9.2 *Suggested Reading*

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Guidelines for Engineering Design for Process Safety

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It is sincerely hoped that the information presented in this volume will lead to an even more impressive safety record for the entire industry; however, neither the American Institute of Chemical Engineers, its consultants, CCPS and/or its sponsors, its subcommittee members, their employers, nor their employers' officers and directors warrant or represent, expressly or implied, the correctness or accuracy of the content of the information presented in this conference, nor can they accept liability or responsibility whatsoever for the consequences of its use or misuse by anyone.

PREFACE

The Center for Chemical Process Safety (CCPS) was established in 1985 by the American Institute of Chemical Engineers (AIChE) for the express purpose of assisting the Chemical and Hydrocarbon Process Industries in avoiding or mitigating catastrophic chemical accidents. To achieve this goal, CCPS has focused its work on four areas:

- establishing and publishing the latest scientific and engineering practices (not standards) for prevention and mitigation of incidents involving toxic and/or reactive materials;
- encouraging the use of such information by dissemination through publications, seminars, symposia and continuing education programs for engineers;
- advancing the state-of-the-art in engineering practices and technical management through research in prevention and mitigation of catastrophic events; and
- developing and encouraging the use of undergraduate education curricula which will improve the safety knowledge and consciousness of engineers.

The current book, *Guidelines for Engineering Design for Process Safety*, is the result of a project begun in 1989 in which a group of volunteer professionals representing major chemical, pharmaceutical and hydrocarbon processing companies, worked with engineers of the Stone & Webster Engineering Corporation. The intent was to produce a book that presents the process safety design issues needed to address all stages of the evolving design of the facility. This book discusses the impact that various engineering design choices will have on the risk of a catastrophic accident, starting with the initial selection of the process and continuing through its final design. This book is concerned with engineering design for process safety. It does not focus on operations, maintenance, transportation, storage or personnel safety issues, although improved process safety can benefit each area. Detailed engineering designs are outside the scope of the work, but the authors have provided an extensive guide to the literature to assist the designer who wishes to go beyond safety design philosophy to the specifics of a particular design.

The book has been organized so as to treat basic design issues first. The first design question addressed is the issue of "Inherently Safer Plants." This reflects the authors' strong belief that the optimum way to achieve process safety is to design safety into the initial design. The latter portion of the book moves to reducing risk through the use of passive and then active devices to prevent and mitigate catastrophic events.

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GLOSSARY

Administrative Controls: Procedural mechanisms, such as lockout/tagout procedures, for directing and/or checking human performance on plant tasks.

Autoignition Temperature: The autoignition temperature of a substance, whether solid, liquid, or gaseous, is the minimum temperature required to initiate or cause self-sustained combustion, in air, with no other source of ignition.

Basic Event: An event in a fault tree that represents the lowest level of resolution in the model such that no further development is necessary (e.g., equipment item failure, human failure, or external event).

Basic Process Control System (BPCS): The control equipment which is installed to support normal production functions.

Boiling-Liquid-Expanding-Vapor Explosion (BLEVE): A type of rapid phase transition in which a liquid contained above its atmospheric boiling point is rapidly depressurized, causing a nearly instantaneous transition from liquid to vapor with a corresponding energy release. A BLEVE is often accompanied by a large fireball if a flammable liquid is involved, since an external fire impinging on the vapor space of a pressure vessel is a common BLEVE scenario. However, it is not necessary for the liquid to be flammable to have a BLEVE occur.

Bonding: The permanent joining of metallic parts to form an electrically conductive path which will assure electrical continuity and the capacity to safely conduct any current likely to be imposed.

Catastrophic Incident: An incident involving a major uncontrolled emission, fire or explosion with an outcome effect zone that extends offsite into the surrounding community.

Combustible: A term used to classify certain liquids that will burn on the basis of flash points. Both the National Fire Protection Association (NFPA) and the Department of Transportation (DOT) define "combustible liquids" as having a flash point of 100°F (37.8°C) or higher. See also, "Flammable." *Importance:* Combustible liquid vapors do not ignite as easily as flammable liquids; however, combustible vapors can be ignited when heated and must be handled with caution. Class II liquids have flash points at or above 100°F, but below 140°F. Class III liquids are subdivided into two subclasses.

Class IIIA: Those having flash points at or above 140°F but below 200°F.
Class IIIB: Those having flash points at or above 200°F.

Common Mode Failure: An event having a single external cause with multiple failure effects which are not consequences of each other.

Continuous Reactors: Reactors that are characterized by a continuous flow of reactants into and a continuous flow of products from the reaction system. Examples are the Plug Flow Reactor and the Continuous-flow Stirred Tank Reactor.

Deflagration: The chemical reaction of a substance in which the reaction front advances into the unreacted substance at less than sonic velocity. Where a blast wave is produced that has the potential to cause damage, the term *explosive deflagration* may be used.

Detonation: A release of energy caused by the extremely rapid chemical reaction of a substance in which the reaction front advances into the unreacted substance at equal to or greater than sonic velocity.

Design Institute for Emergency Relief Systems (DIERS): Institute under the auspices of the American Institute of Chemical Engineers founded to investigate design requirements for vent lines in case of two-phase venting.

Design Institute for Physical Property Data (DIPPR): Institute under the auspices of the American Institute of Chemical Engineers, founded to compile a database of physical, thermodynamic, and transport property data for most common chemicals.

Distributed Control System: A system which divides process control functions into specific areas interconnected by communications (normally data highways) to form a single entity. It is characterized by digital controllers and typically by central operation interfaces.

Distributed control systems consist of subsystems that are functionally integrated but may be physically separated and remotely located from one another. Distributed control systems generally have at least one shared function within the system. This may be the controller, the communication link or the display device. All three of these functions may be shared.

A system of dividing plant or process control into several areas of responsibility, each managed by its own Central Processing Unit, with the whole interconnected to form a single entity usually by communication buses of various kinds.

Dow Fire and Explosion Index (F&EI): A method (developed by Dow Chemical Company) for ranking the relative fire and explosion risk associated with a process. Analysts calculate various hazard and explosion indexes using material characteristics and process data.

Emergency Shutdown (ESD) System: The safety control system which overrides the action of the basic control system when predetermined conditions are violated.

Equipment Reliability: The probability that, when operating under stated environment conditions, process equipment will perform its intended function adequately for a specified exposure period.

Explosion:A release of energy that causes a pressure discontinuity or blast wave.

Fail-Safe: Design features which provide for the maintenance of safe operating conditions in the event of a malfunction of control devices or an interruption of an energy source (e.g., direction of failure of a motor operated valve on loss of motive power).

Features incorporated for automatically counteracting the effect of an anticipated possible source of failure. A system is fail-safe if failure of a component, signal, or utility initiates action that return the system to a safe condition.

Failure: An unacceptable difference between expected and observed performance.

Fireball: The atmospheric burning of a fuel-air cloud in which the energy is mostly emitted in the form of radiant heat. The inner core of the fuel release consists of almost pure fuel whereas the outer layer in which ignition first occurs is a flammable fuel-air mixture. As buoyancy forces of the hot gases begin to dominate, the burning cloud rises and becomes more spherical in shape.

Fire Point: The temperature at which a material continues to burn when the ignition source is removed.

Flammability Limits: The range of gas or vapor amounts in air that will burn or explode if a flame or other ignition source is present. *Importance:* The range represents an unsafe gas or vapor mixture with air that may ignite or explode. Generally, the wider the range the greater the fire potential. See also Lower Explosive Limit/Lower Flammable Limit and Upper Explosive Limit/Upper Flammable Limit.

Flammable: A "Flammable Liquid" is defined by NFPA as a liquid with a flash point below 100°F (37.8°C)

Importance: Flammable liquids provide ignitable vapor at room temperatures and must be handled with caution. Precautions such as bonding and grounding must be taken. Flammable liquids are: Class I liquids and may be subdivided as follows:

Class 1A: Those having flash points below 73°F and having a boiling point below 100°F

Class 1B: Those having flash points below 73°F and having a boiling point at or above 100°F.

Flash Fire: The combustion of a flammable vapor and air mixture in which flame passes through that mixture at less than sonic velocity, such that negligible damaging overpressure is generated.

Flash Point: The lowest temperature at which vapors above a liquid will ignite. The temperature at which vapor will burn while in contact with an ignition source, but which will not continue to burn after the ignition source is removed. There are several flash point test methods, and flash points may vary for the same material depending on the method used. Consequently, the test method is indicated when the flash point is given. A closed cup type test is used most frequently for regulaory purposes. *Importance:* The lower the flash point temperature of a liquid, the greater the chance of a fire hazard.

Frothover: When water is present or enters a tank containing hot viscous oil, the sudden conversion of water to steam causes a portion of the tank contents to overflow.

Hazard: An inherent chemical or physical characteristic that has the potential for causing damage to people, property, or the environment. In this document it is typically the combination of a hazardous material, an operating environment, and certain unplanned events that could result in an accident.

Hazard Analysis: The identification of undesired events that lead to the materialization of a hazard, the analysis of the mechanisms by which these undesired events could occur and usually the estimation of the consequences.

Hazard and Operability Study (HAZOP): A systematic qualitative technique to identify process hazards and potential operating problems using a series of guide words to study process deviations.

A HAZOP is used to question every part of the process to discover what deviations from the intention of the design can occur and what their causes and consequences may be. This is done systematically by applying suitable guide words. This is a systematic detailed review technique for both batch or continuous plants which can be applied to new or existing processes to identify hazards.

Hazardous Material: In a broad sense, any substance or mixture of substances having properties capable of producing adverse effects of the health or safety of human beings. Material presenting dangers beyond the fire problems relating to flash point and boiling point. These dangers may arise from but are not limited to toxicity, reactivity, instability, or corrosivity.

Human Factors: A discipline concerned with designing machines, operations, and work environments so that they match human capabilities, limitations, and needs. Includes any technical work (engineering, procedure writing, worker training, worker selection, etc.) related to the human factor in operator–machine systems.

Inert Gas: A noncombustible, nonreactive gas that renders the combustible material in a system incapable of supporting combustion.

Inherently Safe: A system is inherently safe if it remains in a nonhazardous situation after the occurrence of nonacceptable deviations from normal operating conditions.

Interlock System: A system that detects out-of-limits or abnormal conditions or improper sequences and either halts further action or starts corrective action.

Intrinsically Safe: Equipment and wiring which is incapable of releasing sufficient electrical or thermal energy under normal or abnormal conditions to cause ignition of a specific hazardous atmospheric mixture or hazardous layer.

Likelihood: A measure of the expected frequency with which an event occurs. This may be expressed as a frequency (e.g., events per year), a probability of occurrence during a time interval (e.g., annual probability), or a conditional probability (e.g., probability of occurrence, given that a precursor event has occurred).

Lower Explosive Limit (LEL) or Lower Flammable Limit (LFL): The lowest concentration of a vapor or gas (the lowest percentage of the substance in air) that will produce a flash of fire when an ignition source (heat, arc, or flame) is present. See also Upper Explosive Limit or Upper Flammable Limit.

Importance: At concentration lower than the LEL/LFL, the mixture is too "lean" to burn.

Mitigation: Lessening the risk of an accident event sequence by acting on the source in a preventive way by reducing the likelihood of occurrence of the event, or in a protective way by reducing the magnitude of the event and/or the exposure of local persons or property.

Oxidant: Any gaseous material that can react with a fuel (either gas, dust or mist) to produce combustion. Oxygen in air is the most common oxidant.

Pool Fire: The combustion of material evaporating from a layer of liquid at the base of the fire.

Process Safety: A discipline that focuses on the prevention of fires, explosions, and accidental chemical releases at chemical process facilities. Excludes classic worker health and safety issues involving working surfaces, ladders, protective equipment, etc.

Programmable Electronic System (PES): A system based on a computer connected to sensors and/or actuators in a plant for the purpose of control, protection or monitoring (includes various types of computers, programmable logic controllers, peripherals, interconnect systems, instrument distributed control system controllers, and other associated equipment).

Programmable Logic Controller (PLC): A microcomputer-based control device. A solid-state control system which receives inputs from user-supplied control devices such as switches and sensors, implements them in a precise pattern determined by instructions stored in the PLC memory, and provides outputs for control or user-supplied devices such as relays and motor starters.

Purge Gas: A gas that is continuously or intermittently added to a system to render the atmosphere nonignitable. The purge gas may be inert or combustible.

Quenching: Rapid cooling from an elevated temperature, e.g., severe cooling of the reaction system in a short time (almost instantaneously), "freezes" the status of a reaction and prevents further decomposition.

Runaway: A thermally unstable reaction system which shows an accelerating rate of temperature increase and reaction rate.

Safety Layer: A system or subsystem that is considered adequate to protect against a specific hazard. The safety layer

—is totally independent of any other protective layers
—cannot be compromised by the failure of another safety layer
—must have acceptable reliability
—must be approved according to company policy and procedures
—must meet proper equipment classification
—may be a noncontrol alternative (i.e., chemical, mechanical)
—may require diverse hardware and software packages
—may be an administrative procedure

Unconfined Vapor Cloud Explosion (UCVE): Explosive oxidation of a vapor cloud in a nonconfined space (i.e., not in vessels, buildings, etc.). The flame speed may accelerate to high velocities and produce significant blast overpressure. Vapor cloud explosions in densely packed plant areas (pipe lanes, units, etc.) may show accelerations in flame speeds and intensification of blast.

Upper Explosive Limit (UEL) or Upper Flammable Limit (UFL): The highest concentration of a vapor or gas (the highest percentage of the substance in air) that will produce a flash of fire when an ignition source (heat, arc, or flame) is present. See also Lower Explosive Limit or Lower Flammable Limit.

Importance: At concentrations higher then the UEL, the mixture is too "rich" to burn.

Vapor Density: The weight of a vapor or gas compared to the weight of an equal volume of air; an expression of the density of the vapor or gas. Materials lighter than air have vapor densities less than 1.0 (example: acetylene, methane, hydrogen). Materials heavier than air (examples: propane, hydrogen sulfide, ethane, butane, chlorine, sulfur dioxide) have vapor densities greater than 1.0.

Importance: All vapors and gases will mix with air, but the lighter materials will tend to rise and dissipate (unless confined). Heavier vapors and gases are likely to concentrate in low places —along or under floors, in sumps, sewers and manholes, in trenches and ditches—and can travel great distances undetected where they may create fire or health hazards.

Vapor Pressure: The pressure exerted by a vapor above its own liquid.
Importance: The higher the vapor pressure, the easier it is for a liquid to evaporate and fill the work area with vapors which can cause health or fire hazards.

Venting: Emergency flow of vessel contents out the vessel. The pressure is reduced by venting, thus avoiding a failure of the vessel by overpressurization. The emergency flow can be one-phase or multiphase, each of which results in different flow and pressure characteristics.

ACRONYMS AND ABBREVIATIONS

ACGIH	American Conference of Government Industrial Hygienists
ACI	American Concrete Institute
ACS	American Chemical Society
AGA	American Gas Association
AIChE	American Institute of Chemical Engineers
AIHA	American Industrial Hygiene Association
AISC	American Institute of Steel Construction, Inc.
AISI	American Iron and Steel Institute
AIT	Autoignition temperature
ANSI	American National Standards Institute
APC	Air pollution control
APFA	American Pipe Fittings Association
API	American Petroleum Institute
ASM	American Society for Metals
ASME	American Society of Mechanical Engineers
ASSE	American Society of Safety Engineers
ASNT	American Society of Nondestructive Testing
ASTM	American Society for Testing and Materials
AWS	American Welding Society
BLEVE	Boiling liquid expanding vapor explosion
BPCS	Basic Process Control System
Btu	British Thermal Units
BTX	Benzene, toluene and xylene
CAA	Clean Air Act
CAAA	Clean Air Act Amendments
CCPS	Center for Chemical Process Safety
CEM	Continuous Emissions Monitor
CERCLA	Comprehensive Environmental Response, Compensation, and Liability Act
CFR	Code of Federal Regulations
CGA	Compressed Gas Association
CIA	Chemical Industries Association
CMA	Chemical Manufacturers Association
COT	Coil outlet temperature
CRT	Cathode ray tube
CSTR	Continuous-flow stirred-tank reactor
CWA	Clean Water Act

DAF	Dissolved Air Flotation
dBA	A-weighted decibel level
DCS	Distributed control system
DIERS	Design Institute for Emergency Relief Systems
DIPPR	Design Institute for Physical Property Data
DOT	Department of Transportation
EEGL	Emergency exposure guidance level
EJMA	Expansion Joint Manufacturers Association, Inc.
EPA	Environmental Protection Agency
EPRI	Electric Power Research Institute
ERPG	Emergency Response Planning Guideline
ESCIS	Expert Commission for Safety in the Swiss Chemical Industry
ESD	Emergency shutdown
ET	Eddy Current Testing
FBIC	Flexible Intermediate Bulk Containers
F&EI	Fire and Explosion Index
FMEC	Factory Mutual Engineering Corporation
FRP	Fiber reinforced plastic
GFCI	Ground fault current interrupter
GPM	Gallons per minute
GSPA	Gas Processors Suppliers Association
HAZOP	Hazard and operability study
HEI	Heat Exchanger Institute
hp	Horsepower
HSE	Health and Safety Executive
HVAC	Heating, ventilation, and air conditioning
IChemE	The Institution of Chemical Engineers
ICI	Imperial Chemical Industries
IEEE	Institute of Electrical and Electronics Engineers
IDLH	Immediately Dangerous to Life or Health
IGC	Intergranular corrosion
IRI	Industrial Risk Insurers
ISA	Instrument Society of America
ISGOTT	International Safety Guide for Oil Tankers and Terminals
ISO	International Standards Organization
kA	Kiloampere
kV	Kilovolt
LEL	Lower explosive limit
LFL	Lower flammable limit
LNG	Liquified natural gas
LOC	Limiting oxidant concentration
LPG	Liquified petroleum gas
mA	Milliampere

MCC	Motor control center
MIE	Minimum ignition energy
mJ	Millijoule
MSDS	Material safety data sheet
MSS	Manufacturers Standardization Society
MT	Magnetic particle testing
NACE	National Association of Corrosion Engineers
NAS	National Academy of Science
NBIC	National Board Inspection Code
NEC	National Electrical Code
NEMA	National Electrical Manufacturers Association
NESC	National Electrical Safety Code
NDE	Nondestructive examinatio
NFPA	National Fire Protection Association
NIOSH	National Institute of Occupational Safety and Health
NPCA	National Paint and Coatings Association
NPDES	National Pollutant Discharge and Elimination System
NPSH	Net positive suction head
NRC	National Research Council
NSPS	New Source Performance Standards
NTIAC	Nondestructive Testing Information Analysis Center
OSHA	Occupational Safety and Health Administration
PCB	Polychlorinated biphenyl
PEL	Permissible exposure limit
PES	Programmable Electronic System
PFD	Process Flow Diagram
PLC	Programmable logic controller
P&ID	Piping and instrumentation diagram
PHA	Process Hazard Analysis
PID	Proportional Integral derivative
POT	Pass outlet temperature
ppm	Parts per million
pS	PicoSiemen
PSA	Pressure swing adsorption
PT	Liquid penetrant testing
PVRV	Pressure-vacuum relief valve
RCRA	Resource Conservation and Recovery Act
RP	Recommended Practice
RT	Radiographic testing
RTD	Resistance temperature detector
SCBA	Self-contained breathing apparatus
SCC	Stress corrosion cracking
scf	Standard cubic foot

SCR	Silicon conductor rectifier
SAE	Society of Automotive Engineers
SIS	Safety Interlock System
SPCC	Spill Prevention Control and Countermeasures
SPEGL	Short-term public emergency guidance level
SPFE	Society of Fire Protection Engineers
SSPC	Steel Structures Painting Council
TEMA	Tubular Exchanger Manufacturer Association
TLV	Threshold limit value
TOC	Total organic compounds
TSCA	Toxic Substance Control Act
UBC	Uniform Building Code
UEL	Upper Explosive Limit
UFL	Upper Flammable Limit
UL	Underwriters Laboratory Inc.
UPS	Uninterruptible power supply
UT	Ultrasonic testing
VOC	Volatile organic compound
VP	Vapor Pressure
WEEL	Workplace environmental exposure limit

16

FIRE PROTECTION

16.1 INTRODUCTION

The intent of fire protection in a chemical facility is to minimize the loss of life, property, and business due to fire and/or explosion. The design and extent of fire protection systems depend primarily upon the types and degree of hazards involved. The peril of fire when processing, handling, and storing flammable and combustible materials is very serious in light of historical fire losses in the processing industry. Loss data for the hydrocarbon processing industries (Norstrom 1992) indicate that the frequency and size of losses is increasing (Figures 16-1, 16-2).

Many possible reasons are suggested for the trends, including

- Larger plants
- Older Equipment
- Increased congestion through debottlenecking, installation of energy conservation equipment, and environmental concerns.
- Longer production runs between maintenance turnarounds
- Change of ownership
- Changes in environmental regulations and toxic material clean-up requirements.

Other possible reasons include

- Reductions in staff
- Increased mobility of operators and managers

The possible consequences from a fire include loss of life, property, raw materials and products in addition to the detrimental effects on production schedules, economics, and public opinion. In an effort to minimize the economic and social impact of a fire, appropriate equipment and fire fighting techniques should be utilized. Fires occur even though efforts are made to control sources of fuel and ignition. Therefore adequate fire fighting facilities and emergency procedures must be in-place and utilized effectively.

Contamination of the environment by toxic chemicals and combustion products has become a major concern for facilities handling chemicals. The use of fire protection water, applied through sprinklers, water spray systems, monitor nozzles or hand lines can spread the contaminants, polluting the soil and groundwater supplies. The fire itself may create toxic combustion products and unburned materials.

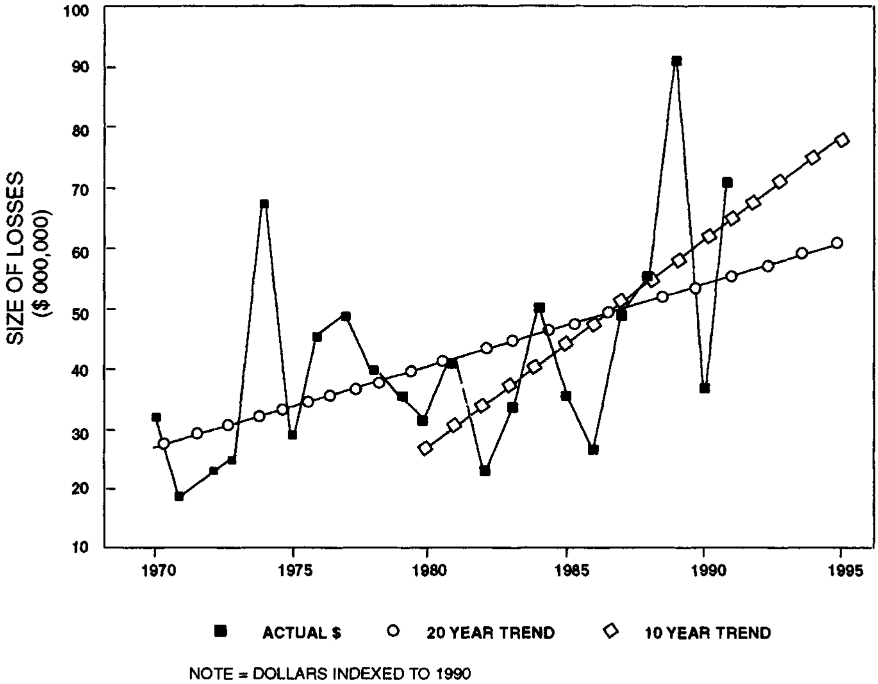
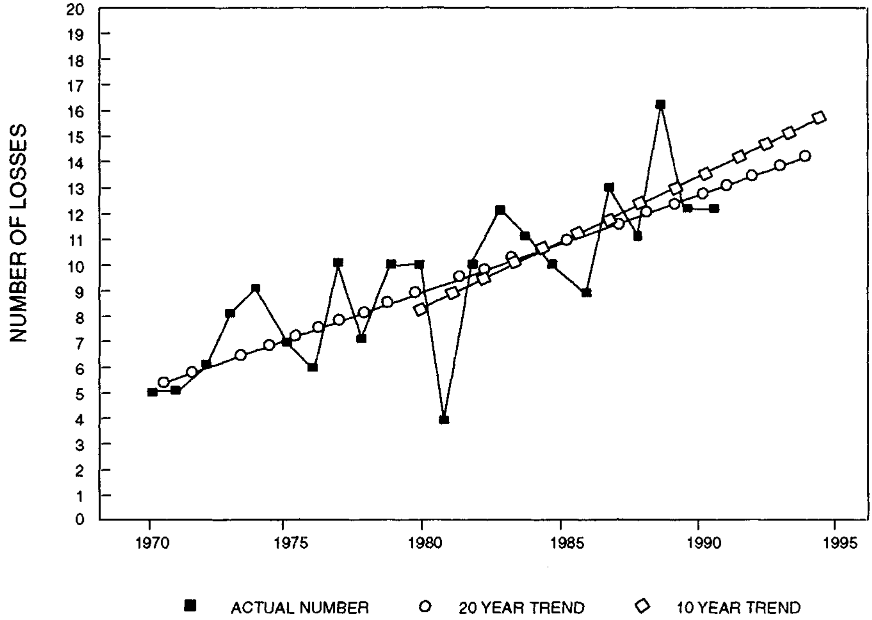


Figure 16-1 Average property damage losses greater than $10 million in the hydrocarbon processing industries (Norstrom 1992).

The fire triangle describes the three elements required for fire to occur. These are fuel, heat, and oxidant. If any one of these elements is not present, fire will not occur. Most fire protection and prevention efforts concentrate on removing one or more of the elements in the fire triangle. A more detailed discussion of fire and fire protection methods can be found in the NFPA *Fire Protection Handbook* (1991).

In most cases, extinguishment produces a safer condition than controlled burning; however, extinguishing the fire is not always the best approach. With jet gas fires, this is generally not the case, since a gas release is subject to reignition or explosion. Isolation of the fuel source is the best approach when fighting this type of fire.

In the following sections, fire protection methods and practices are discussed, beginning with detection and personnel notification, continuing with discussions of active and passive protection, and concluding with response and control. It must be emphasized that adequate fire protection may be achieved in many ways, including reducing the potential for a large fire. This chapter is intended only to introduce basic concepts and alternatives for consideration. An understanding of fire characteristics and behavior of flam-



NOTE = DOLLARS INDEXED TO 1990

Figure 16-2 Frequency of losses greater than $10 million in the hydrocarbon processing industries (Norstrom 1992).

mable materials both when contained and when released, is necessary so that correct responses may be designed into a facility or planned action to be taken. Fire protection and prevention specialists should be consulted in the early stages of process designs or modifications so that all of the alternatives can be evaluated.

16.2 DETECTION AND ALARM SYSTEMS

16.2.1 General

Most fires begin small. When a fire does occur, the actions taken in the first few minutes are usually the most important and can eliminate the need for hours of fire fighting. Therefore, it is important to detect a fire, or adverse condition that could lead to a fire, as quickly as possible so that action can be taken. Since it is not possible to prevent all fires, nor to have personnel available to detect every fire as soon as ignition occurs, detection and alarm systems are often installed.

Detection and alarm systems provide prompt detection of a potentially hazardous condition. Prompt detection provides timely notification of personnel and/or activation of automatic fire suppression and control systems during the early stages of an incident, thereby reducing the impact of the fire. Combustible gas detectors can detect a gas release or vapors from a liquid spill before a fire occurs. Fire detectors include those which recognize heat, smoke or flame. Many of these are discussed in the following sections. NFPA 72E, "Standard on Automatic Fire Detectors" should be reviewed for minimum design, installation, testing, and maintenance requirements. NFPA standards in the 70, 71, and 72 series cover issues pertinent to detection and alarm systems such as connection of system components, power supplies, and system integration.

A key aspect of detection and alarm systems is the continuous supervision of circuits and equipment to ensure reliable operation and to notify personnel of abnormal conditions. This supervision is inherent in approved equipment, when the system is designed and installed in accordance with NFPA standards, and is necessary because these systems normally function in a standby mode. Approved equipment means devices that have been listed or approved by a nationally recognized testing laboratory such as Underwriters Laboratories (UL) or Factory Mutual (FM).

The type and design of the fire alarm, control, and annunciation system should be selected to best meet the needs of the facility. Facilities which have a central process control center may desire to have the fire detectors and alarms monitored there. However, fire alarm systems and annunciators should remain separate and distinct from process controls. In any case, the primary location of the fire alarm annunciation must be in an area continuously occupied by attentive trained personnel in order to ensure prompt and adequate response to all emergencies.

16.2.2 Combustible Gas Detection

Gas detection is employed to detect the presence of potentially flammable vapor/air mixtures before they reach the Lower Flammable Limit (LFL) and become a potential source of fire or explosion. Gas detectors used for fire protection differ from the detectors used for industrial hygiene monitoring which function in low concentration ranges such as parts per million. Gas detection systems for fire protection are used widely in the chemical industry in both process and storage areas. Combustible gas detectors are often used for areas of a facility that are subject to accidental flammable vapor releases (potential leak sources) or where accumulations of flammable vapors could come in contact with ignition sources. They are used to detect large releases, where the potential for a vapor cloud exists, and to detect smaller releases from potential leak sources. These areas include, but are not limited to, the following:

- Selected pump or compressor facilities and liquid hose transfer stations handling highly flammable fluids.
- Tank car and tank truck facilities handling highly flammable fluids.
- Electrical centers or control rooms in the vicinity of potential large flammable gas releases.
- Air inlets to ventilation and pressurization systems in classified areas and in the vicinity of accidental large flammable gas releases.
- Aerosol filling areas.
- Ditches, trenches, sumps, and other low points where heavy flammable vapors could accumulate.

Most gas detection system set points are chosen based on a percentage of the LFL, with a two-tiered approach (one alarm for warning and manual response and a higher set point alarm to initiate predetermined emergency measures) being common. Alarms are generally initiated at 10–30% of the LFL and the high level, shutdown, or other action initiated at 30–50% of the LFL. Detection systems are sometimes used to shutdown processes or equipment and activate inerting, fire protection (water spray, water curtains, etc.), and emergency ventilation systems (Greenawalt n.d.). Emergency shutdown of electrically energized equipment in the presence of combustible gas could cause an explosion since electrical arcing produced from opening energized contacts could be an ignition source. Set points should be chosen to ensure that equipment is deenergized before vapors reach dangerous levels.

The location of gas detectors should take into consideration such factors as the gas density, wind direction analysis, gas detector sensitivity, potential ignition sources, and potential flammable release points. Detectors may be provided either on an area basis, or located to detect leaks from specific locations, or a combination of the two philosophies. There are no standards for gas detector placement, and it is important that detectors be located in accordance with the manufacturer's recommendations. Access for maintenance and calibration must also be considered when locating detectors since an inaccessible detector is unlikely to be maintained.

There are several types of combustible gas detectors used for fire protection. Most fall into two general categories, spot types and sampling types. Spot type detectors are generally faster than sampling detectors since the gas does not have to travel through the sample tube from the sampling point to the detection instrument. The most common detectors include diffusion head type catalytic oxidation (spot type), infrared spectroscopy (sampling type), and thermal incineration (sampling type). Catalytic oxidation detectors oxidize the gas, heating an internal element and changing its electrical resistance. Infrared detectors detect a change in infrared radiation as higher gas concentrations absorb more infrared radiation. Incineration detectors pass the gas though a constant flame and detect the increased heat generated by a combustible gas. Diffusion head type catalytic detectors are generally recommended unless they are not compatible with materials that may be released.

Gas detectors have potential problems. Catalytic detectors are subject to catalyst poisoning. Exposure to silicones, lead, sulfur, and other materials can quickly make the detectors inoperable. Exposure to chlorine, chlorinated compounds, or corrosive materials can reduce the life of the sensor and cause maintenance problems. Calibration can also be a problem, since calibration of many detectors is dependent on the specific gas to be detected. Catalytic type detectors exposed to hydrocarbons such as ethane, ethylene, and propane at 20% of their LFL may give different results for each gas. Thermal incineration detectors contain an ignition source. Absorption of infrared radiation by a gas depends on the gas's molecular structure, and therefore infrared detectors are designed for use with specific gases. The concentration indicated by detectors may not be accurate when several different gases may be released or a gas mixture is present. Some detectors are also sensitive to changes in humidity, temperature or atmospheric pressure.

Gas detectors should be maintained and calibrated periodically in accordance with the manufacturer's instructions. In hazardous areas, the detector housing should be opened only when safe conditions can be ensured. Portable gas sensors or sniffers should be used to determine the possible presence of flammable vapor–air concentrations before opening the sensor housing.

16.2.3 Fire Detectors

A fire will affect its environment in many ways. Fire detectors attempt to recognize these changes and respond with an alarm. Fire detectors respond to heat, particulates (smoke), or radiant energy. Heat and smoke detectors are the most common, although detectors that respond to radiant energy are used where extremely fast response is critical. A more detailed discussion of fire detectors can be found in the NFPA *Handbook.*

Certain fire detectors may be used for detection and alarm only, or may be utilized to actuate a fire suppression system and/or shut down equipment. Detectors should not be considered a substitute for suppression systems where those systems are appropriate.

16.2.3.1 Thermal Detection

Thermal detectors are of either fixed temperature, rate-compensated fixed temperature, or rate-of-rise design. Spot-type are the most common. Line type detectors are useful in certain specific applications, such as conveyors and cable trays. The spot-type thermal detector is considered to be one of the most reliable and trouble-free types of thermal fire detector.

Fixed temperature detectors are designed to operate at a specific temperature, while rate-of-rise detectors respond to temperatures which rise faster than the design rate rather than at a specific temperature. Rate-compensated fixed temperature detectors are a combination of both types and reduce a fixed temperature detector's time lag in rapidly growing fires. Rate-of-rise detectors may react faster than fixed temperature detectors to a rapidly growing fire, but may never operate during a slowly developing fire.

Recommended maximum spacing for thermal detectors inside buildings should be in accordance with NFPA 72E and UL Listing/FM Approval requirements. Thermal detectors installed outdoors require special consideration, such as closer spacing, and should be addressed on a case-by-case basis. In addition, thermal detectors located outdoors may need special shielding devices to prevent snow and ice accumulation which might delay response.

Heat detectors are often used to isolate flammable liquids in the event of a fire. Fusible link operated shut-off valves can be used on tank outlets to prevent tank contents from emptying in the event a line fails in a fire. Fusible plugs, or plastic tubing can be used as a heat detector to automatically close pneumatically operated valves (valves should be air-to-open) in flammable liquid lines to isolate the fuel from a fire.

16.2.3.2 Smoke Detection

The technology for sensing airborne particles of combustion includes ionization, photoelectric, and incipient stage/early detection devices. In general, flaming fires are more quickly detected by ionization detectors, and smoldering or slow-developing fires are more quickly detected by photoelectric detectors. Ionization detectors have widespread use and are suitable for many applications. Selection of the proper detector type depends on the nature of the hazard; refer to the NFPA Handbook and/or fire protection specialists. Smoke detectors are commonly located in areas such as

- Control rooms
- Computer rooms
- Instrument rooms
- Office areas
- Electrical equipment rooms

In areas where smoke detection is used to actuate fire suppression systems, cross-zoning or other voting type detection schemes are often used for actuation. Subfloor and above-ceiling areas containing electrical and instrumentation cabling or other combustibles may also need smoke detection. Critical and high value control cabinets or panels which are not ventilated may require internal smoke detection since an incipient stage fire could escalate beyond control inside a cabinet prior to room detection.

Numerous conditions in chemical facilities can have a negative impact on smoke detector performance. These conditions can result in false alarms. Some detectors are sensitive to humidity and dirty atmospheres. Ionization detectors are also sensitive to chlorine, hydrogen chloride, hydrogen fluoride, phosgene, trichlorethylene, and other chemicals.

Smoke detectors are commonly used in electrical equipment rooms, control rooms, and other areas containing electrical equipment. Often the detectors are located at the ceiling. Electrical equipment failures often generate "cold smoke," which will not rise to the ceiling where the detectors are normally located. Additional detectors may be required at the bottom of electrical cabinets or rooms to sense this condition.

16.2.3.3 Optical Flame Detection

Optical flame detectors are devices which respond to radiant energy. Ultraviolet (UV) radiation and infrared (IR) radiation detectors are the most common. These have proven to provide prompt detection, but have not always been proven reliable as single source detection devices. However, there are several techniques which reduce false alarms and failures. Two commonly used techniques are dual IR and combination UV/IR detection devices. Dual IR and combination UV/IR detection devices reduce false alarms from sources such as welding arcs, flickering sunlight, hot bodies, or flashing lamps

The sensitivity of optical sensors depends upon the cleanliness of the lens. Sensors installed where dust or other materials may accumulate on the lens should be of the self cleaning type or be located where routine maintenance can be readily performed.

Optical flame detectors are best employed in areas where very fast response is required for actuation of protective or emergency shutdown systems. The actual detector placement depends on the area or equipment being monitored (physical dimensions, complexity, production importance, etc.), detector cone of vision, and sensitivity level of the sensor. Installation should closely adhere to the manufacturers recommendations. Optical flame detectors may also be provided with swivel bases to allow for optimum sensor positioning.

Optical flame detectors used as the primary detection device are considered a suitable alternate for standard thermal detection devices. Optical flame detectors find wide acceptance in enclosures where suppression or inerting systems require immediate actuation. To enhance reliability, additional control safeguards are often utilized, such as cross-zone or voting logic.

16.2.4 Manual Alarms

Manual alarm stations are usually simple contact closing devices. Two of the most common fire alarm stations are of either pull-lever or break-glass design requiring two distinct operations to avoid accidental operation.

Manual alarm stations should be located with respect to normal means of egress from all areas and as may be required by local codes. All buildings and process blocks should have at least one station in clear view, readily accessible to personnel from any point within the facility, with the maximum travel distance to a station no greater than 200 feet.

16.3 WATER-BASED FIRE PROTECTION SYSTEMS

Two types of fixed fire protection exist, active and passive, and chemical process plants often employ a mixture of both types to provide a total and reliable fire protection scheme. Active fire protection systems include water and chemical application systems for controlling fires. Passive systems are discussed in Section 16.5.

16.3.1 General

An adequate and reliable water based fire protection system is the basis for a sound plant fire protection program. Facilities use water to control or extinguish fires involving combustible materials or liquids, and for containment of fires involving flammable gases and liquids. Water is also directly applied to equipment and structures to protect them from damage caused by the heat of a flammable or combustible liquid fire. In cases where water alone cannot be expected to extinguish a fire, application of water will serve to limit the damage until fire extinguishment is attained by other means.

In many cases, large quantities of water will be required in a concentrated area to supply sprinkler systems, water spray systems, hydrants, monitor nozzles, foam systems and other water based fire protection systems. The design of the water supply and distribution systems is therefore critical. The NFPA *Fire Protection Handbook,* Section 5 (1991), and the various NFPA Fire Codes (NFPA 11, 13, 14, 15, 16, 16A, 20, 22, 24, 30, 231, 231C, and others) provide general information on fire protection system design and installation. Other valuable references are also listed at the end of this chapter.

16.3.2 Water Based Fixed Systems

Water based fixed systems are used to apply water to a fire and can be manual or automatic. Most facilities use a combination of both manual and automatic systems. With decreasing staffing levels at many sites, automatic systems have become very important, even in those facilities that have traditionally relied on manual fire fighting efforts. The basic approach to these systems varies depending on the size of the facility and quantity of flammable and combustible materials handled. Small indoor specialty chemical operations require a different design than large outdoor oil or petrochemical processing facilities.

Automatic sprinkler systems, designed in accordance with NFPA 13, "Installation of Sprinkler Systems" are the most commonly used water based extinguishing system. These systems should generally be installed in all buildings of combustible construction or occupancy. Most manufacturing buildings, warehouses, research laboratories, and other important buildings have sufficient combustibles and value to be provided with sprinklers. Fires involving flammable and combustible liquids used in many chemical facilities result in fires that develop faster and burn hotter than ordinary combustibles such as wood or paper. The increased quantities of flammable liquids in chemical processes often require designs for Extra Hazard occupancies as defined in NFPA 13.

Storage and warehousing areas present unique challenges in the design of fire protection systems. The storage of flammable or combustible liquids, especially in plastic containers, presents a severe fire challenge. In some cases, materials of extremely high value (e.g., pharmaceuticals, herbicides, catalysts, etc.) are produced and stored. Careful attention to the sprinkler design is required to limit losses. NFPA 231, "General Storage" and NFPA 231C, "Rack Storage of Materials" provide basic guidelines for the protection of materials in warehouses. Specific guidance for the protection of flammable liquid warehouses can be found in NFPA 30, "Flammable and Combustible Liquids Code." It should be noted that considerable research is being conducted to improve the protection for flammable and combustible liquids in containers. Many feel that current guidelines are inadequate. Design guidelines are constantly changing and many companies, insurers, fire protection specialists and other authorities having jurisdiction may recommend specific guidelines that are more stringent than NFPA 30. The use of foam water sprinkler systems may provide better protection than water alone in areas where flammable liquids are handled.

Process equipment and structures may be protected with water spray systems. Water spray systems are extremely efficient at cooling equipment exposed to fire and are used to provide exposure protection for valuable or critical equipment and for equipment which has the potential for large liquid or gas release upon its failure. Where an explosion hazard exists, deluge valves should be barricaded and piping arranged to limit explosion damage. Protection is usually provided for vessels with large hold-up (reactors, columns, storage tanks, and other vessels), pumps, compressors, pipe racks, and manifolds, loading racks, cable trays, and structural steel, none of which can be effectively protected, especially in the first few minutes of a fire, by manual means. To provide effective cooling, specific water spray application densities are necessary as established by the National Fire Protection Association (see NFPA 15, "Standard for Water Spray Fixed Systems for Fire Protection," for additional information) or by recognized testing laboratories for special hazards and applications. Operating companies have sponsored tests of specific applications and designs which have proven beneficial to the industry. Application rates of 0.25 gpm per square foot of protected area and higher are often used. Many insurance companies and other authorities have specific recommendations for water spray system design.

Manual water based protection is usually provided by monitor nozzles, hydrants, and hose lines. Fire water monitor nozzles are recommended to provide large amounts of cooling water to vessels and equipment exposed by fire. Monitors can be affixed to fire hydrants or located independently. Monitor nozzles have an advantage over ordinary hydrants in that they can be quickly placed into service by a single person and can operate unattended once placed into service. It is generally recommended that all critical areas be covered by at least two monitor nozzles. In congested plant areas (e.g., tank farms) where full benefit of grade level monitors would not be realized, elevated monitors should be considered. Remote operated and automatic oscillating monitors are also available.

Fire hydrants are needed throughout the facility to assist with the manual fire attack and for salvage operations. Hydrants should be equipped as a minimum with two 2½-inch capped hose outlets. A 4-inch pumper connection can be used to supply a hydrant mounted monitor or provide water to a fire truck pumper if it is necessary to boost the available pressure. Hydrant spacing in process areas is often as frequent as 75–100-foot intervals. The exact location and spacing of hydrants in any individual area requires knowledge of the layout, hazards, drainage systems, and other factors to make sure that they will be accessible during emergency conditions. Hydrant spacing for plant administrative and other less hazardous areas should not exceed 250–300-foot intervals.

16.3.3 Fire Water Supplies

There are two critical factors to consider when designing the water supplies for a chemical facility. These are adequacy and reliability. Adequacy of the system is determined by the capability of the supply to meet the flow and system pressure requirements for the anticipated fire duration, typically 2 to 4 hours. The system must also be reliable under adverse conditions such as those following an explosion, so redundancy is often provided. Also, the onsite dedicated fire water storage should have the capability of replenishment within 24 hours.

The water supply and distribution system must be able to deliver large quantities of water to many areas of a facility. The actual volume and pressure required depends on the specific hazard to be protected. The water supply should be capable of supplying the maximum instantaneous and continuous demands which may result from an explosion or fire within the facility being protected. When evaluating the demands for a specific hazard, consider the maximum number of fixed systems that may be expected to operate simultaneously (e.g., multiple water spray, deluge, or foam systems) and the water to be used for manual fire fighting from monitors and hose lines. The total demand could be as low as 1000 gpm for administrative areas to 10,000 gpm and higher for large process areas. These flows should be available at a minimum of 100 psi within the protected area in most cases.

Reliability of the system can be enhanced in several ways. First, fire protection water supplies should be dedicated for fire protection and not combined with process water needs. Many facility water supplies are not capable of providing adequate fire water protection from existing water systems without reinforcement, such as from booster pumps. Process water systems may not be designed for the pressures required for fire fighting. Combined systems are much more likely to be out of service when needed, and when large quantities of water are used for fire fighting, it can rob critical cooling water from processes, resulting in unstable process conditions, increasing the severity of an emergency condition.

Second, the facility supply should be capable of providing much of the anticipated demand with any "impairment" to the system. An impairment could be the loss of a single fire pump, reduced suction supply, a break in the distribution piping, a shut valve, or other adverse condition. This means that looped and redundant water supplies should be provided to minimize any single failure.

In all but the most unusual circumstances, dedicated fire water pumps and dedicated water storage facilities should be provided to meet the maximum fire water demand. Most public water systems are inadequate to supply the volumes and pressures required. Gravity tanks are also usually of inadequate volume and pressure to be of significant benefit in all but small facilities. Due to the large volumes of water required, many facilities arrange their pumps to take suction from rivers, lakes or ponds. Reliance should not be placed on water supplies located in adjacent plants (i.e., those owned by another company) except in the most unusual circumstances.

Where fire water pumps are installed, they should be provided with all necessary features to allow for independent and reliable operation should other systems fail. This is achieved by providing self-contained diesel engine driven pumps. Loss experience has shown (Garrison 1988) that when fire pumps fail during an incident, more than 90% of the failures involve electric motor or steam turbine driven pumps. NFPA 20, "Standard for the Installation of Centrifugal Fire Pumps" (1990) should be reviewed relative to system requirements.

Fire pumps should be located to avoid the potential loss of all pumping supplies at the same time. Locate fire pumps away from severe process hazards so that they will not be damaged by explosion overpressures. Explosion debris has landed on fire pump buildings and destroyed suction tanks making the systems inoperable even when located remotely. At least two pumping stations are desirable. Fire department connections should be provided in convenient locations to boost the pressure for sprinklers and other fire protection systems which may become overtaxed or somehow isolated from the water supply.

16.3.4 Fire Water Distribution Systems

Fire water systems should be designed to supply sufficient quantities of water to all areas of a facility. The fire water distribution system should be sized to limit the friction loss from the supply to the greatest hazard and to meet the maximum fire water demand including expected fire hose and monitor nozzle requirements. Future plans should be included in any design. NFPA 24, "Standard for the Installation of Private Fire Service Mains and Their Appurtenances" should be consulted for minimum installation requirements.

When laying out the fire water distribution system the following are usually considered:

- Sizing distribution mains to take advantage of the water supplies available. Large pumping capacities can be wasted if the water distribution system cannot deliver the water to the desired areas at effective pressures. This usually means a looped or gridded distribution system.
- Sizing the distribution piping to meet anticipated demands with any part of the distribution system out of service.
- Providing adequate backflow prevention where public or other potable supplies connect to the system.
- Providing a separate connection to the distribution system for each source of supply.
- Burying distribution piping even in climates where freezing is not a problem to prevent an explosion within the facility from impairing the system.
- Providing adequate valving to isolate damaged sections of the system. Water supply mains generally should have indicating-type sectional valves located at appropriate locations on the grid. The sectional valves should be installed at other appropriate points in order to minimize the extent of impairments. The isolating valves should be placed so that hydrants, monitors, deluge systems, sprinkler systems or other fire protection systems could still operate by isolating the problem using the valves. Sectional valves should be arranged so that no more than four to seven pieces of equipment (hydrant, deluge valve, monitor, etc.) will be impaired at any one time. Multiple impairment scenarios may be con-

sidered, and the possible need of large diameter temporary water transmission hose should be considered for supplemental fire water supply in extreme emergencies.

16.4 CHEMICAL AND SPECIAL AGENT EXTINGUISHING SYSTEMS

16.4.1 General

Although fire water application is most often an adequate confinement and control agent, it may not be the best agent for extinguishment of flammable liquids or flammable gas fires, and it requires special precautions when used on energized electrical equipment. Dry chemical, foam, carbon dioxide, and other special extinguishing agents have application in many facilities handing chemicals. Portable or fixed manual chemical or special agent systems are often provided as first aid response to limit the spread of small fires, and supplement automatic safety systems.

16.4.2 Foam Systems

The wide range of fire fighting foams available today is the result of over forty years of development which has produced steady improvement in applications and effectiveness. Foams were originally developed to extinguish fires in specific types of materials. However, there has been considerable effort to develop foams which can extinguish fires involving as wide a range of materials as possible. The extinguishment mechanism is mainly through exclusion of oxygen by smothering, assisted to a degree by cooling water released from the foam blanket.

Modern foams are produced mechanically by proportionately mixing foam concentrate with water and then aerating the solution for expansion. Foams are classified by their expansion ratio. Low-expansion foams have less than a 20 : 1 expansion ratio. Medium-expansion foams can have up to 200 : 1 expansion, and high-expansion foams have expansion between 200 : 1 and 1000 : 1. NFPA 11 and 11 A, "Standards for Low, Medium, and High Expansion Foams," NFPA 16, 16A, and NFPA 25, should be reviewed for specific requirements for design, installation, operation, testing, and maintenance of foam systems.

Two foam types widely used in the chemical industry are protein and synthetic foams. Advanced protein foams include fluoroprotein (FP) and film forming fluoroprotein (FFFP) foams which are both available in 3% and 6% concentrations, depending on equipment design and application, and are intended for low to medium expansion. FP foams are derivatives of basic protein foams with the addition of fluorosurfactants to improve fuel compatibility and fire knockdown performance. FFFP foams are based on fluoroprotein foams with the addition of film forming fluorosurfactants. FP foam is best employed as a subsurface injection agent on storage tanks and FFFP can be used for both subsurface and general application protection.

Improved synthetic foams include Aqueous Film Forming Foam (AFFF) and Alcohol Resistant (AR) foams, which are available in 1%, 3%, and 6% concentrations. These are primarily employed for low-expansion applications but some medium expansion applications exist.

AFFF provides extinguishment primarily by forming a vapor sealing aqueous film on the surface of a hydrocarbon liquid. AFFF spreads quickly over the liquid surface allowing for rapid flame knockdown and rapid reseal of the film surface when broken. AFFF does not provide long term protection against reignition. AFFF is very effective when used in water spray, monitor nozzle, and hand-held hose systems. NFPA 16, "Standard for Deluge Foam–Water Sprinkler Systems and Foam–Water Spray Systems" should be reviewed for specific design and installation requirements.

Alcohol Resistant foams including AFFF alcohol type concentrates (ATC) have been developed to deal with fires involving polar solvents and water miscible fuels such as alcohol. AFFF–ATC provides enhanced capabilities over standard AFFF since it has been proven to be highly successful in extinguishment of both water soluble polar solvents and water insoluble hydrocarbon liquids. Slightly aspirated AFFF–ATC foam is more fluid than normally aspirated AFFF (due to the lower expansion ratio) and can be applied more forcefully to water miscible fuels providing rapid fire extinguishment and good vapor suppression, lending itself to hose and monitor nozzle applications on pool fires.

Special synthetic foams made from surfactants are used for most medium and high expansion applications. Medium and high expansion foams are normally used to flood indoor areas and confined spaces. The use of medium expansion foam may be acceptable on water reactive materials in some cases. Refer to NFPA 49 for recommendations with specific chemicals. High expansion foams are also used to flood warehouses containing combustible liquids. High expansion foam is also used in LNG vapor and fire control.

Hazardous material (Hazmat) and stabilized foams have been developed for suppressing toxic vapor releases and long term sealing of flammable liquid spills. Hazmat foams are effective on products which destroy standard foams due to the difference in pH; however, hazmat foams generally are not used for fire fighting. Specialized Hazmat foams are available for use on alkaline materials, such as ammonia and alkylamines, and on acid materials. Stabilized foam is the product of simultaneously proportioning the foam concentrate and a stabilizing agent with water. The stabilized foam solution forms a gel on the surface of flammable liquids within 1 to 3 minutes through a polymerization reaction.

16.4.3 Dry Chemical Systems

Dry chemical systems are considered the most effective agents for extinguishment of combustible metals and many materials that are incompatible with water (see NFPA 49), flammable liquids, and gas fires. However, dry chemical systems are usually far less effective in preventing reignition of flammable liquid pool fires then is foam. Therefore, extreme care and judgment must be given to its application. Twin or combined agent systems utilizing foam and dry chemical can effectively be employed. Refer to NFPA 10 for portable dry chemical extinguishers, to NFPA 11 for combined agent systems, and to NFPA 17 for fixed dry chemical systems.

Dry chemical fire extinguishers are listed by UL and other testing organizations for use on various types of fires and are rated based on their relative effectiveness. Acceptable extinguisher location (determined by the travel distance between the extinguisher and the hazard and the maximum area capable of being protected by each extinguisher) is a function of the extinguisher rating and hazard(s). Based on these criteria, portable, wheeled, or stationary dry chemical extinguishers are strategically positioned throughout the protected facility.

There are a number of different types of dry chemical agents; among the most effective and most commonly used are potassium bicarbonate (Purple K), sodium bicarbonate (regular dry chemical), and monoammonium phosphate (ABC dry chemical). Regular dry chemical and Purple K are effective on flammable liquid and energized electrical fires (Class BC) while the ABC or multipurpose type is also effective on ordinary combustible fires (Class ABC). Refer to NFPA 10 for a detailed discussion of extinguisher classifications. Although dry chemical agents are very effective on electrical fires, their residue after discharge usually requires extensive clean up.

Special dry powders are used for the protection of combustible metals. Chapter 5-21 of the NFPA *Fire Protection Handbook* (1991) provides a good discussion of the various agents used with combustible metals.

Fixed dry chemical systems are normally used to protect small hazards and are not often used in chemical plants. Large systems have proven applicable in high risk areas such as flammable liquid storage, process areas, compressor, and pump rooms. Local application dry chemical systems have also been used for vent stack extinguishment.

16.4.4 Halon Systems and Alternatives

Halon systems extinguish fires by inhibiting the chemical chain reaction of the combustion process. Halon is used for both manual and fixed system applications. Halon 1211 (bromochlorodifluoromethane) is employed as portable application on Class ABC fires and primarily for manual protection of electrical control rooms. Halon 1301 (bromotrifluoromethane) systems are used primarily for total room flooding, fixed protection of sensitive computer control centers, switchgear, motor control center rooms, and inside turbine enclosures. NFPA 12A and 12B should be reviewed for design application of Halon 1301 and Halon 1211, respectively.

Halon 1301 systems can be designed to provide either suppression or inerting concentrations. Suppression concentrations are usually below 7% by volume of protected area; most inerting concentrations are above 7% by volume. Concentrations above 7% and products of Halon decomposition may be hazardous to human occupants and caution is recommended in its application. Although human exposure to concentrations below 7% is safe and the effects of exposure above 7% are usually reversible upon removal from the exposure, prewarning of pending Halon discharge is recommended.

6.4.4.1 Halon Alternatives

Halons are suspected to be detrimental to the ozone layer and as indicated by the Montreal Protocol Assessment (United Nations Environmental Program, 1989), the Halon Technical Options Committee seeks to achieve Halon reductions without jeopardizing the provision of necessary fire protection. Complete phaseout is required by the end of 1993 in the United States. Work is continuing on the development of "clean agents" to replace Halon, and a committee has been formed to develop NFPA 2001 which will cover clean agents and their selection. Several promising agents are under development; however, none are direct Halon replacements. The use of Halon should be avoided except in extreme cases.

Alternatives to Halon include carbon dioxide and automatic sprinklers. Computer and control rooms can be protected by a combination of sprinklers in the room and CO_2 for any underfloor space and equipment enclosures where Halon would normally be provided. Water damage to sensitive equipment from sprinklers may be minimized by incorporating emergency procedures which include: disconnecting power, removing smoke and other contaminants, and preventing startup until dryness is achieved. Rapidly reducing the humidity in the affected area is important to prevent corrosion from products of combustion prior to cleaning the equipment.

16.4.5 Carbon Dioxide Systems

Carbon dioxide systems are used to extinguish fires by excluding oxygen and smothering fires. Carbon dioxide can be used in both manual and fixed applications and in local and total flooding systems. Manual (portable) carbon dioxide extinguishers are most often used on electrical fires since the agent is nonconductive and leaves no residue. NFPA 12, "Standard on Carbon Dioxide

Extinguishing Systems" should be reviewed for minimum requirements for use and design application of fixed systems.

Portable carbon dioxide extinguishers are recommended in power generation facilities, control rooms, and switchgear rooms, but due to a limited discharge range, these extinguishers should only be used indoors. Like other portable extinguishers, carbon dioxide extinguishers are classified and rated for use and effectiveness and are located accordingly.

A carbon dioxide fixed system, total flooding application requires an atmosphere of about 34% carbon dioxide by volume which also displaces oxygen to a level which will no longer sustain human life. Due to this life safety hazard, carbon dioxide total flooding systems should be provided with appropriate safeguards to protect personnel.

16.4.6 Inerting Systems

Inerting systems prevent the formation of explosive air–vapor mixtures. The inert gas takes up space, displacing the oxygen, thus preventing accumulation of sufficient oxygen to support combustion. Nitrogen, and occasionally carbon dioxide, are usually used as inerting agents for such applications. Inert gases such as argon have special application for materials such as zirconium that burn in nitrogen. The limiting oxygen concentration (LOC) to support combustion can vary depending on the inert gas used, and flammability tests may be needed with complex mixtures to experimentally measure the lower limits of flammability based on the volumetric concentration of the combustible gas.

Inerting systems are commonly employed to pad or blanket the space above flammable liquid storage tanks or other vessels including mixing tanks, ball mills, centrifuges, and other equipment. Inerting is also used to reduce the concentration of flammable vapor in a vessel prior to cleaning or maintenance. In this case, purging the enclosure with the inert material reduces the concentration of the flammable material below its lower flammable limit without the vapor space passing through the flammable range by eliminating the oxygen. Once the flammable vapors have been removed, the inert gas must be replaced with oxygen and confined space entry procedures followed before the vessel can be entered. Inerting systems for combustible gas releases by vent stacks have been employed to control accidental ignitions. NFPA 69, "Explosion Prevention Systems" provides guidance on the design and calculation methods used in these systems and those designed to prevent accumulation of flammable vapors.

Water as an inert diluent has been used for many years in steam smothering systems in process plants. Care is needed since the steam can condense out and the space become flammable again. Also, steam discharge can cause static charge accumulation. Atmospheres such as methane and air that would otherwise be explosive can be made inert by the addition of fine water fogs with water droplet size of approximately 1 micron. However, since highly atomized water spray systems typically produce 100- to 200-micron droplets which are far too large, water spray inerting is not as practical as one might assume.

16.5 PASSIVE FIRE PROTECTION

16.5.1 General

Passive fire protection inherently provides protection against fires and, as its name implies, does not require any electrical, mechanical or manual action to function. As such, passive fire protection is usually regarded as more reliable than active fire protection systems. However, passive fire protection is often neglected and allowed to deteriorate, actually becoming less reliable. It is essential, therefore, that passive fire protection, like active fire protection systems, be inspected on a routine basis and maintained as necessary.

The types of passive fire protection which are commonly employed include the following:

- Fire barriers
- Fireproofing and fire-resistant construction
- Thermal insulation
- Separation distances
- Drainage/spill control systems

Each of these types is discussed in the following sections.

16.5.2 Fire Barriers

The purpose of fire barriers is to minimize fire damage by limiting the spread of fire. Fire barriers are typically constructed of noncombustible materials such as masonry, concrete, or gypsum-board. Fire barriers are most often provided inside buildings but are occasionally used outside to separate process units or other hazardous operations.

Fire barriers are designed to prevent the passage of heat and flames for a specified period of time as designated by a "fire resistance rating." Fire resistance ratings are typically specified in hours, ranging from 30 minutes to 4 hours. The *UL Fire Resistance Directory* (1992) provides details on tested wall and floor/ceiling assemblies and their achieved fire resistance ratings. The National Fire Protection Association is currently developing a new standard, NFPA 221, covering fire walls.

There are two basic types of fire barriers, fire "walls" and fire "partitions." Fire walls provide better protection against fire spread than "partitions" and have fire resistance ratings of 3 hours or more. Fire walls are non–load-bearing, and have parapets (usually 30 inches in height) which extend above adjacent roof lines and are designed so that the wall will remain standing in the event of structure collapse on either side as a result of a fire. A "standard fire wall" is a parapetted, masonry wall with no openings or other penetrations, such as for conduits or piping, and at least 4 hours fire resistance. Standard fire walls are sometimes referred to as "Maximum Foreseeable Loss" or MFL walls. If the exterior wall configuration would allow the fire to spread around the wall, a wingwall or endwall should be provided. While fire walls should be freestanding, there are other designs such as a tied fire wall or double one-way fire walls that are acceptable.

Fire partitions provide less protection against fire than do fire walls. Fire resistance ratings are typically 3 hours or less and they do not extend through the roof, and do not have all of the same features as fire walls, such as parapets and "free standing" design. The type, location, and design of fire barriers, including the fire resistance rating, depends on many factors. These include: type and severity of fire hazards, size and configuration of areas under consideration, type and criticality of operations, building code and insurance company requirements, company standards, and other features. Due to the number of factors that need to be considered, persons experienced in fire protection should be consulted in the location and design of fire barriers. In general, however, fire barriers should be provided to reasonably minimize loss potential consistent with company risk management philosophies and code requirements. Examples of where fire barriers should be considered include the following:

- Between dissimilar occupancy types, such as warehouses and production areas
- Between separate and unrelated processes.
- Between areas normally occupied by personnel, such as control rooms or offices, and high fire hazard areas (process areas, warehouses, etc.).
- Between critical operations, such as electrical or instrument rooms, and high fire hazard areas.

Fire barriers should be designed and constructed in accordance with local building code requirements and accepted engineering designs (such as UL or FM). It is important to note, however, that fire resistance ratings for fire barriers are determined based on ASTM test method E-119 (or UL 263 or NFPA 251) which simulates the heat developed from a fire involving ordinary combustibles (paper, cardboard, etc.) and is not representative of the heat produced by burning hydrocarbons. Thus, the actual fire resistance rating of a fire barrier in a process plant setting could be significantly less than otherwise indicated by its rating. Where an explosion hazard is present, special designs must be used if the wall is to resist the explosion forces.

Openings in fire barriers, such as doorways, windows, ventilation openings, air handling ducts, conveyor openings, etc., should be provided with automatic closing (or normally closed) fire doors, shutters or dampers. These devices should have fire resistance ratings commensurate with the fire resistance rating of the fire barrier, and if left open, should be equipped with some means to automatically close the device in the event of a fire (such as fusible links or smoke detectors). In some cases, two devices, one on each side of the fire barrier, may be necessary to provide the necessary opening protection. Because these devices are mechanical in nature, they must be tested and serviced on a routine basis to ensure they will close properly in the event of a fire. NFPA 80, "Fire Doors and Windows," provides more information on the installation and testing of these devices.

Penetrations in fire barriers, such as for conduit, piping, cable trays, electrical bus ducts, etc., also need to be protected to maintain the integrity of the fire barrier. A number of approaches exist for protection of such penetrations. The *UL Fire Resistance Directory* provides details on many of these. Again, however, these assemblies are evaluated based on ASTM E-119 and may not reflect the actual performance in cases where high fire hazard materials exist. Piping, wiring or cable trays penetrating fire walls should be made as close to the bottom of the wall as possible to avoid them pulling the wall down when building collapse occurs on one side of the wall. Cable for cable trays should be coiled loosely on either side of the barrier to prevent them from pulling on the wall. Alternatively, piping, cables, and other penetrations can be routed around or above the fire barrier rather than through it.

Fire barriers should be inspected on a routine basis to ensure that they have not been damaged (such as by vehicle traffic) and that any openings and penetrations which have been created since the barrier was constructed are properly protected.

16.5.3 *Fireproofing*

Structural steel which is exposed to a fire can lose its tensile strength and eventually fail, depending on the quantity of heat generated and the duration of the fire. If steel failure occurs, equipment and piping could rupture or fall, potentially releasing additional fuel and other hazardous materials. It is desirable therefore to protect structural steel where the potential exists for the release of large quantities of flammable or combustible materials. Water spray (deluge sprinkler) protection can be used to provide this protection, but fireproofing is often preferred because of its passive nature and improved resistance to explosion overpressures.

Like fire barriers, fireproofing is designed to protect steel for a specified period of time as designated by a "fire resistance rating." Construction details for various fireproofing system designs with different fire resistance ratings can be found in the *UL Fire Resistance Directory* (1992). Resistance ratings for fireproofing typically range from 1 to 4 hours and are determined based on one of two test methods, ASTM E-119 (UL 263) or UL 1709. ASTM E-119, as discussed previously, simulates the heat developed from fires involving ordinary combustibles and is not reflective of the rapid and high heat release from burning hydrocarbons. UL 1709, also known as the Rapid Rise Fire Test, on the other hand, simulates the heat release from burning hydrocarbons and thus is better suited for determining the fire resistance rating of fireproofing used in chemical process plants (A comparison of ASTM and UL test methods is illustrated in Figure 16-3).

There are three basic types of fireproofing systems:

- *Spray-on/Coated Systems*—These systems consist of fireproofing materials which are sprayed or coated directly onto the structural steel, often with some means of reinforcement. The materials used are one of two types:

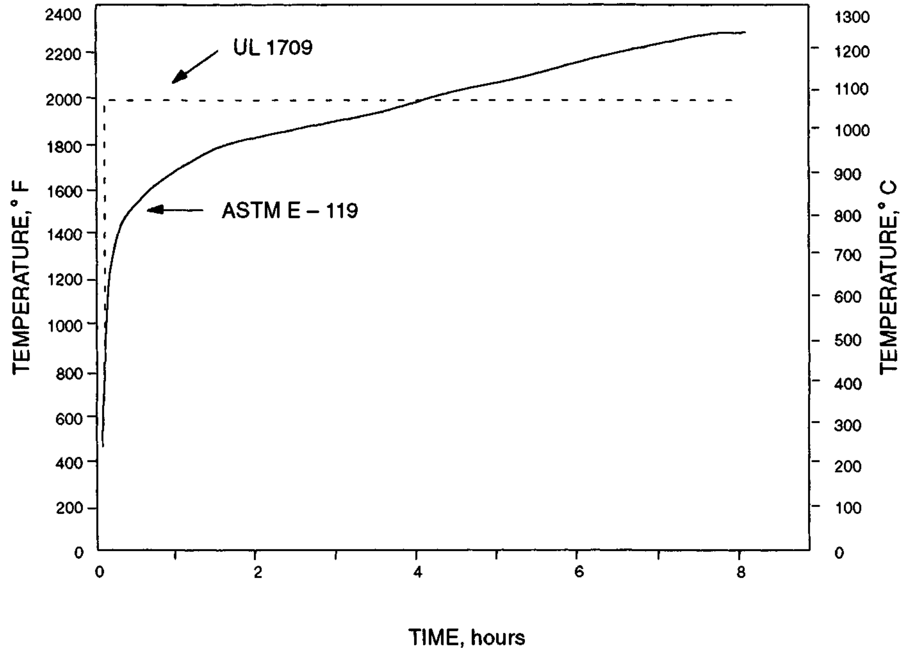


Figure 16-3 Comparison of methods to test fireproofing. Time–temperature curves show the reaction of concrete encased columns to fire severities represented by ASTM E-119 and UL 1709. Preparation of samples and test conditions are described in IM.2.5.1. (IRI 1990).

heat reactive or inert insulating (e.g., concrete, vermiculite, gunite, and cementitious mixtures). Heat reactive materials absorb heat via their reactive mechanisms and are sacrificial in nature.

- *Wrap Systems*—These systems consist of flexible sheeting or mats which are wrapped around structural steel members. The sheeting or mats are then secured in place.
- *Box Systems*—These systems consist of a "box" which is constructed around the structural steel member using noncombustible insulating materials such as mineral, fiber or gypsum boards; mineral wool bats; gypsum; or cementitious mixtures. Laths are needed for some of these materials.

The extent of fireproofing, including the fire resistance rating, depends on a number of factors, including: volume of flammable/combustible liquid which could be released, release scenarios, hazards of materials in the process (toxicity, flammability, reactivity, etc.), criticality of operations, liquid drainage systems, elevation and proximity of steel to potential fire, building code and insurance company requirements, company standards, and other protective features. Initially, however, consideration should be given to fireproofing load-bearing steel 9–12 m (30–40 feet) above grade (or above other solid surfaces where flammable/combustible liquids could pool) and within 4–8 m (15–25 feet) of a potential fire (including the drainage path of burning liquids). It should be emphasized that these are general guidelines and that more or less fireproofing may be warranted depending on the specific situation and hazards. For this reason, persons experienced in fire protection should be consulted when specifying the installation of fireproofing. Additional information can also be found in API 2218, "Fireproofing Practices in Petroleum and Petrochemical Processing Plants"; NFPA 30, "Flammable and Combustible Liquids Code"; and various insurance company publications.

Load-bearing steel for which fireproofing should be considered includes structure columns and beams. (Wind and cross bracing will generally not warrant fireproofing if failure of such members will not adversely affect the structural integrity of the structure).

It is common practice not to apply spray-on/coated type fireproofing on the top flanges of beams which will be used to support open-type floor grating. This is due to the difficulty in achieving adequate fireproofing application without affecting the quality (and safety) of the walking surface and without creating corrosion problems. According to some sources (Castle and Castle 1987) this is acceptable since the principal fire exposure is often from pool fires underneath the beam. It is important however that the interface between the fireproofing and the steel at the flange edge be properly sealed with caulk or other materials to prevent water and chemicals from penetrating beneath the fireproofing.

- Equipment supports, such as vessel legs, skirts, and saddles (skirts may warrant fireproofing on the inside if there are internal leakage sources or if there are sufficiently large openings in the skirt which would allow heat from an external fire to enter; also, fireproofing of saddles is not necessary if the height of the saddle at its lowest point is 12 inches or less).
- Pipe supports (racks).

Fireproofing is also sometimes applied to process equipment and electrical/instrument cables to protect them from fire.

While installation in general is important to the performance of fireproofing, two aspects are especially critical with respect to spray-on/coated fireproofing: surface preparation and final finish (top) coating. If the steel surface is not properly prepared, the fireproofing material may not adhere to adequately to the steel and could even delaminate during a fire. It is therefore important to follow the manufacturer's recommendations for surface preparation and to test the adhesion of the applied fireproofing. Top coating is not always necessary, but it may be desirable where highly corrosive materials are present. Top coating also allows for easier cleaning of the fireproofing.

Fireproofing should routinely be inspected for physical damage, delamination or other deterioration. Any deteriorated fireproofing should be completely removed and promptly repaired.

16.5.4 Thermal Insulation

Insulation is sometimes used to protect vessels or equipment from heat during a fire. This can be particularly useful with respect to design of emergency relief systems as use of thermal insulation may allow a reduction in the vent size. When credits for insulation of equipment are used, care should be taken to insure that the insulation will withstand the exposure from the fire and hose stream application. See Chapter 8 for a more detailed discussion of thermal insulation, and Chapter 6 for a discussion on the protection of gasketed flanges exposed to fire.

16.5.5 Separation Distances

Fires, particularly those involving hydrocarbons, can generate significant amounts of both radiant and convective heat. Except for the immediate area of the fire, radiant heat is of primary concern. For example, an 80 foot diameter pool fire of *n*-octane can generate sufficient radiant heat to warp steel 95 feet from the pool edge. As a result, protection against radiant heat from potential fires is often necessary for chemical plant facilities.

While protection against radiant heat can be provided by the passive fire protection methods discussed previously or by active fire protection systems, such as sprinklers, physical separation is a frequently used method and the most desirable since it also provides protection from explosions in adjacent areas. In some cases, however, physical space is limited and the appropriate separation distances cannot be provided; in such cases, other protective measures must be employed. In addition, it is not unusual for separation distances to be compromised as the result of subsequent plant expansions, process changes or other modifications. For this reason, it is essential that minimum separation distances be clearly defined and maintained if at all possible. If future plant modifications are anticipated which might impact separation distances, consideration should be given to employing larger initial separation distances and/or other protective means.

Adequate separation is often achieved by dividing up a plant into process blocks of similar or like hazards, for example, process units, tank farms, loading/unloading operations, utilities, waste treatment, and support areas, and then separating individual operations or hazards within each block. The block approach also serves to reduce the loss potential from catastrophic events, such as unconfined vapor cloud explosions, and to improve accessibility for emergency operations (see Chapter 3, Plant Design).

Two methods exist for determining minimum separation distances within chemical process plants. The first method is to use recommended separation distances for generic plant hazards, such as those covered in Chapter 3. These distances are generally conservative and will cover most situations. Tables of recommended separation distances are available from several sources, including API and some insurance companies.

The second method of determining minimum separation distances is by calculating the heat flux—the amount of heat received by an object—and the resulting surface temperatures that would be expected from a fire involving the actual hazards in question. While this method generally results in more realistic separation distances, the calculations are often complex and should only be performed by persons familiar with the concepts involved. In addition, the calculations should consider all possible scenarios. Space does not permit complete discussion of this subject; however, additional information can be found in the SFPE *Handbook of Fire Protection Engineering* (SPFE 1988) as well as various technical journal articles. Computer programs are also commercially available which can be used to estimate radiant heat from fires, although the sophistication and accuracy of these programs vary.

NFPA 30 also provides minimum separation distances, particularly with respect to storage tanks.

In addition to radiant heat exposure, other factors which should be considered in determining separation distances and plant layout include topography, prevailing winds (for normal and accidental vapor/gas releases), liquid drainage paths (for accidental liquid spills), location of fire protection equipment and accessibility for emergency vehicles.

16.5.6 Drainage/Spill Control Systems

Large quantities of water may be used to fight fires in facilities handling chemicals. Since most flammable materials float on water, there is the potential for fire protection water to spread the fire. In addition, many chemicals have the potential to contaminate the soil and groundwater. Water used for fire fighting can disperse these chemicals spreading the pollution. As a result of all these factors, there is a need for drainage systems to control water runoff. An equally important point to make is that drainage systems can control flammable liquid spills.

Drainage facilities should be designed to simultaneously carry flammable liquids and fire protection water away from buildings, structures, storage tanks, pipe racks, and process equipment. Drainage systems should not expose adjacent plant facilities to burning or toxic materials during an incident. This may require diversionary curbs, trenches, collection sumps, skimmers, and holding ponds or basins.

In many cases, the water and chemicals collected during an incident will need to be "pretreated" prior to disposal in a waste water treatment facility, or the rate that these materials are introduced to the treatment process controlled. Small holding ponds for specific process areas should be sized to hold 30–60 minutes of discharge as a minimum. Where there is the potential for fires of long duration, such as in petrochemical or oil refining facilities, special precautions will be necessary. It may be possible to separate organics from fire water prior to disposal, thus reducing the size of the required holding area. As noted in the introduction to this section, the potential for soil and water contamination should not be used as a reason to avoid providing fire protection or drainage systems.

Drainage of liquids may not be desirable in some cases, since this may actually result in more serious concerns (such as large vapor clouds or contamination of drinking water), and in other cases, drainage and remote containment may not be practical due to space limitations or other reasons. In such cases, additional automatic fixed fire protection measures such as foam or waterspray may be necessary to ensure adequate protection is afforded.

Drainage/spill control systems are typically comprised of a combination of features to achieve the necessary spill control depending on the particular situation. These features include the following:

- Sloped surfaces (typically minimum 1%)
- Trenches
- Flumes or sluiceways
- Drains (with traps to prevent flashback)
- Curbs or dikes
- Sumps or pits (to contain small spills)
- Separators or skimmers (to separate contaminants from water)

- Remote containment basins or tanks
- Reactivity of chemicals with water or other chemicals in the drainage system

The design of drainage/spill control systems can be complex. Space does not permit a complete discussion of this subject, but some of the factors which should be considered in the design of drainage/spill control systems include the following:

- Volume of liquid which could be released as well as the rate and mode of release
- Properties of the liquid which could be released, including extinguishability, viscosity, water solubility, specific gravity, and volatility.
- Expected flow from water based fire extinguishing systems, such as sprinklers, foam systems, hoses, and monitor nozzles
- Surface type (earth, gravel, concrete, etc.)
- Topography
- Spacing and location of facilities
- Rainfall (containment facilities should normally contemplate some rainfall in capacity design)
- Expected duration of fire (or time to implement contingency plans)
- Risk of environmental contamination (proximity to water supplies, geology, etc.)
- Local codes and regulations
- Need to separate organics from water to prevent drainage to rivers

NFPA 30 and the appendix of NFPA 15, "Water Spray Fixed Systems" should be consulted for details on the design of drainage/spill control systems. Additional guidance can be obtained from insurance company publications.

Drainage/spill control systems should be inspected on a regular basis to ensure they are in good condition. In particular, drains and trenches should be examined to ensure they do not contain any blockages. Rainwater should be drained or pumped out of containment facilities following each rainfall.

16.6 REFERENCES

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2

INHERENTLY SAFER PLANTS

2.1 INTRODUCTION

In a 1988 report "Survey of Chemical Engineering Research: Frontiers and Opportunities," the National Research Council identified inherently safer plant designs as a critical element for the continuing improvement of the good safety record of the chemical and petrochemical industries. The report particularly recognizes the importance of process selection on safety, stating that "few basic decisions affect the hazard potential of a plant more than the initial choice of technology" ("Design" 1988).

An inherently safer plant relies on chemistry and physics—the quantity, properties and conditions of use of the process materials—to prevent injuries, environmental damage and property damage rather than on control systems, interlocks, alarms and procedures to stop incipient incidents. In the long term, inherently safer plants are often the most cost effective. Smaller equipment operating at less severe temperature and pressure conditions will be cheaper and have lower operating costs. A process that does not require complex safety interlocks and elaborate procedures will be simpler, easier to operate, and more reliable. The need for an ongoing commitment of resources to maintain the safety systems will be eliminated. The safety of nuclear power plants relies heavily on complex instrumentation and safety systems, and the cost associated with those systems is high. Forsberg (1990) has estimated that 30–60% of the operating costs of a typical nuclear power plant are associated with safety.

In recent years there has been considerable interest in inherently safer plants in the chemical process industries. A number of papers and two excellent books by Kletz (1983, 1984, 1989, 1990, 1991a,b,c) provide an overview of the general concepts of inherently safer plants, and describe many specific examples. Recent papers by Englund (1990, 1991a,b) and several other authors (Althaus and Mahalingam 1992; Dale 1987; Doerr and Hessian 1991; Hendershot 1988, 1991a; Prugh 1992) also review inherently safer plants and processes and provide many specific examples of inherently safer designs.

Although a process or plant can be modified to increase inherent safety at any time in its life cycle, the potential for major improvements is greatest at the earliest stages of process development. At these early stages, the process engineer has maximum degrees of freedom in the plant and process specification. The engineer is free to consider basic process alternatives such as fundamental technology and chemistry and the location of the plant. Imperial

Chemical Industries (ICI) describes six stages of hazard studies, including three during the process design phase and three during construction, startup and routine plant operation. The identification of inherently safer process alternatives is most effectively accomplished between the first and second process design hazard studies (Preston and Turney 1991). At this stage the conceptual plant design meets the general rule for an optimization process—that a true optimum can be found only if all of the parameters are allowed to vary simultaneously (Gygax 1988).

2.1.1 Process Risk Management Strategies

Risk has been defined as a measure of economic loss or human injury in terms of both the incident likelihood and the magnitude of the loss or injury (CCPS 1989). Thus, any effort to reduce the risk arising from the operation of a chemical processing facility can be directed toward reducing the likelihood of incidents (incident frequency), reducing the magnitude of the loss or injury should an incident occur (incident consequences), or some combination of both. In general, the strategy for reducing risk, whether directed toward reducing frequency or consequence of potential accidents, falls into one of the following categories:

- *Inherent, or Intrinsic*—Eliminating the hazard by using materials and process conditions that are nonhazardous (e.g., substituting water for a flammable solvent).
- *Passive*—Eliminating or minimizing the hazard by process and equipment design features that do not eliminate the hazard, but do reduce either the frequency or consequence of realization of the hazard without the need for any device to function actively (e.g., the use of higher pressure rated equipment).
- *Active*—Using controls, safety interlocks, and emergency shutdown systems to detect potentially hazardous process deviations and take corrective action. These are commonly referred to as engineering controls.
- *Procedural*—Using operating procedures, administrative checks, emergency response and other management approaches to prevent incidents, or to minimize the effects of an incident. These are commonly referred to as administrative controls.

Risk control strategies in the first two categories, inherent and passive, are more reliable and robust because they depend on the physical and chemical properties of the system rather than the successful operation of instruments, devices and procedures. Inherent and passive strategies are not the same and are often confused. A truly inherently safer process will completely eliminate the hazard (Kletz 1991a). The discussion and examples in this chapter include both inherent and passive strategies to manage risk. Table 2-1 gives some

Table 2-1 Examples of Process Risk Management Strategies

Risk Management Strategy Category	Example	Comments
1. Inherent	An atmospheric pressure reaction using nonvolatile solvents which is incapable of generating any pressure in the event of a runaway reaction.	There is no potential for overpressure of the reactor because of the chemistry and physical properties of the materials.
2. Passive	A reaction capable of generating 150 psig pressure in case of a runaway, done in a 250 psig reactor.	The reactor can contain the runaway reaction. However, 150 psig pressure is generated and the reactor could fail due to a defect, corrosion, physical damage or other cause.
3. Active	A reaction capable of generating 150 psig pressure in case of a runaway, done in a 15 psig reactor with a 5 psig high pressure interlock to stop reactant feeds and a properly sized 15 psig rupture disk discharging to an effluent treatment system.	The interlock could fail to stop the reaction in time, and the rupture disk could be plugged or improperly installed, resulting in reactor failure in case of a runaway reaction. The effluent treatment system could fail to prevent a hazardous release.
4. Procedural	The same reactor described in Example 3 above, but without the 5 psig high pressure interlock. Instead, the operator is instructed to monitor the reactor pressure and stop the reactant feeds if the pressure exceeds 5 psig.	There is a potential for human error, the operator failing to monitor the reactor pressure, or failing to stop the reactant feeds in time to prevent a runaway reaction.

Note: These examples refer only to the categorization of the risk management strategy with respect to the hazard of high pressure due to a runaway reaction. The processes described may involve trade-offs with other risks arising from other hazards. For example, the nonvolatile solvent in the first example may be extremely toxic, and the solvent in the remaining examples may be water. Decisions on process design must be based on a thorough evaluation of all of the hazards involved.

examples of the four risk management strategy categories. The categories are not rigidly defined, and some strategies may include aspects of more than one category.

Marshall (1990, 1992) discusses managerial approaches to accident prevention, control of occupational disease and environmental protection in terms of strategic and tactical approaches. Strategic approaches have a wide significance and represent "once and for all" decisions. The inherent and passive categories of risk management would usually be classified as strategic approaches. In general, strategic approaches are best implemented at an early stage in the process or plant design. Tactical approaches, the active and procedural risk management categories, include safety interlocks, operating procedures, protective equipment and emergency response procedures. These approaches tend to be implemented much later in the plant design process, or even after the plant is operating, and often involve much repetition, increasing the costs and potential for failure.

In general it is probably not appropriate to talk about an *inherently safe* plant, but rather to use the term *inherently safer*. An absolute definition of safe is difficult, and risk cannot be reduced to zero. However it is possible to say that one process alternative is inherently safer than another alternative. For example, under the wrong circumstances water can be an extremely hazardous chemical—thousands of people drown every year. However, for the potential exposure scenarios in a chemical plant, water is clearly an inherently safer solvent than other materials.

Process alternatives may also involve trade-offs, where the increased inherent safety from the viewpoint of one hazard results in a less safe process from the viewpoint of a different hazard. The note to Table 2-1 describes a possible scenario where the increased inherent safety of a process option based on the risk of runaway reaction pressure may result in a less safe process with respect to the toxicity of the materials used. Another example, described by McQuaid (1991) considers the safety tradeoffs of one and two story houses. A one story house is inherently safer with regard to the risk of falling down steps. However, in an incident in Belgium in the 1970s, people woke up one morning in their second floor bedrooms and found that their domestic animals on the ground had been killed by a dense gas cloud from a chlorine leak at a nearby chemical plant. Considering the risk of being exposed to a dense toxic gas cloud, it is inherently safer to sleep in a second floor bedroom.

Another example of tradeoffs, frequently in the news in recent years, is the use of chlorofluorocarbon refrigerants in place of other materials such as ammonia and propane. Chlorofluorocarbons are clearly inherently safer from the viewpoint of acute toxicity (compared to ammonia) and flammability (compared to ammonia or propane). However, the suspected long term environmental impact of chlorofluorocarbon discharges to the atmosphere is resulting in their phase out in many applications. This illustrates the importance of understanding all of the hazards associated with material, process or plant design options. Then all hazards can be evaluated so that the best decision on which alternative results in the greatest overall benefit can be made.

2.1.2 Safety Layers

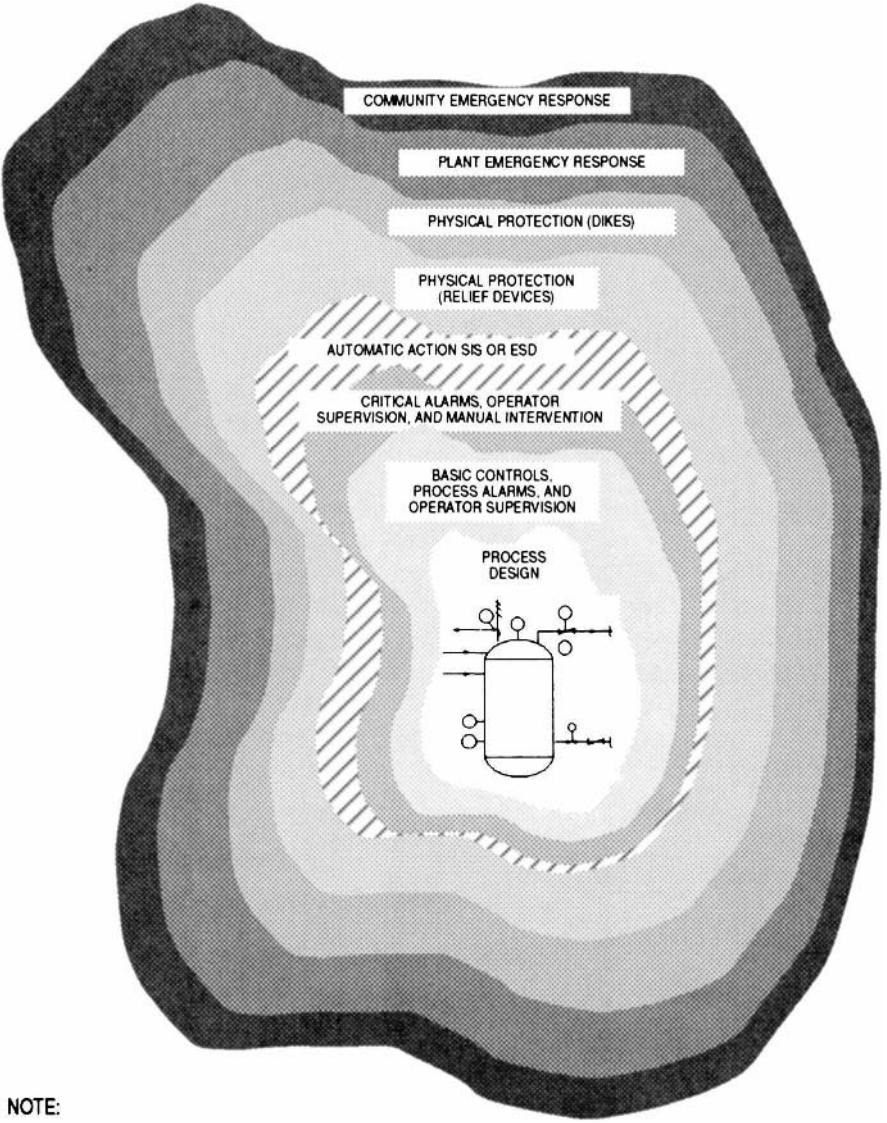
Process safety relies on multiple safety layers, or defense in depth, to provide protection from a hazardous incident (Drake and Thurston 1992; CCPS 1993; Johnson 1990). These layers of protection start with the basic process design and include control systems, alarms and interlocks, safety shutdown systems, protective systems and response plans as illustrated in Figure 2-1. Inherent and passive approaches to safety can be a part of several layers of protection. For example, proper dike design can minimize the evaporation of a spilled material. However, a truly inherent safety approach will be directed at the innermost layer of protection—the process design. The best first line of defense is to design a process in which hazardous incidents cannot happen. If such a process can be designed, or if potential incidents are small enough that they cannot hurt anybody, damage the environment or damage property if they do occur, then there will be no need for many of the additional layers of protection.

2.1.3 Design Approaches for Inherently Safer Plants

Approaches to the design of inherently safer plants have been categorized into five major groups by Kletz (1984, 1991d):

- *Intensification*—Using small quantities of hazardous substances
- *Substitution*—Replacing a material with a less hazardous substance
- *Attenuation*—Using less hazardous conditions or a less hazardous form of a material
- *Limitation of Effects*—Designing facilities that minimize the impact of a release of hazardous material or energy
- *Simplification/Error Tolerance*—Designing facilities that make operating errors less likely, and that are forgiving of errors that are made

The remainder of this chapter will discuss strategies for inherently safer plant design in more detail and provide some specific examples, using these categories to organize the discussions.



NOTE:

Protection layers for a typical process are shown in the order of activation expected as a hazardous condition is approached.

ESD – Emergency Shutdown
SIS – Safety Interlock System

Figure 2-1 Typical layers of protection in a modern chemical plant (CCPS 1993).

2.2. INTENSIFICATION

2.2.1 Reactors

Reactors often represent a large portion of the inventory of hazardous material in a chemical process. A reactor may be large because the chemical reaction is slow. However, in many cases the chemical reaction actually occurs very quickly, but it appears to be slow due to inadequate mixing and contacting of the reactants. Innovative reactor designs that improve mixing may result in much smaller reactors. Such designs are usually cheaper to build and operate, as well as being safer due to smaller inventory. In many cases, improved product quality and yield also result from better and more uniform contacting of reactants. A complete understanding of reaction mechanism and kinetics is essential to the optimal design of a reactor system. With a thorough understanding of the reaction, the designer can identify reactor configurations that maximize yield and minimize size, resulting in a more economical process, reducing generation of by-products and waste, and increasing inherent safety by reducing the reactor size and inventories of all materials.

2.2.1.1 Continuous Stirred Tank Reactors

Continuous stirred tank reactors (CSTR) are often much smaller for a specific production rate when compared to a batch reactor. In addition to reduced inventory, a CSTR usually results in other benefits which can also enhance safety, reduce costs, and improve product quantity. For example:

- Mixing in the smaller CSTR is generally better, which may improve product uniformity and reduce by-product formation
- Greater heat transfer surface per unit of reactor volume can be provided improving temperature control and reducing the risk of thermal runaway
- It may be more practical to build a small reactor for a high design pressure, allowing containment of a runaway reaction.

In one reported example, the same quantity of a material can be manufactured either in a 3000 gallon (~11 m^3) batch reactor or a 100 gallon (~0.4 m^3) CSTR. The reaction is exothermic and a runaway reaction could result in reactor rupture. Table 2-2 compares the overpressure resulting from reactor rupture at distances of 50 (15 m) and 100 feet (30 m) from the reactor for the two cases, assuming both reactors have the same design and rupture pressure (Hendershot 1991a). To put these numbers into perspective, 1 psig overpressure is sufficient to cause partial demolition of houses, and 2–3 psig overpressure shatters unreinforced concrete or cinder block walls (CCPS 1989).

In considering the relative safety of batch and continuous processing it is important to fully understand any differences in chemistry and processing conditions, which may outweigh the benefits of reduced size of a continuous

Table 2-2 Effect of Size on Overpressure Due to Vessel Rupture[a]

Distance (feet)	Overpressure from Vessel Rupture (psig)	
	3000 Gallon Batch Reactor	100 Gallon Continuous Reactor
50	3.4	0.62
100	1.1	0.27

[a] Hendershot 1991a

reactor. For example, Englund (1991a) describes continuous latex processes which have enough unreacted monomer in the continuous reactor that they may be less safe than a well designed batch process. Kletz (1991d) discusses a generic case where more severe processing conditions may result in a more severe hazard from a smaller reactor.

2.2.1.2 Tubular Reactors

Tubular reactors often offer the greatest potential for inventory reduction. In addition, they are usually extremely simple in design, containing no moving parts and a minimum number of joints and connections that could leak. In many cases a relatively slow reaction can be completed in a long tubular reactor. There are many devices available for providing mixing in tubular reactors, including jet mixers, eductors, and static mixers.

Caro's acid is an equilibrium mixture of sulfuric acid, water and peroxymonosulfuric acid (H_2SO_5) that can be used in the metal extraction and separation industries and other applications where an extremely powerful oxidizing agent is needed. It is manufactured by reacting concentrated sulfuric acid with hydrogen peroxide. Whiting (1992) describes a process for the manufacture of 300 kg/day of Caro's acid using a 30 liter agitated isothermal reactor with a 30 minute residence time. The reactor must operate at less than 0°C to avoid product decomposition. An improved process uses an adiabatic tubular reactor with a volume of 20 milliliters and a residence time of less than 1 second to produce 1000 kg/day of Caro's acid, a reactor size reduction of 1500:1. The process requires an elevated temperature, but the short residence time, and immediate reaction of the product with the solution to be treated, minimize decomposition at the elevated temperature.

A batch process for the manufacture of a nonhazardous product from several hazardous raw materials is shown in Figure 2-2. The batch stirred tank reactor has a volume of several thousand gallons. A new process, as shown in Figure 2-3, was developed using a tubular reactor containing static mixing

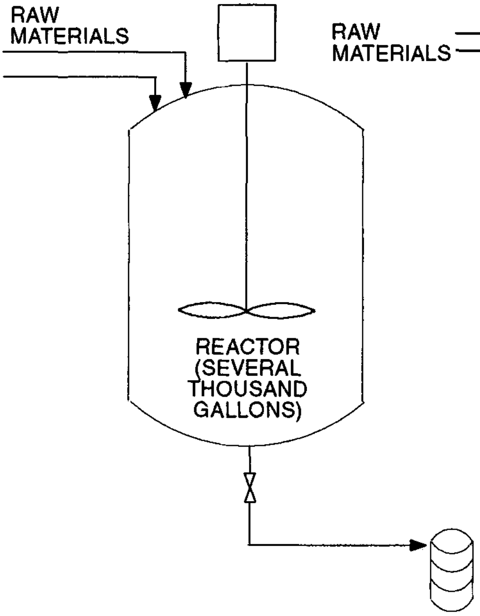


Figure 2-2. A large batch reactor to manufacture a product

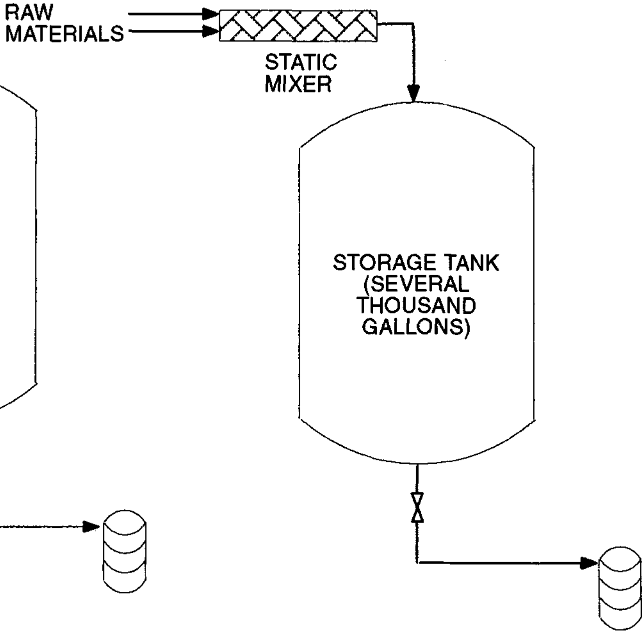


Figure 2-3. A tubular reactor to manufacture the product of Figure 2-2.

elements to replace the batch process. The new reactor was so much smaller that when a group of people who had seen the original plant toured the new manufacturing facility, they looked for a large reactor and finally mistook the final product storage tank for the reactor. Paul (1988) emphasizes the importance of a thorough study of the chemical reaction mechanisms and kinetics in several examples from the pharmaceutical industry, allowing the process designers to identify optimal reactor configurations using novel designs including tubular reactors with static mixing elements.

2.2.1.3 Gas–Liquid Reactions

Mass transfer is often the rate limiting step in gas–liquid reactions, and novel reactor designs that increase mass transfer can reduce reactor size and also improve process yields. As an example (Koestler 1992), an organic material was originally chlorinated in a glass-lined batch stirred tank reactor, with chlorine fed through a dip pipe. Replacement of the stirred tank reactor with a loop reactor, with chlorine fed to the recirculating liquid stream through an eductor, reduced reactor size, increased productivity and reduced chlorine usage as summarized in Table 2-3.

Table 2-3 Effect of Reactor Design on Size and Productivity for a Gas-Liquid Reaction[a]

Reactor Type	Batch Stirred Tank Reactor	Loop Reactor
Reactor Size (liters)	8000	2500
Chlorination Time (hr)	16	4
Productivity (kg/hr)	370	530
Chlorine Usage (kg/100 kg product)	33	22
Caustic Usage in Vent Scrubber	31	5

[a] Koestler 1992

2.2.1.4 *Some Additional Examples of Intensification*

Nitroglycerine formerly was manufactured in batch reactors containing more than one ton of material. Newer CSTR processes significantly reduce the inventory, and the Nobel AB process uses a mixing eductor reactor to reduce inventory to about 1 kg (Dale 1987, Kletz 1984, 1991d). Some ethylene oxide derivatives can be manufactured in a continuous tubular reactor rather than a batch reactor containing a potentially flammable vapor space (Kletz 1991d). Adipic acid can be manufactured in an internally cooled plug flow reactor rather than an externally cooled CSTR (Kletz 1984). Kletz (1984, 1991d) provides additional examples of intensification through improved reactor design.

2.2.2 Storage and Material Transfer

Raw material and in-process storage tanks often represent a major portion of the risk of a chemical plant. Hazardous material transfer lines can also be a significant hazard. Attention to the design of storage and transfer equipment can reduce hazardous material inventory.

2.2.2.1 *Storage*

Storage tanks for raw material and intermediates are often much larger than really necessary, usually because this makes it "easier" to operate the plant. The operating staff can pay less attention to ordering raw materials on time, or can accept downtime in a downstream processing unit, because upstream production can be kept in storage until the downstream unit is back on line. This convenience in operation can come at a significant cost in risk of loss of containment of the hazardous materials being stored. The process design engineers must question the need for all intermediate hazardous material storage, and minimize quantities where such storage is really needed. Similarly, hazardous raw material storage should also be minimized, with greater attention being given to "just in time" supply. Inventory reduction can also result in lower inventory costs, as well as increasing the inherent safety of the manufacturing facility.

The reduction in inventory resulting from greater attention to plant operations and design of unit interactions can be extremely large. Wade (1987) gives several excellent examples:

- An acrylonitrile plant eliminated 500,000 pounds (~277,000 kg) of in-process storage of hydrogen cyanide by accepting a shutdown of the entire unit when the product purification area shut down. This applied pressure to the plant to solve the problems that caused shutdown of the purification area.
- Another acrylonitrile plant supplied by-product hydrogen cyanide to various other units. An inventory of 350,000 pounds (~159,000 kg) of hydrogen cyanide was eliminated by having the other units draw directly from the acrylonitrile plant. This required considerable work to resolve many issues related to acrylonitrile purity and unit scheduling.
- A central bulk chlorine system with large storage tanks and extensive piping was replaced with a number of small cylinder facilities local to the individual chlorine users. Total inventory of chlorine was reduced by over 100,000 pounds (~45,360 kg).

2.2.2.2 *Transfer Piping*

Inventory in transfer lines can be a major factor in overall facility risk. For example, a quantitative risk analysis of a chlorine storage and supply system identified the pipeline from the storage area to the manufacturing area as the most important contributor to total risk (Hendershot 1991b). To minimize the risk associated with transfer lines, their length should be minimized by careful attention to unit location and pipe routing. Pipe size should be sufficient to convey the required amount of material and no larger. However, it is important to remember that small bore piping is less robust and less tolerant of abuse when compared to large piping, and that additional attention to proper support and installation will be required (IChemE 1987). In some cases, for example, chlorine for water treatment applications, it may be possible to transfer material as a gas rather than a liquid with a large reduction of inventory in the transfer line.

Options to reduce the inventory in a pipeline will reduce the downwind distance to a particular concentration of concern of a toxic or flammable material. For example, Table 2-4 compares the downwind distance to a 25 ppm chlorine concentration as a result of the rupture of various size liquid and vapor chlorine pipes.

Table 2-4 Effect of Various Options to Reduce Inventory on the Hazard Zone Resulting from the Rupture of a 500-Foot Chlorine Transfer Pipe[a]

Pipe Diameter (in)	Chlorine State	Inventory (kg)	Downwind Distance to Atmospheric Chlorine Concentration of 25 ppm (m)
2	Liquid	430	2400
1	Liquid	110	1700
1	Vapor	2	650

[a] Hendershot 1991a

2.2.3 *Distillation*

Some suggestions for inventory reduction in conventional distillation systems include:

- Minimize the size of reflux accumulators and reboilers (Dale 1987).
- Use internal reflux condensers and reboilers where practical (Dale 1987).
- Use column internals that minimize holdup without sacrificing operation efficiency (Dale 1987).
- Reduce the amount of material in the base of the column by reducing the diameter of the base (Kletz 1991d).
- Remove toxic, corrosive, or otherwise hazardous materials early in a distillation sequence, reducing the spread of such materials throughout a process (Wells and Rose 1986)

Low-inventory distillation equipment, such as the thin film evaporator, is also available and should be considered for hazardous materials. This equipment offers the additional advantage of short residence time and is particularly useful for reactive or unstable materials.

The use of Higee rotating distillation equipment, invented by Imperial Chemical Industries (ICI), can reduce inventory by a factor of 1000. The distillation occurs in a rapidly rotating bed containing a packing with a high specific surface area. Vapor is fed to the outside and moves to the center, contacting liquid fed at the center and moving outward. Extremely effective separations are possible with a small in-process inventory and very short residence time. This technology is described in more detail by Kletz (1991d).

Table 2-5 Surface Compactness of Heat Exchangers[a]

Type of Exchanger	Surface Compactness (m^2/m^3)
Shell and tube	70-500
Plate	120-225 up to 1,000
Spiral plate	Up to 185
Shell & finned tube	65-270 up to 3,300
Plate fin	150-450 up to 5,900
Printed circuit	1,000-5,000
Regenerative-rotary	Up to 6,600
Regenerative-fixed	Up to 15,000*
Twin screw extruder	"High"
Human lung	20,000

[a] Kletz 1991d

*Some types have a compactness as low as $25m^2/m^3$.

2.2.4 *Heat Transfer*

Heat transfer equipment has a great variation in heat transfer area per unit of material volume. Table 2-5 compares the surface compactness of a variety of heat exchanger types. Process inventory can be minimized by using heat exchangers with the minimum volume of hazardous process fluid for the heat transfer area required.

2.3 SUBSTITUTION

2.3.1 *Chemistry*

Inherent safety of the manufacturing process for a material can be greatly increased by development of alternate chemistry using less hazardous raw material or intermediates, reducing inventories of hazardous materials, or operating at less severe processing conditions. Identification of catalysts to enhance reaction selectivity or allow desired reactions to be carried out at a lower temperature or pressure is often a key to development of inherently safer chemical synthesis routes. The following are some specific examples of innovations in process chemistry that result in inherently safer processes.

Halogenated polymers can be manufactured by conducting the polymerization step first, followed by halogenation of the polymer. This avoids

Halogenated polymers can be manufactured by conducting the polymerization step first, followed by halogenation of the polymer. This avoids manufacture and handling of hazardous halogenated monomers (Burch 1986; Kharbanda and Stallworthy 1988).

The insecticide carbaryl, the product manufactured at Bhopal, can be produced by several routes, some of which do not use methyl isocyanate, the material that was released in the Bhopal accident, or that generate only small quantities of methyl isocyanate as an in-process intermediate (Kletz 1991d). DuPont has developed a proprietary process for manufacture of carbamate insecticides which generates and immediately consumes methyl isocyanate. Total methyl isocyanate inventory in the process is no more than 10 kilograms (Kharbanda and Stallworthy 1988).

Acrylonitrile can be manufactured by reacting acetylene with hydrogen cyanide:

$$CH{\equiv}CH + HCN \rightarrow CH_2{=}CHCN$$

A newer ammoxidation process uses less hazardous raw materials (propylene and ammonia) (Dale 1987; Puranik et al. 1990):

$$CH_2{=}CHCH_3 = NH_3 + \frac{3}{2}O_2 \rightarrow CH_2{=}CHCN + 3H_2O$$

The Reppe process for manufacture of acrylic esters uses hazardous raw materials, acetylene and carbon monoxide, and a catalyst with high acute toxicity, nickel carbonyl, to react with an alcohol to make the corresponding acrylic ester:

$$CH{\equiv}CH + CO = ROH \xrightarrow[HCl]{Ni(CO)_4} CH_2{=}CHCO_2R$$

The newer propylene oxidation process uses less hazardous materials to first manufacture acrylic acid followed by esterification with the appropriate alcohol (Hochheiser 1986).

$$CH_2{=}CHCH_3 + \frac{3}{2}O_2 \xrightarrow{catalyst} CH_2CHCO_2 + H_2O$$

$$CH_2CHCO_2H + ROH \xrightarrow{H^+} CH_2{=}CHCO_2R + H_2O$$

Polymer supported reagents, catalysts, protecting groups and mediators can be used in place of the corresponding small molecule materials (Sherrington 1991). The reactive species is tightly bound to a macromolecular support which immobilizes it. This generally makes toxic, noxious or corrosive material much safer. The use of polystyrene sulfonic acid catalyst for

$$CH_3OH + CH_2{=}C(CH_3)_2 \xrightarrow{\textit{Polystyrene Sulfonic Acid}} CH_3OC(CH_3)_3$$

Sherrington (1991) provides several additional examples and suggestions for future development.

Chemistry of side reactions and by-products may also offer opportunities for increasing the inherent safety of a process. For example, a process involving a caustic hydrolysis step uses ethylene dichloride as a solvent. Under the reaction conditions a side reaction between sodium hydroxide and ethylene dichloride produces small but hazardous quantities of vinyl chloride:

$$C_2H_4Cl_2 + NaOH \rightarrow C_2H_3Cl + NaCl = H_2O$$

An alternative nonreactive solvent has been identified which eliminates the hazard (Hendershot 1987).

Phase transfer catalysis ("Phase Transfer" 1990; Starks 1987; Starks and Liotta 1978) processes for the synthesis of many organic materials use less, or sometimes no, organic solvents, may use less toxic solvent, may allow use of less hazardous raw materials (for example, aqueous HCl instead of anhydrous HCl), and operate at milder conditions. Some types of reactions where phase transfer catalysis has been applied include:

- esterification
- nucleophilic aromatic substitution
- etherification
- dehydrohalogenation
- oxidations
- alkylation
- aldol condensations

Rogers and Hallam (1991) provide a number of additional examples of chemical approaches to inherent safety, involving synthesis routes, reagents, catalysts and solvents.

2.3.2 Solvents

Replacement of volatile organic solvents with aqueous systems or less hazardous organic materials improves safety of many processing operations and final products. Some examples include:

- Water based paints and adhesives in place of solvent based products
- Aqueous or dry flowable formulations for agricultural chemicals instead of organic solvent formulations
- British computer manufacturer ICL has eliminated chlorofluorocarbons from its manufacturing processes, replacing them with aqueous cleaning systems for flux removal ("Technology" 1991). In the United States, IBM

Table 2-6 Some Examples of Solvent Substitutions[a]

Chloroform → Acetone → Ethyl Acetate → Ethanol
Dichloromethane → Ethanol
Trichloroethylene → Aqueous System
Acetic Acid → Aqueous System
Propanol → 1,2-Propanediol → Aqueous System

[a] Adapted from Goldschmidt and Filskov 1990

has reduced or eliminated chlorofluorocarbons, chloroform, methylene chloride, and other hazardous solvents, replacing them with nonhazardous materials (Kelley 1992). Apple Computer reports the elimination of all chlorofluorocarbons for cleaning electronic assemblies and has converted to water based processes (*Chemical Week Newswire* 1992).

- The United States Air Force is evaluating a process called Coldjet which removes paint from airplanes using a jet of frozen carbon dioxide pellets in place of hazardous paint removal solvents (Welter 1991).
- Consumer paint removal products based on less volatile organic esters are now available as substitutes for products based on hazardous solvents such as methanol, toluene, acetone and methylene chloride ("Paint Removers" 1991).
- A Danish survey (Goldschmidt and Filskov 1990) confirms the feasibility of solvent substitution as a way of reducing workplace exposure to hazardous materials, particularly organic degreasing solvents. Table 2-6 lists some of the substitutions identified by this industrial survey.

2.3.3 *Utility Systems*

Utility and plant services systems must also be examined for options to increase the inherent safety of a plant or process. For example:

- Use water or steam as a heat transfer medium rather than flammable or combustible oils (Kharbanda and Stallworthy 1988; Kletz 1991d).
- Use high flash point oils or molten salt if water or steam is not feasible (Dale 1987; Kletz 1991d).
- Chlorofluorocarbon refrigerants have been cited as inherently safer alternatives to refrigerants such as ammonia and propane. Many chlorofluorocarbons are now being phased out because of suspected adverse environmental impact. This creates new challenges for industry in identifying new refrigerants that have the low acute toxicity and fire hazards

of chlorofluorocarbons but that do not have long term adverse environmental impacts.
- Alternatives to chlorine are available for water treatment and disinfection applications. For example, sodium hypochlorite has been used both in industrial and municipal water treatment applications (Governale 1989; Somerville 1990), and calcium hypochlorite is another possible alternative.
- Use magnesium hydroxide slurry to control pH, rather than concentrated sodium hydroxide (Englund 1991a).

2.4 ATTENUATION

Attenuation means using materials under less hazardous conditions. This can be accomplished by strategies that are either physical (e.g., lower temperatures, dilution) or chemical (e.g., development of a reaction chemistry that operates at less severe conditions).

2.4.1 Dilution

Dilution reduces the intrinsic hazards associated with storage of a low-boiling hazardous material in two ways: by reducing the storage pressure and by reducing the initial atmospheric concentration in the event of a release. Materials that boil below normal ambient temperature have often been stored in pressurized systems under their ambient temperature vapor pressure. The pressure in such a storage system can be lowered by diluting the material with a higher boiling solvent. This reduces the driving force (the pressure difference between the storage system and the outside environment) in case of a leak in the system, reducing the rate of release. As an example, Table 2-7 shows the effect of water dilution on the vapor pressure of ammonia and of monomethylamine solutions. Handling of these materials as a sufficiently dilute aqueous solution allows them to be stored at atmospheric pressure rather than in a pressurized system.

A distinct benefit of storage in the diluted form is the reduced partial pressure of the hazardous component in the solution. In the event of a loss of containment accident, the atmospheric concentration of the hazardous material at the spill location will be reduced. The reduced atmospheric concentration at the source results in a smaller hazard zone downwind of the spill.

Table 2-7 Vapor Pressure of Aqueous Ammonia and Monomethylamine Solutions[a]

Ammonia (21°C)		Monomethylamine (20°C)	
Concentration (wt %)	Vapor Pressure (atm)	Concentration (wt. %)	Vapor Pressure (atm)
100.0	8.80	100.0	2.80
48.6	3.00	50.0	0.62
33.7	1.10	40.0	0.37
28.8	0.75		
19.1	0.31		

[a] Hendershot 1991a

The effect of water dilution of monomethylamine, a flammable and toxic material, on the vapor cloud resulting from a loss of containment incident is shown in Figure 2-4. Monomethylamine boils at –6.7°C and has a vapor pressure of about 50 psig at 25°C. Figure 2-4 shows the relative hazard zones, defined as the distance from the source within which the monomethylamine vapor concentration will exceed a specified value. The loss of containment event in this example is the complete failure of a 1-inch liquid pipe under a specific atmospheric condition for (A) anhydrous monomethylamine and (B) a 40% aqueous monomethylamine solution. The hazard zone extends to a much greater distance in the case of ambient storage of anhydrous monomethylamine.

Many materials can be handled in a dilute form to reduce the risk of handling and storage. Some other examples include:

- muriatic acid in place of anhydrous HCl
- dilute nitric acid in place of concentrated fuming nitric acid
- sulfuric acid in place of oleum (SO_3 solution in sulfuric acid) for sulfonation reactions

If a chemical process requires the concentrated form of a material, it may be feasible to store it as a more dilute form and concentrate the material, by distillation or some other technique in the plant prior to introduction to the process. This reduces the inventory of material with greater intrinsic hazard to the minimum amount required to operate the process.

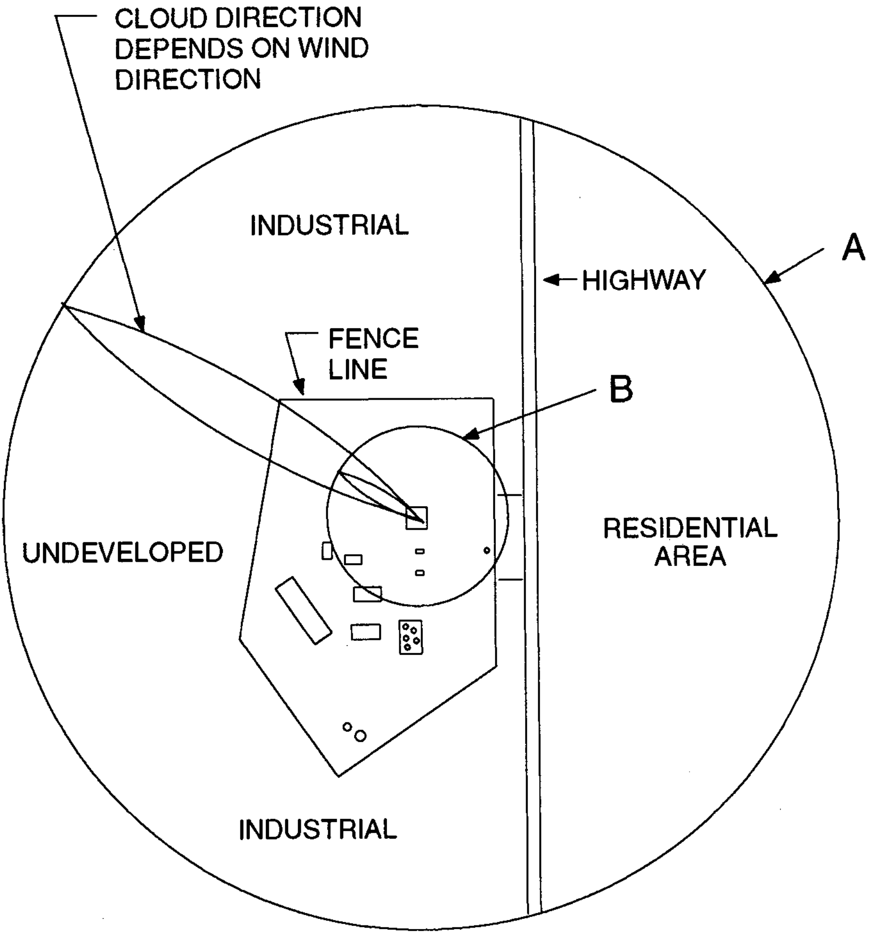


Figure 2-4. Relative hazard zones for anhydrous and aqueous monomethylamine releases—relative distances within which a specified concentration of monomethylamine is exceeded upon rupture of a 1-inch liquid pipe at summer ambient temperature for (A) anhydrous monomethylamine and (B) aqueous monomethylamine (Hendershot 1988).

2.4.2 *Refrigeration*

Many hazardous materials such as ammonia and chlorine (Puglionesi and Craig 1991; Somerville 1990) can be stored at or below the atmospheric boiling point using practical refrigeration systems. The atmospheric pressure boiling points of some common materials for which refrigerated storage may be a viable option are summarized in Table 2-8.

Table 2-8 Atmospheric Pressure Boiling Point of Selected Hazardous Materials[a]

Material	Atmospheric Pressure Boiling Point (C)
Chlorine	–34
Ammonia	–33
Methyl Chloride	–24
Sulfur Dioxide	–10
Monomethylamine	–7
1,2–Butadiene	–4
Dimethylamine	+7
Phosgene	+8
Hydrogen Fluoride	+19
[a] Hendershot 1991a	

Refrigerated storage reduces the magnitude of the consequences of a release from a hazardous material storage facility in three ways: by reducing the storage pressure, by reducing the initial flash in the event of a leak, and by reducing or eliminating liquid aerosol formation in the event of a leak.

Refrigeration, like dilution, reduces the vapor pressure of the material being stored, reducing the driving force (pressure differential) for a leak to the outside environment. If possible, the hazardous material should be cooled to its atmospheric pressure boiling point. At this temperature the rate of flow of a liquid leak will depend only on liquid head or pressure, with no contribution from vapor pressure. The flow through any hole in the vapor space will be minimal and will be limited to breathing and diffusion.

Material stored at or below its atmospheric pressure boiling point has no superheat. Therefore there will be no initial flash of liquid to vapor in case of a leak. Vaporization will be controlled by evaporation from the pool formed by the leak, with potential for reducing the rate through secondary containment design as well as emergency response countermeasures.

Many materials, when released from storage in a liquefied state under pressure, form a jet containing an extremely fine liquid aerosol. The fine aerosol droplets formed may not rain out onto the ground, but instead may be carried downwind as a dense cloud. The amount of material contained in the cloud may be significantly higher than would be predicted based on an equilibrium flash calculation assuming that all of the liquid phase rains out (Johnson and Diener 1991). This phenomenon has been observed experimentally for many materials, including propane (Brown et al. 1987), ammonia (Kaiser 1989), hydrogen fluoride (Tilton and Farley 1990), and monomethylamine (Lantzy et al. 1990). Refrigeration of a liquefied gas to a temperature near its atmospheric pressure boiling point eliminates the two-phase flashing jet, and the liquid released will rain out onto the ground. Containment and remediation measures such as spill collection, secondary containment, neutralization and absorption may then be effective in preventing further vaporization of the spilled liquid.

Brown et al. (1987) have estimated the relative release rates of propane from a pipe containing gas, refrigerated liquid, and pressurized liquid at ambient temperature, as shown in Figure 2-5. Refrigeration clearly has a significant benefit in terms of reducing the rate of vapor release to the atmosphere.

Refrigerated storage greatly reduces the size of a hazard zone. The effect of refrigeration on the hazard zone, defined as the distance from the release within which the atmospheric concentration exceeds a specified hazardous concentration, for a monomethylamine release is shown in Figure 2-6. The accident scenario is the rupture of a 1-inch pipe containing liquid monomethylamine, (A) stored at ambient temperature under its vapor pressure of about 50 psig, and (B) stored at its atmospheric boiling point of about –7°C.

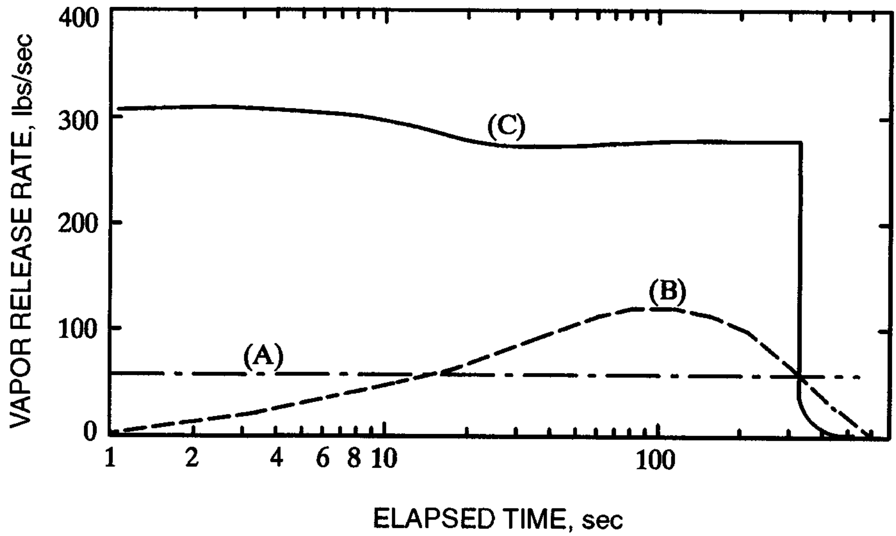


Figure 2-5. Effect of release conditions on vapor release rate for a 6-inch propane line: (A) gas phase release, (B) refrigerated liquid release, (C) two-phase release (Brown et al. 1987).

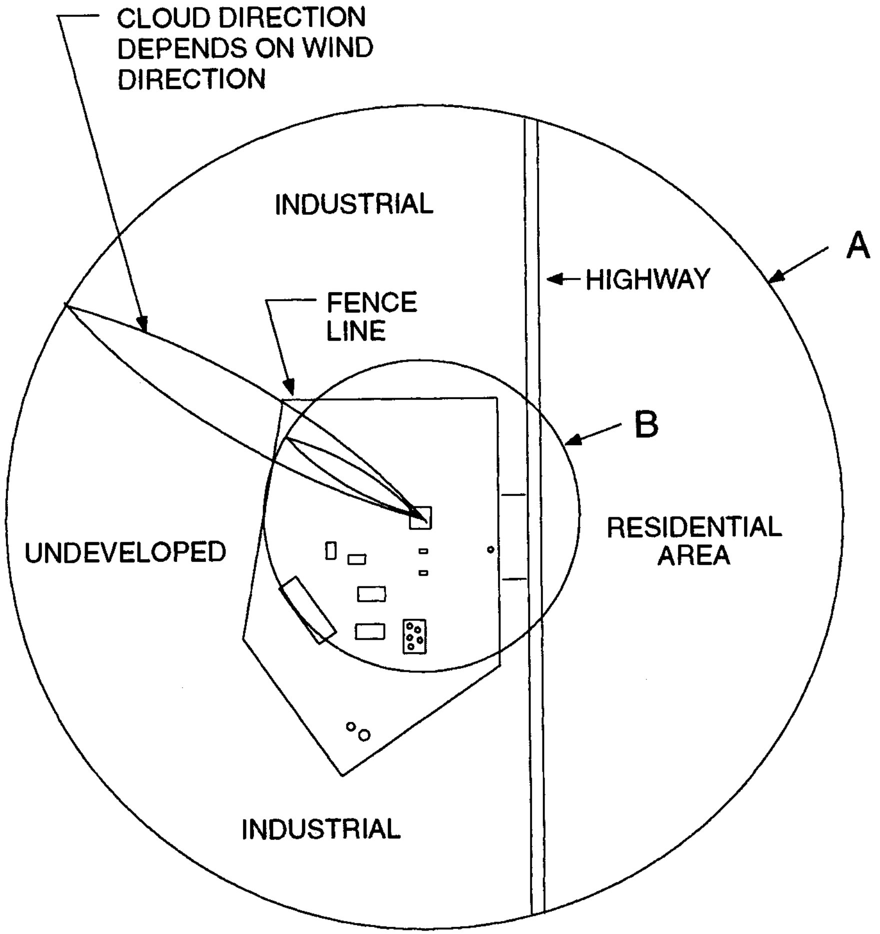


Figure 2-6. Relative hazard zones for ambient and refrigerated storage of monomethylamine releases—relative distances within which a specified concentration of monomethylamine is exceeded upon rupture of a 1-inch liquid pipe containing liquid anhydrous monomethylamine (A) at summer ambient temperature and (B) refrigerated to its atmospheric pressure boiling point (Hendershot 1988).

Figure 2-7 is an example of a refrigerated storage facility for chlorine. A similar installation has also been proposed for phosgene storage (Puglionesi and Craig 1991; Somerville 1990).

2.4.3 *Solids Handling*

Handling solids in the form of larger particle size granules or pellets rather than a fine powder reduces the potential for worker exposure (Burch 1986). If

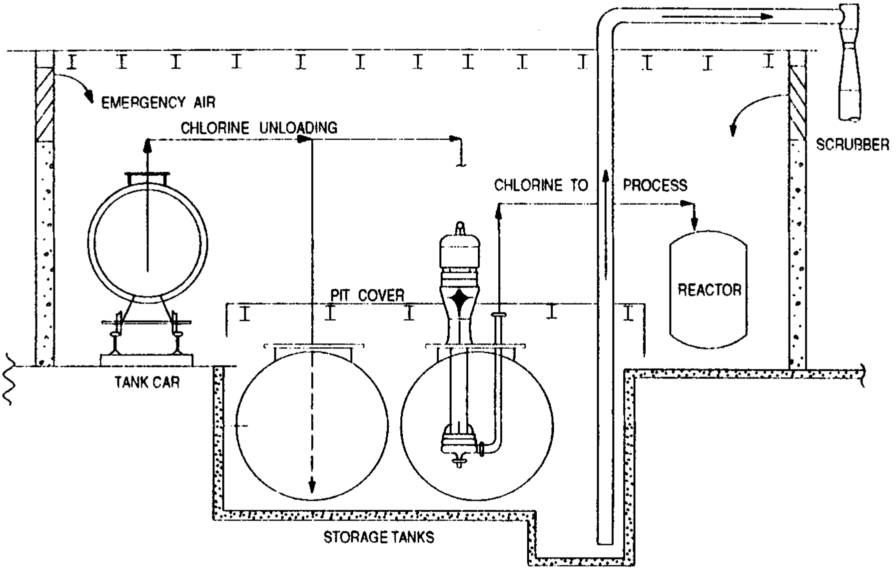


Figure 2-7. A chlorine storage system (Somerville 1990).

the solid is combustible, the dust explosion hazard can be greatly reduced or even eliminated by using a larger particle size material (Englund 1990, 1991a). For example, Figure 2-8 shows the effect of particle size on dust explosion properties for several combustible dusts. However, it is important to consider the possibility of particle attrition which can occur during handling and processing, resulting in the generation of small particles which could increase dust explosion hazards.

Handling of solids as a wet paste or slurry can also reduce hazards. For example, using wet benzoyl peroxide instead of dry reduces the hazards of this extremely reactive material (Yoshida et al. 1991). Worker exposure hazards are reduced by formulating dyes as liquids or wet pastes rather than dry solids or powders (Burch 1986).

2.4.4 Attenuation of Process Conditions

Processing under less severe conditions, particularly lower temperature and pressure, increases the inherent safety of a chemical process. Some examples include:

- Improvements in ammonia manufacturing processes have reduced operating pressures. In the 1930s ammonia plants operated at pressures as high as 600 bar. In the 1950s, process improvements had reduced operating pressures to 300–350 bar. By the 1980s, ammonia processes operating

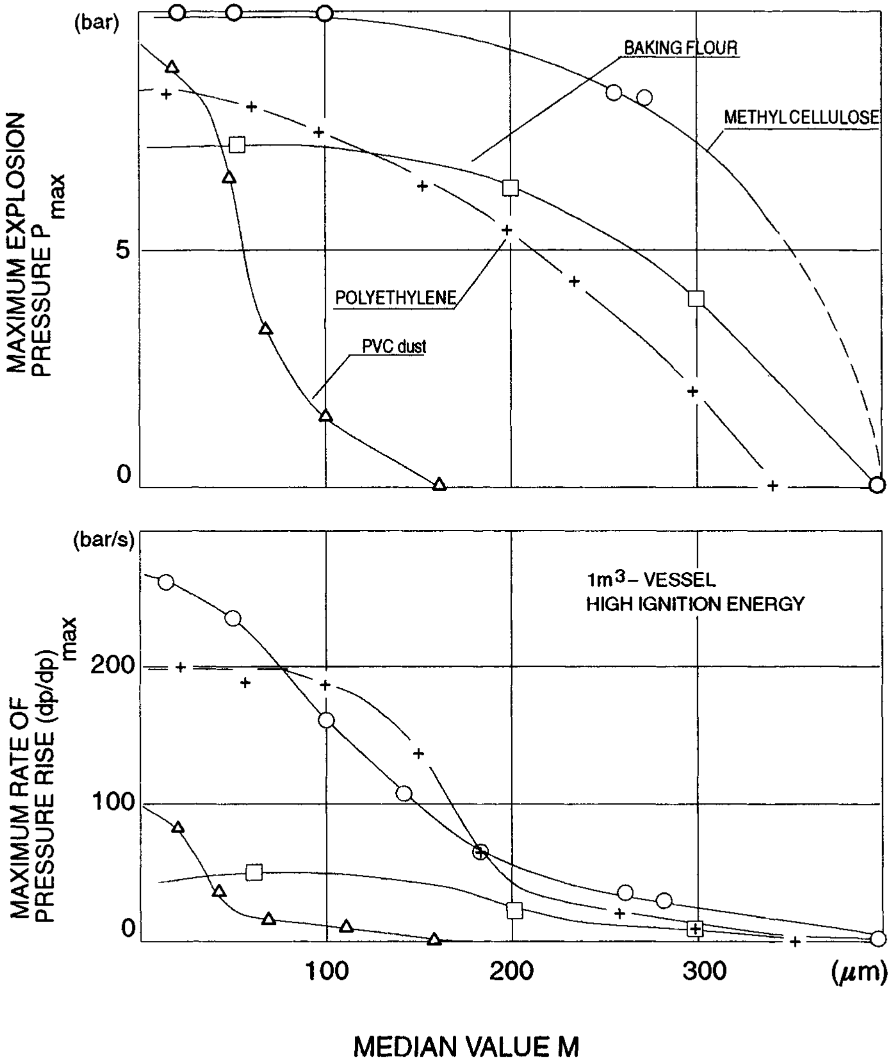


Figure 2-8. Influence of particle size on explosion properties of combustible dusts.

in the 100–150 bar range were being built. Besides being safer, the lower pressure plants are also cheaper and more efficient (Kharbanda and Stallworthy 1988).

- Catalyst improvements allow methanol plants and plants using the Oxo process for aldehyde production to operate at lower pressures (Dale 1987).

Next Page

- Improvements in polyolefin manufacturing technology have resulted in lower operating pressures (Althaus and Mahalingam 1992; Dale 1987).
- Use of a higher boiling solvent may reduce the normal operating pressure of a process and will also reduce the maximum pressure resulting from an uncontrolled or runaway reaction (Wilday 1991).

2.5 LIMITATION OF EFFECTS

2.5.1 Isolation by Siting/Location

Proper siting of hazardous material processing facilities impacts inherent safety in two ways: by reducing the impact of a release of material and/or energy on surrounding people and equipment and by reducing the potential for one incident to initiate another incident in a nearby facility ("knock-on effects"). Adequate distances between hazardous material unloading, storage, and processing facilities must be maintained. Toxic and flammable materials should be stored as far as possible from the controlled site boundary or fence. Buffer zones between hazardous installations and on-site population concentrations or the surrounding community should be maintained. The size of the required buffer zones can be determined by estimating the consequences of potential credible accident scenarios (Crossthwaite and Crowther 1992). Relocation of manufacturing facilities can eliminate the need for storage and transport of hazardous materials (Wade 1987) or can provide greater separation of hazardous material handling facilities from surrounding population (Orrell and Cryan 1987).

Process siting decisions should include consideration of opportunities to eliminate the transport of hazardous materials and to minimize storage inventories. The three step process of Figure 2-9(A) requires shipment of a hazardous intermediate and also a large storage tank at two separate plant locations. The relocation of the second manufacturing step to Plant 1 eliminates the need for transport of the hazardous material and reduces total inventory. In general, an overall manufacturing process will be inherently safer if hazardous materials are manufactured as needed and immediately consumed at a single manufacturing location.

2.5.2 Batch Reactors

Semi-batch or gradual addition batch processes increase safety by limiting the supply of one or more reactants (Englund 1982, 1990, 1991a; Hendershot 1987; Wilday 1991). For an exothermic reaction, this limits the total energy of reaction available in the reactor at any time. Ideally, the limiting reactant will be consumed rapidly as it is fed, and there will be no buildup of unreacted

12

ELECTRICAL SYSTEM HAZARDS

The two principal hazards of electricity are electric arcs (sparks) and electrical shock. Sparks and arcs may ignite flammable mixtures, resulting in fire or explosion. Although electrical and thermal energy burns and electrical shocks can cause serious injuries to personnel, this will not be addressed in this chapter since our focus is the avoidance of catastrophic events.

In designing an electrical system in a facility that handles chemicals, an engineer must pay special attention to the safe and reliable application of electrical apparatus, hazards associated with static electricity and methods of grounding and lightning protection. This chapter addresses the control of ignition from electrical sources and conditions that generate sparks.

12.1 ELECTRICAL EQUIPMENT HAZARDS

12.1.1 Electrical Area Classification

The classification of areas inside a facility that handles flammable gases, liquids and dusts is the basis for correct selection of electrical apparatus and enclosures for electrical components. Area classifications are defined in the National Electrical Code, NFPA 70, Article 500, Hazardous (Classified) Locations, and summarized in Appendix 12A, beginning on page 365.

Locations are classified according to the properties of the material being used and its surrounding atmosphere. Elements that affect the area classifications may include availability of flammable or explosive material, flammability or explosibility of the material, operating temperature and pressure, flash points, autoignition temperature, vapor density of the material, resistivity of dust or fibers, explosive pressures, dust layer ignition temperature, open or sealed conduit, and ventilation. Definitions for flammable and combustible liquids are given in NFPA 30.

Each room, section, or area must be considered individually in determining its classification. The overall classification of the area is also considered. For instance, consider the control building within a processing unit. Although the unit may be Division 2, the control building could be purged to nonclassified, and rooms within the control building also nonclassified. A representative (but far from complete) list of industrial facilities and operating areas where equipment is required to operate in hazardous locations is given in Table 12-1.

Table 12-1 Typical Hazardous Locations

Class I Locations

- Petroleum refining facilities
- Dip tanks containing flammable or combustible liquids
- Plants manufacturing organic coatings
- Spray finishing areas
- Solvent extraction plants
- Plants manufacturing or using pyroxylin (nitrocellulose) or other plastics
- Utility gas plants, operations involving storage and handling of liquified petroleum gas
- Petrochemical plants such as olefins, benzene, toluene, xylene, vinyl, polypropylene
- Polyvinyl chloride/monovinyl chloride, methanol, ammonia and other related facilities
- Chemical plants making or using flammable organics

Class II Locations

- Manufacture and storage of magnesium and aluminum powder
- Manufacture and storage of polyethylene fluff
- Manufacture and storage of starch
- Areas for packing and handling pulverized sugar and cocoa
- Facilities for coal or coke preparation and handling
- Confectionery manufacturing plants
- Chemical plants making or using powders or bulk solids

Class III Locations

- Textile mills
- Cotton gins and cotton seed mills

Sources: Adapted from IEEE 142

12.1.2 Types of Enclosures

To use electrical equipment in a hazardous atmosphere, specific types of enclosures are used to house the equipment. In order to make the correct application, it is necessary to recall the definitions given by the National Electrical Code (NEC) to the terms "explosionproof" and "dust-ignition-proof."

Explosionproof Apparatus: "Apparatus enclosed in a case capable of containing an explosion of a specified gas or vapor which may occur within it and preventing the ignition of a specified gas or vapor surrounding the enclosure by sparks, flashes or explosion of the gas or vapor within, and which operates at such an external temperature that a surrounding flammable atmosphere will not be ignited thereby" (NEC). These enclosures use a threaded joint or a ground joint to cool the escaping hot gases.

Arcing devices used in Class I, Division 1 and 2 locations, must have explosionproof housings, NEMA Type 7. There are several manufacturers that provide these enclosures which must be designed to withstand a hydrostatic pressure test of four times the maximum pressure from an explosion within the enclosure.

Dust-ignitionproof means "enclosed in a manner that will exclude ignitible amounts of dusts or amounts that might affect performance or rating and that, where installed and protected in accordance with this Code [NEC], will not permit arcs, sparks or heat otherwise generated or liberated inside of the enclosure to cause ignition of exterior accumulations or atmospheric suspensions of a specified dust on or in the vicinity of the enclosure" (NEC, Article 502).

Class II locations require dust-ignitionproof enclosures, NEMA Type 9, that exclude all dust from the interior of the box and at the same time are designed such that enclosed heat generating devices will not cause external surfaces to reach temperatures capable of igniting or discoloring dust on the enclosure or igniting dust–air mixtures in the surrounding atmosphere.

While the explosionproof and dust-ignitionproof enclosures are the most frequently used in hazardous areas, there are other NEMA type enclosures for electrical equipment located in nonhazardous areas (Table 12-2).

For ignition to occur, three components of the fire triangle must be present:

- flammable vapor, dust, or liquid mist within ignitible concentration limits
- presence of an oxidant
- presence of a sufficiently energetic ignition source, for minimum duration of contact

Ignition is prevented by removing any one of the three components. For example, one may

- alter the concentration of material, that is, move it out of flammable or explosive range (for example, purge with inert gas);
- eliminate the oxidant;
- remove the ignition source (or physically enclose or separate it), for example, use intrinsically safe equipment, explosionproof enclosures; prevent static.

12.1.3 Intrinsically Safe Equipment

Intrinsically safe equipment and wiring is defined as that incapable of releasing sufficient electrical energy at standard temperature and pressure to cause ignition of a specific hazardous substance in its most easily ignited concentration. Intrinsically safe equipment is primarily limited to process control instrumentation with low energy requirements. Several commercial devices in this category are listed by Underwriters Laboratories, Inc. (UL), and Factory Mutual Engineering Corp. (FMEC). It must be noted that intrinsically safe

Table 12-2 NEMA Definitions of Enclosures

DEFINITIONS PERTAINING TO NONHAZARDOUS LOCATIONS

Type 1 Enclosures are intended for indoor use primarily to provide a degree of protection against limited amounts of falling dirt.
NEMA Standard 7-15-1991.

Type 2 Enclosures are intended for indoor use primarily to provide a degree of protection against limited amounts of falling water and dirt.
NEMA Standard 1-10-1979.

Type 3 Enclosures are intended for outdoor use primarily to provide a degree of protection against the rain, sleet, windblown dust, and damage from external ice formation.
NEMA Standard 7-15-1991.

Type 3R Enclosures are intended for outdoor use primarily to provide a degree of protection against rain, sleet, and damage from external ice formation.
NEMA Standard 7-15-1991.

Type 3S Enclosures are intended for outdoor use primarily to provide a degree of protection against rain, sleet, windblown dust, and to provide for operation of external mechanisms when ice laden.
NEMA Standard 7-15-1991.

Type 4 Enclosures are intended for indoor or outdoor use primarily to provide a degree of protection against windblown dust and rain, splashing water, hose-directed water, and damage from external ice formation.
NEMA Standard 1-10-1979.

Type 4X Enclosures are intended for indoor and outdoor use primarily to provide a degree of protection against windblown dust and rain, splashing water, hose-directed water, and damage from external ice formation.
NEMA Standard 1-10-1979.

Type 5 Enclosures are intended for indoor use primarily to provide a degree of protection against settling airborne dust, falling dirt, and dripping noncorrosive liquids.
NEMA Standard 5-25-1988.

Type 6 Enclosures are intended for indoor or outdoor use primarily to provide a degree of protection against hose-directed water, the entry of water during occasional temporary submersion at a limited depth, and damage from external ice formation.
NEMA Standard 7-15-1991.

Type 6P Enclosures are intended for indoor or outdoor use primarily to provide a degree of protection against hose-directed water, the entry of water during prolonged submersion at a limited depth, and damage form external ice formation.
NEMA Standard 7-15-1991.

Type 12 Enclosures are intended for indoor use primarily to provide a degree of protection against circulating dust, falling dirt, and dripping noncorrosive liquids.
NEMA Standard 7-15-1991.

Type 12K Enclosures with knockouts are intended for indoor use primarily to provide a degree of protection against circulating dust, falling dirt, and dripping noncorrosive liquids.
NEMA Standard 7-15-1991.

Type 13 Enclosures are intended for indoor use primarily to provide a degree of protection against dust, spraying of water, oil, and noncorrosive coolant.
NEMA Standard 1-10-1979.

Table 12-2 NEMA Definitions of Enclosures—*Continued*

DEFINITIONS PERTAINING TO HAZARDOUS (CLASSIFIED) LOCATIONS

Type 7 Enclosures are intended for indoor use in locations classified as Class I, Groups A, B, C or D, as defined in the National Electrical Code.
NEMA Standard 7-15-1991.

Type 8 Enclosures are intended for indoor or outdoor use in locations classified as Class I, Groups A, B, C or D, as defined in the National Electrical Code.
NEMA Standard 7-15-1991.

Type 9 Enclosures are intended for indoor use in locations classified as Class II, Groups E, F or G, as defined in the National Electrical Code.
NEMA Standard 7-15-1991.

Type 10 Enclosures are constructed to meet the applicable requirements of the Mine Safety and Health Administration.
NEMA Standard 1-10-1979.

Source: NEMA 250, 1991.

equipment and its associated wiring must be installed so they are purposely separated from nonintrinsically safe circuits by vapor impermeable barriers (ANSI/ISA RP 12.6). *Intrinsic Safety* by Magison (1984) is a good general text on the subject, focusing on design of safe equipment and systems but also including installation, inspection, and maintenance practices.

Design tests and evaluation of intrinsically safe systems are provided in ANSI/UL 913. Notes regarding installation of such devices are summarized in Article 504 of the 1990 NEC. It is permissible to use general purpose enclosures as housing for intrinsically safe wiring and apparatus instead of the more expensive explosionproof or dust-ignitionproof enclosures that are mandatory for conventional (not intrinsically safe) arcing equipment. This represents an improvement in that a safe system is provided while avoiding the long delivery and high cost of explosionproof fittings and boxes or dust-ignitionproof enclosures.

Nonincendive equipment and wiring are incapable of releasing sufficient electrical or thermal energy, during *normal* operating conditions, to ignite a specific hazardous atmosphere mixture (FMEC 1984b)

12.1.4 Purging and Pressurized Enclosures

Another option to allow the use of conventional (not intrinsically safe) electrical arcing equipment in hazardous areas is to create an enclosure that is less hazardous (or nonhazardous) by means of dry air or nitrogen purging and pressurization systems. Arrangements for purging are discussed in NFPA 496. Positive-pressure ventilation is addressed in NFPA 70, Article 500. Appropriate safeguards must be provided against ventilation failure.

For example, a local panel for a large process compressor may require a large number of electrical components like relays, switches and push buttons that won't fit into a cast metal enclosure. A valid alternative is to design a pressurized sheet metal enclosure, typically NEMA type 4 or 12, and create and maintain a nonhazardous atmosphere inside the enclosure. Several types of purged enclosures (known as X, Y, Z types) are described in FMEC 1976. "Type X purging reduces the classification within an enclosure from Class I, Division 1 to nonhazardous. Type Y purging reduces the classification within an enclosure from Class I, Division 1 to Class I, Division 2. Type Z purging reduces the classification within an enclosure from Class I, Division 2 to nonhazardous" (FMEC 1976).

A purged enclosure requires:

- A source of clean, dry air or an inert gas such as nitrogen.
- A compressor (or compressed air cylinder) or mechanical ventilation system to maintain positive pressure inside the enclosure.
- Interlocks to prevent the power from being applied before the enclosures have been purged, and to deenergize the system should the pressure fall below a safe value.

Purged enclosures are difficult to maintain; therefore, they should be used as a last resort. NFPA 496 explains the different types of purging systems that can be used depending on the degree a hazardous area is declassified to a less hazardous one or to a nonhazardous area.

Pressurization is mostly used in areas with large volumes such as a control room or a switchgear building. In this case, the fresh air intake is positioned to insure clean air. A draft fan maintains internal positive pressure.

12.2 LIGHTNING PROTECTION

Lightning protection systems are intended to minimize damage to facilities that may be subject to atmospheric stroke. The damage caused by lightning may be thermal (fire), electrical (flashover) and/or mechanical (torsional forces). The energy in a lightning stroke can ignite flammable vapors and damage the equipment and structures by the flow of lightning discharge current through any resistance in its path. In process plants, electrical equipment, all equipment containing hazardous liquids and gases, outdoor metal structures, vessels or other tall equipment subject to lightning strokes should be properly grounded. In addition, buildings or structures made of nonmetallic materials, those normally occupied by personnel, or those that if seriously damaged could result in a major loss either to the structure itself or from the effect on other facilities, also require lightning protection systems.

12.2.1 *Lightning Phenomena Theory*

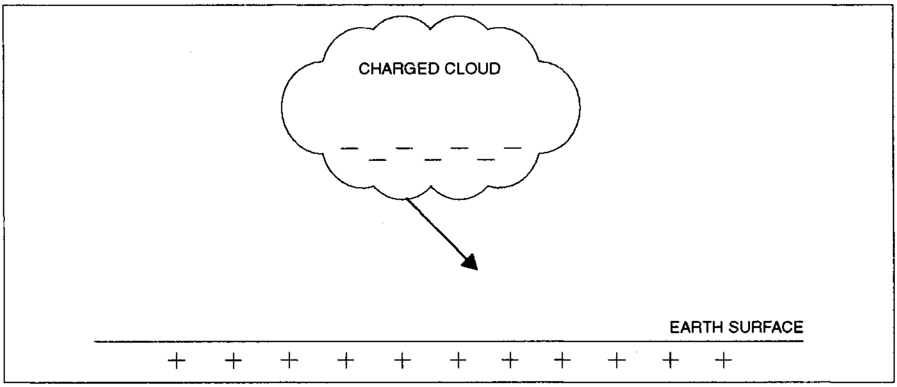
Lightning is the discharge of electricity from a charged cloud to another cloud or the ground. An atmospheric discharge to ground is shown in Figure 12-1. The last part of the distance travelled by the downward leader is the most critical for a lightning protection, because at that point the stroke may be influenced to take a specific path which provides protection to a given structure. The current that may be discharged during a lightning stroke varies widely between 2 and 200 kiloamperes, with some exceptional cases as high as 300 kA (EPRI 1987). Any lightning protection system will have to deal with large currents draining to earth in a very short period of time. However, it must be pointed out that the probability of occurrence of thunderstorms also influences design of a lightning protection system. Statistics have been compiled for this probability and are presented on a map by isokeraunic lines that designate geographic areas of equal frequency of thunderstorm activity (Figure 12-2). The value read from the isokeraunic line is the number of days per year that thunder was heard in that particular region. Isokeraunic levels are particularly useful for transmission line design.

12.2.2 *Lightning Protection Systems*

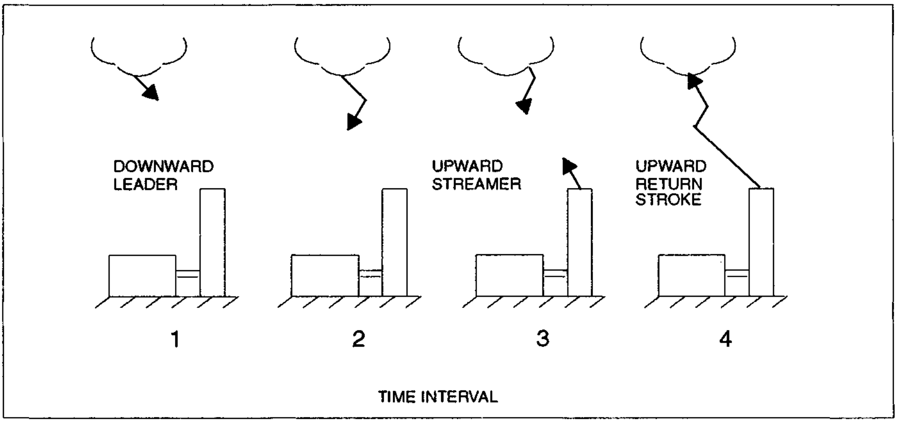
The basic theory of protection against direct lightning strikes is to provide terminals projecting into the air above the highest parts of a given structure with interconnecting grounding conductors that provide a path of minimum resistance to earth. The tallest structure in a group is the likeliest target and it determines the degree of protection for lower structures. Lightning strokes, which might otherwise fall inside the zone, are attracted to the mast. In a petrochemical plant, taller structures like splitters, strippers, absorbers, and fractionating columns shield lower structures like reactors or drums.

A well-designed lightning protection system protects against direct lightning strikes as well as induced lightning voltages. Protection against direct strikes may be accomplished in buildings, cooling towers, and stacks by the use of air terminals (lightning rods) connected into the grounding system in addition to metal ground bonds. Steel process towers are by nature lightning rods and do not require additional air terminals. Suppression of induced lightning voltages is achieved by means of lightning arresters and surge capacitors at strategic locations particularly if a bare aerial power distribution line is exposed to direct lightning stroke.

The protected zone for structures is determined by spanning a 100-foot arc, as shown in Figure 12-3 both for a single mast and for a rig of four masts with overhead ground wires. In both cases the striking distance radius is the same. It is at this distance that the upward streamer is formed and the downward leader is attracted to the mast.



a. Thundercloud–to–earth charge distribution



b. Lightning stroke formation

NOTE: A storm cloud produces a charge of one polarity distributed within the base of the cloud and a corresponding, but opposite, charge distributed on the surface of the earth under the cloud. The process starts with a downward corona–like streamer from the cloud defined as a stepped leader. This leader transports the electric charge from the cloud to the earth following several unpredictable paths depending on atmospheric ionization of the air in a series of hesitating steps. As the top streamer approaches earth, another upward stream of electric charge builds up almost instantaneously aimed at encountering the top streamer. If a plasma channel is established within properly ionized air the two streamers meet and lightning occurs, establishing a path for conduction of a large electric current, defined as the return stroke, which equalizes the charge between the two equipotential planes. The total elapsed time for a leader to complete its path from cloud to earth is less than 10 milliseconds.

Figure 12-1 Lightning formation. (Copyright © 1987, Electric Power Research Institute. EPRI–EL–5036 Grounding and Lightning Protection. Reprinted with permission.)

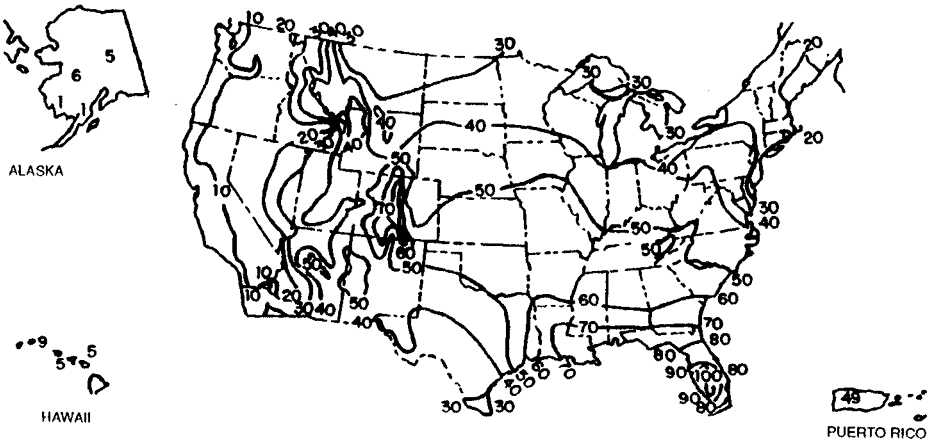
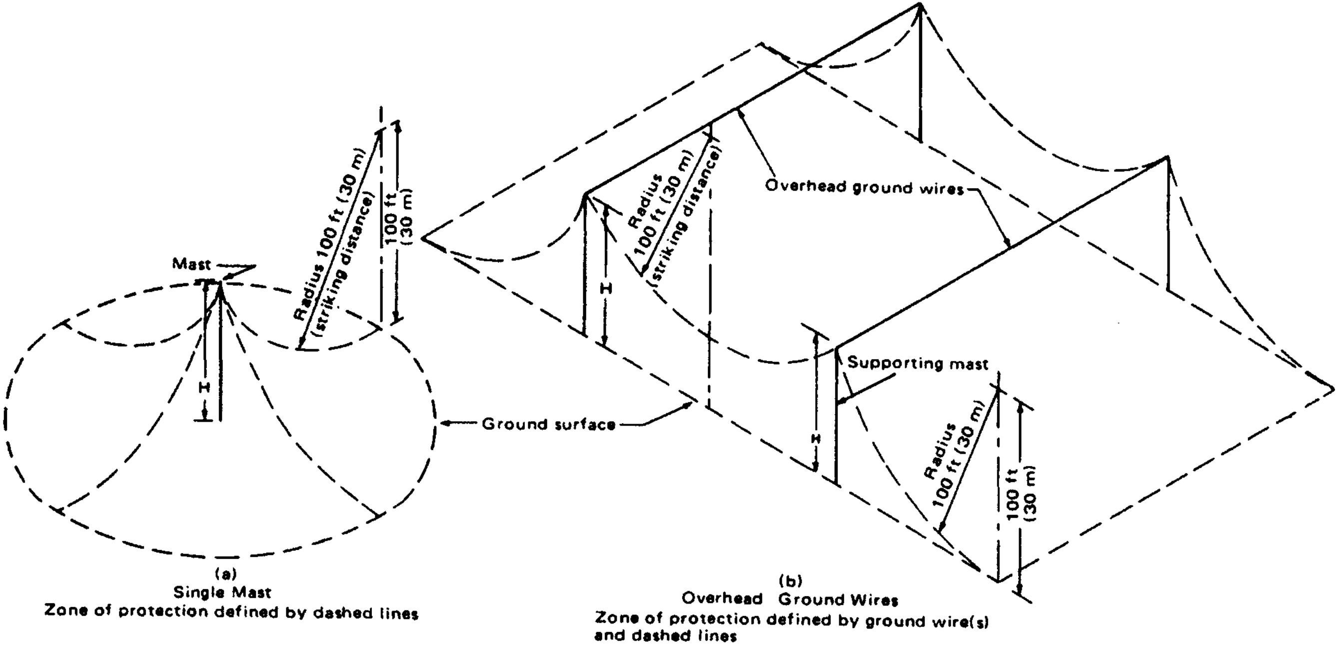


Figure 12-2 Mean annual days of thunderstorm activity in the United States. (Copyright © 1982, Electric Power Research Institute. EPRI–EL–5036 Grounding and Lightning Protection. Reprinted with permission.)

Conventional steel structures, at least 3/16 inch in thickness, such as process columns, vessels, steel storage tanks and steel stacks of petroleum and petrochemical processing plants, will not be damaged by direct lightning strokes. Still, it is necessary to adequately ground the structures to prevent damage to the foundation, dissipate the energy and to provide a zone of protection for electrical apparatus and other equipment in the vicinity. Grounded tanks containing flammable liquids or liquified petroleum gas under pressure do not require specific lightning protection since they are inherently self-protecting if adequately grounded. Atmospheric storage tanks with nonmetallic roofs must have lightning protection with air terminals. Structures, cooling towers, or buildings made entirely of nonconductive materials and located outside of the zone of protection of another structure require full lightning protection as indicated in NFPA 78. A typical arrangement of air terminal spikes is shown in Figure 12-4. The terminals are all interconnected and the down conductor bends and turns are minimal.

Incoming utility substations, as well as outdoor pumping stations, that have a large number of major electrical apparatus and which provide extremely important process functions also require lightning protection. The lightning protection system for a typical industry substation includes:

- Masts or steel lattice extensions to provide cones of protection to the equipment within the substation. The shield angle for a single mast is 30°, but increases to 60° for a shielding angle that lies within the masts.
- Overhead static wires on incoming transmission to protect phase conductors. The static wire(s) should be connected to one of the masts or lattice extensions within the substation.



(a)
Single Mast
Zone of protection defined by dashed lines

(b)
Overhead Ground Wires
Zone of protection defined by ground wire(s) and dashed lines

Figure 12-3 (a) Single mast zone of protection. (b) Overhead ground wires. (Reprinted with permission from NFPA 780-1992 *Lightning Protection Code*, Copyright © 1992, National Fire Protection Association, Quincy, Massachusetts 02269. This reprinted material is not the complete and official position of the National Fire Protection Association on the referenced subject, which is represented only by the standard in its entirety.)

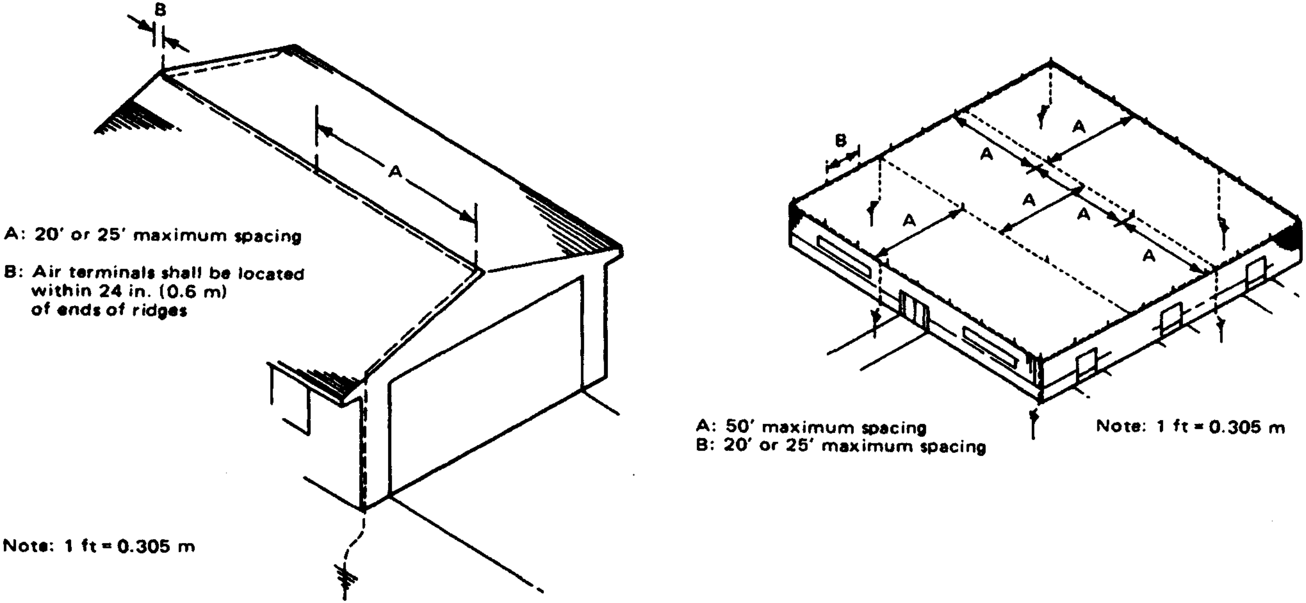


Figure 12-4. Structural lightning protection using air terminals. (Reprinted with permission from NFPA 780-1992 *Lightning Protection Code*, Copyright © 1992, National Fire Protection Association, Quincy, Massachusetts 02269. This reprinted material is not the complete and official position of the National Fire Protection Association on the referenced subject, which is represented only by the standard in its entirety.)

- Messenger cable grounded at frequent intervals to provide protection to aerial cables.
- Metallic conduits and metal sheaths need to be grounded and bonded at each end. Feeders in metallic conduits or with metal sheaths are essentially self-protecting.

Lightning arresters will also be required to protect electrical equipment connected to a distribution system exposed either directly or indirectly to lightning strokes. A lightning arrester is a device that drains to ground high currents at surge voltages just like the ones created by an atmospheric discharge. Lightning arrester applications are covered in IEEE Standard 242. The best locations for arresters are:

- At the exposed high bushings and sometimes at the low voltage bushings of power transformers.
- At the terminals of a dry type transformer when fed from an overhead line.
- At the junction of an aerial distribution line and a cable pothead.
- At the terminals of medium voltage motors, 1500 HP and above, fed from an aerial line directly (API RP 540), supplied by a transformer connected to an overhead feeder. The scheme is usually coupled with a surge capacitor specifically rated to reduce the rate of rise of voltage surges. For ideal protection the leads between the surge protection devices mentioned and the motor should be as short as possible.

12.3 BONDING AND GROUNDING

The most common method of preventing ignition hazards is charge dissipation by means of bonding and grounding. Bonding between two bodies provides a conductive path through which static charges can recombine. Therefore, no charge can accumulate and thus no spark can occur since the difference in electrical potential is zero. Bonding (metallically connecting two objects) will eliminate static sparks between the two objects at loading and unloading facilities that involve handling of flammable and combustible liquids; grounding prevents static sparks between the objects and the ground.

Grounding of electric power systems and equipment is necessary in order to limit voltage disturbances due to lightning, line surges, or unintentional contact with higher voltage sources, and to provide safe return paths to the power source during ground fault conditions. Grounding is a conducting connection, intentional or accidental, between an electrical circuit or equipment and the earth.

The grounding system serves several functions; the power system ground is related to electrical circuit protection (ground fault protection or voltage surge); the equipment safety ground deals with lightning, static charge, electric shock, and personnel protection. A third function is equalizing voltage potential to reduce possibility of arcing.

12.3.1 Power System Ground

A power system ground is required to stabilize and limit the voltage to ground (earth) of the electrical system by essentially restricting the system to earth potential. The main function of this portion of the grounding system is to facilitate the operation of protective equipment such as breakers, fuses or relays. It also limits the voltage to which cable system to ground insulation is stressed during a ground fault and provides a relatively stable system with a minimum of transient overvoltages. Power system grounding methods are extensively covered in the IEEE Standard 142 and further discussion of this subject is beyond the scope of this publication. It is important to properly ground plant control systems and safety shutdown systems (FIPS 1983).

12.3.2 Safety Ground

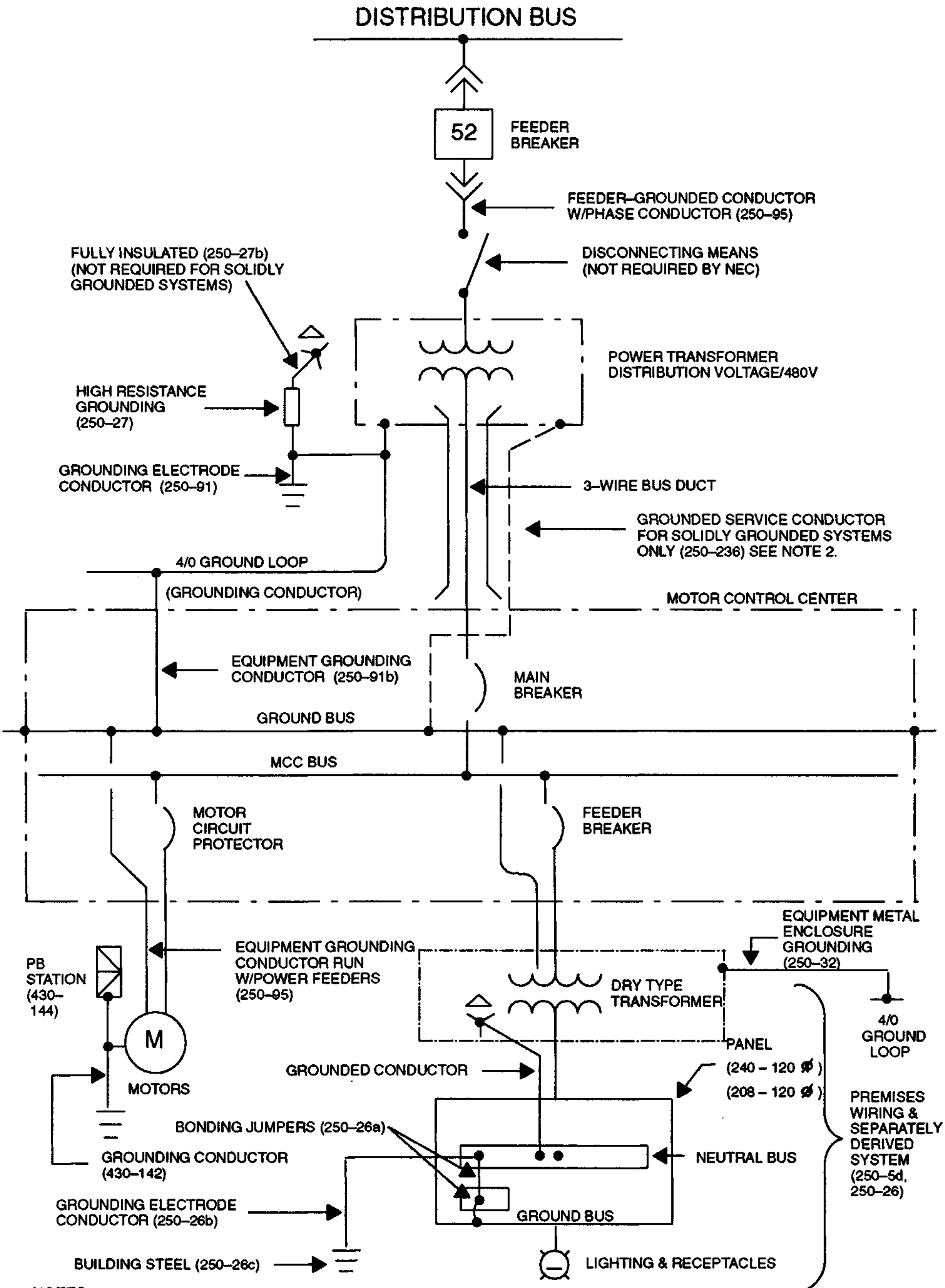
A safety ground is required to protect personnel and equipment from the effects of electric shock, lightning and static electricity. Serious injury can be caused by relatively low electric current not cleared by overcurrent protective devices (Dalziel 1972). The National Electrical Code (NEC), Article 250, addresses requirements for grounding and bonding of electrical equipment and installations. A typical grounding system illustrating the use of the above terms is shown schematically in Figure 12-5.

The NEC outlines methods, types, sizes and locations of grounding connections and conditions under which guards, isolation or insulation may be substituted for grounding.

Section 9 of the NEC, *Grounding Methods for Electric Supply and Communications Facilities* should be followed. The purpose of Section 9 is to "provide practical methods of grounding, as one of the means of safeguarding employees and the public from injury that may be caused by electrical potential."

12.3.3 Testing for Grounds

Ground resistance testing is conducted to assure the continued integrity and continuity of ground connections. The standard 3-terminal, fall of potential test for ground resistance; the 3-terminal slope test; and the Direct 2-terminal test are described in IRI's IRInformation Manual (1992).



NOTES:

1. APPLICABLE NEC ARTICLE IS GIVEN IN PARENTHESES.
2. FOR A SOLIDLY GROUNDED SYSTEM:
   A. ALL CONNECTIONS REMAIN AS SHOWN EXCEPT FOR RESISTOR.
   B. THE SYSTEM GROUNDED CONDUCTOR TO THE MCC BUS MUST BE ADDED AS SHOWN DASHED.

Figure 12-5 Typical grounding system.

12.3.4 *Static Electricity Protection*

The basic philosophy for static electricity protection is to provide a means whereby charges separated by whatever cause may recombine harmlessly or be dissipated before sparking potentials are attained. In addition, corrective measures are devised to avoid spark gaps where such harmful discharges could occur. If hazardous static conditions cannot be deleted during certain operations, it is necessary to assure that there are no ignitable mixtures at the locations where sparks may be present. The most widespread practice against static electricity hazards is to prevent buildup of electrostatic charge by means of bonding. Other techniques such as humidification and ionization are discussed in NFPA 77.

As discussed in Chapter 11, static electricity may develop in flowing liquids. When liquid flows, charging occurs because the adsorbed ions are separated from the free ions that are carried into the body of the liquid by turbulence (Figure 12-6). The opposite charge is usually conducted through the metallic pipe wall in the same direction because of the natural attraction between opposite charges. The rate of electrostatic generation increases with the rate of flow, ionic content, material turbulence and surface area of the interface.

A typical situation of static charge generation during a tank truck loading operation is illustrated in Figure 12-7. When a fluid is pumped through the pipe at constant velocity, the electric potential of the liquid will stabilize at a value where charge generation is balanced with charge dissipation. If the liquid is conducted into a smaller pipe, the liquid velocity will increase, which in turn increases the charge generation rate. If a filter is placed in the pipe, the generation of charge increases by 10 to 200 times because of the large surface area and small pore openings which yields an intimate contact between all of the fuel and the filter surface. The high charge developed by the filter decreases as the liquid continues down the pipe. Usually a relaxation time of 30 seconds will discharge the fluid to safe levels and it is normally attained by providing piping downstream of the filter long enough to transfer the liquid for that

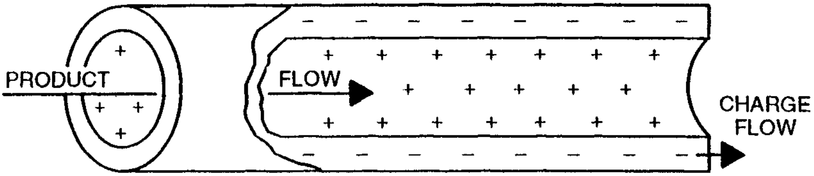


Figure 12-6 Charge separation in a pipe. (APIRP 2003. Reprinted courtesy of the American Petroleum Institute.)

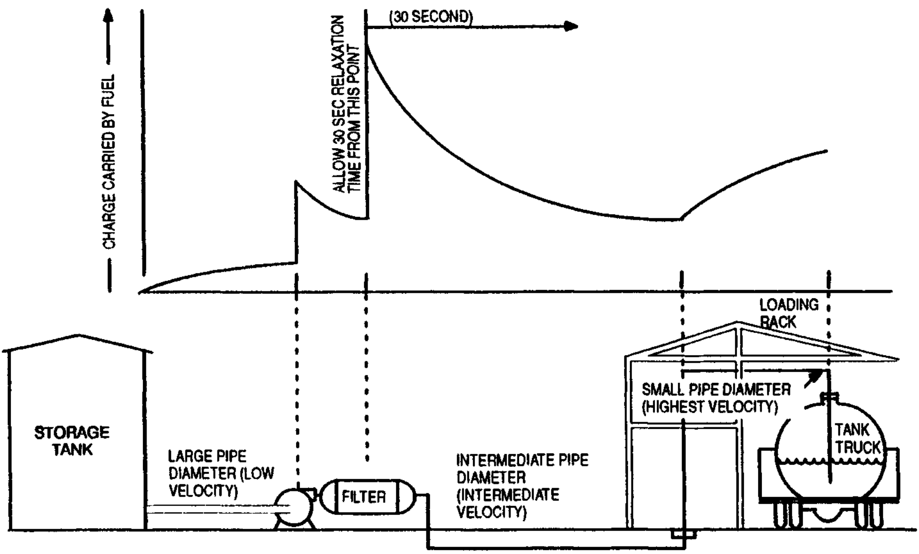


Figure 12-7 Charge generation during tank truck loading. (APIRP 2003. Reprinted courtesy of the American Petroleum Institute.)

period of time. Alternatively, the piping may be enlarged or a relaxation tank can be provided.

To avoid static electricity generation, nonconductive flammable liquids should never be added to a vessel by splashfilling. The liquids can be added by filling through a bottom nozzle or filling through a dip leg (Figure 12-8).

Bonding and grounding are used at tank-car loading racks to eliminate sparks between the fill pipe and tank car dome (Figure 12-9). Bonding for container filling operations keeps the filling nozzle and container at the same electrical potential in order to prevent a possible static spark. Bonding and grounding at marine terminals is a complex issue; local facilities may have specific requirements (see Section 11.5.3.3).

Recent investigations (Bredthauer 1990) have concluded that there is a possibility of sparks at enclosure joints during the acceleration of large electric motors (typically 5000 hp and 6.9 kV and above) with multisection enclosures. Installation of adequately sized equipotential bonding across the enclosure joints is recommended.

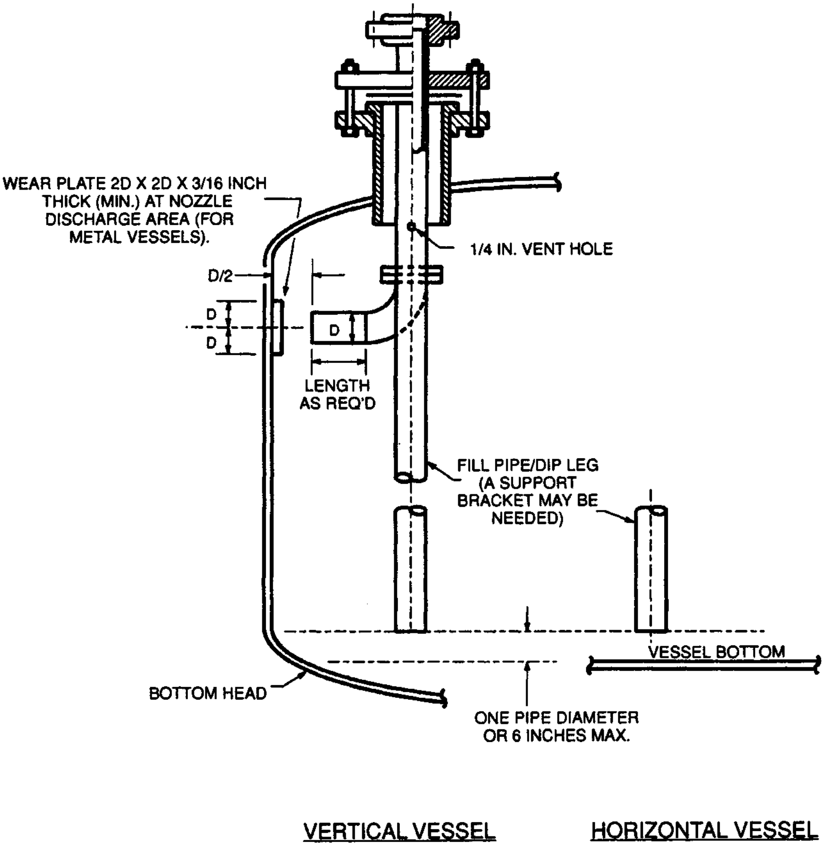


Figure 12-8 Vessel fill pipe/dip leg arrangement to avoid static electricity problems (Grossel 1992).

APPENDIX 12A
SUMMARY OF NEC AREA CLASSIFICATIONS (NFPA 70, 1990, ARTICLE 500.3 SPECIAL PRECAUTION)

Note: Fine Print Notes and Exceptions have not been included here. Consult the original document.

Class I Group Classifications

Group A: Atmospheres containing acetylene.

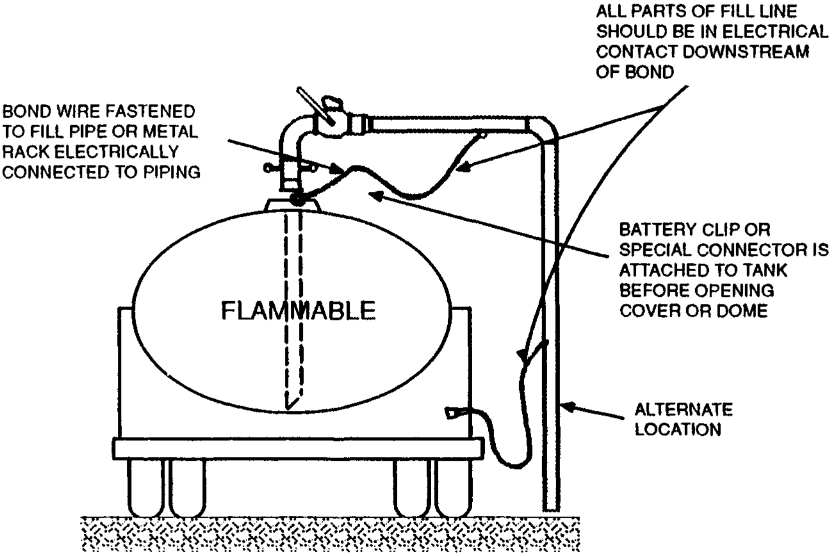


Figure 12-9 Filling tank truck through open dome. Note: The bond connection during the loading of tank vehicles should be made before the dome is opened and shall remain in place until filling is completed and all dome covers have been closed and secured. The connection consists of a metallic bond wire permanentlly electrically connected to the fill stem or to some part of the rack structure in electrical contact with the fill stem. The free end of such wire is provided with a clamp or equivalent device for convenient attachment to some metallic part in electrical contact with the cargo tank of the vehicle. (Reprinted with permission from NFPA 77-1988 *Static Electricity,* Copyright © 1988, National Fire Protection Association, Quincy, Massachusetts 02269. This reprinted material is not the complete and official position of the National Fire Protection Association on the referenced subject, which is represented only by the standard in its entirety.)

Group B: Atmospheres containing hydrogen, fuel and combustible process gases containing more than 30 percent hydrogen by volume, or gases or vapors of equivalent hazard, such as butadiene, ethylene oxide, propylene oxide, and acrolein.

Group C: Atmospheres such as ethyl ether, ethylene, or gases or vapors of equivalent hazard.

Group D: Atmospheres such as acetone, ammonia, benzene, butane, cyclopropane, ethanol, gasoline, hexane, methanol, methane, natural gas, naphtha, propane, or gases or vapors of equivalent hazard.

Class II Group Classifications

Group E: Atmospheres containing combustible metal dusts, including aluminum, magnesium, and their commercial alloys, or other combustible dusts whose particle size, abrasiveness, and conductivity present similar hazards in the use of electrical equipment.

Group F: Atmospheres containing combustible carbonaceous dusts, including carbon black, charcoal, coal or coke dusts that have more than 8 percent total entrapped volatiles or dusts that have been sensitized by other materials so that they present an explosion hazard.

Group G: Atmospheres containing combustible dusts not included in Group E or F, including flour, grain, wood, plastics, and chemicals.

This summarized material is not the complete and official position of the National Fire Protection Association on the referenced subject, which is represented only by the standard in its entirety.

12.4 REFERENCES

12.4.1 Regulations, Code of Practice, and Industry Standards

The editions that were in effect when these *Guidelines* were written are indicated below. Because standards and codes are subject to revision, users are encouraged to apply only the most recent edition.

ANSI C2. 1987. *National Electrical Safety Code*. American National Standards Institute, New York.

ANSI/UL 913. 1988. *UL Standard for Safety Intrinsically Safe Apparatus and Associated Apparatus for use in Class I, II, & III, Division I, Hazardous (Classified) Locations.* American National Standards Institute, New York/Underwriters Laboratories, Northbrook, Illinois.

ANSI/ISA RP12.6. 1987. *Installation of Intrinsically Safe Instrument Systems in Class I Hazardous Locations.* American National Standards Institute, New York/Instrument Society of America, Research Triangle Park, N.C.

API RP 500. 1991. *Recommended Practice for Classification of Locations for Electrical Installations at Petroleum Refineries*. American Petroleum Institute, Washington, D.C.

API RP 540. 1982. *Electrical Installations in Petroleum Processing Plants.* American Petroleum Institute, Washington, D.C.

API RP 2003. 1982. *Protection Against Ignition Arising Out of Static, Lightning and Stray Currents*. American Petroleum Institute, Washington, D.C.

IEEE Std 142. 1982. *Recommended Practice for Grounding of Industrial and Commercial Power Systems (ANSI) (Green Book)*. Institute of Electronic and Electrical Engineers, Piscataway, New Jersey. ISBN 1-55937-141-2.

IEEE Std. 242. 1986. Reaff 1991. *Recommended Practice for Protection and Coordination of Industrial Commercial Power Systems (ANSI) (Buff Book)*. Institute of Electronic and Electrical Engineers, Piscataway, New Jersey. ISBN 471-85392-5

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NFPA 70. 1990. *National Electrical Code*. National Fire Protection Association, Quincy, Massachusetts.

NFPA 77. 1988. *Recommended Practice on Static Electricity*. National Fire Protection Association, Quincy, Massachusetts.

NFPA 496. 1989. *Standard for Purged and Pressurized Enclosures for Electrical Equipment in Hazardous (Classified) Locations*. National Fire Protection Association, Quincy, Massachusetts.

NFPA 497A. 1986. *Recommended Practice for Classification of Class I Hazardous (Classified) Locations for Electrical Installations in Chemical Process Areas*. National Fire Protection Association, Quincy, Massachusetts.

NFPA 497B. 1991. *Classification of Class II Hazardous (Classified) Locations for Electrical Installations in Chemical Process Areas*. National Fire Protection Association, Quincy, Massachusetts.

NFPA 497M. 1991. *Manual for Classification of Gases, Vapors, and Dusts for Electrical Equipment in Hazardous (Classified) Locations*. National Fire Protection Association, Quincy, Massachusetts.

NFPA 654. 1988. *Prevention of Fire and Dust Explosions in the Chemical, Dye, Pharmaceutical, and Plastics Industries*. National Fire Protection Association, Quincy, Massachusetts.

NFPA 78. 1986. *Lightning Protection Code*. National Fire Protection Association, Quincy, Massachusetts. (Note: Commencing with the 1992 Edition, NFPA 78 will be identified as NFPA 780)

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UL (Underwriters Laboratories) 913. *Standard for Intrinsically Safe Apparatus and Associated Apparatus for use in Class I, II, and III, Division 1, Hazardous (Classified) Locations.* Underwriters Laboratories, Northbrook, Illinois.

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5

MATERIALS SELECTION

5.1 INTRODUCTION

Equipment service life is influenced by many factors, such as materials of construction, design details, fabrication techniques, operating conditions, and inspection and maintenance procedures. In recent years there have been many cases where materials have failed either without warning or with warnings ignored. Material failures, while relatively infrequent, can be extremely severe, resulting in catastrophic accidents. The best way to reduce the risk of material failure is to fully understand the internal process, the exterior environment and failure modes, select materials for the intended application, apply proper fabrication techniques and controls, and provide good maintenance and inspection and repair techniques. Material failures due to mechanical and structural failures are addressed in numerous other publications. This chapter will focus on premature failure of materials due to corrosion, since corrosion failure is the major unpredictable route to catastrophic loss of containment of hazardous materials.

Corrosion refers to the degradation or breakdown of materials due to chemical attack. Corrosion is one of the most important process factors in material selection and yet the most difficult to predict. In general, equipment service life can be predicted from well established general corrosion data for specific materials in specific environments. However, localized corrosion is unpredictable, difficult to detect and can greatly reduce service life. Even more insidious are subsurface corrosion phenomena.

5.1.1 Properties of Materials

The basis for selection is performance under design conditions, that is, how the material will function in the process environment, not only at standard operating conditions but also under startup, shutdown, and upset conditions. The behavior of a material in a process environment is determined by its physical, chemical, and mechanical properties. These properties determine how the material will be affected by process chemicals as well as how the material will affect the process.

Chemical and physical properties are normally considered as a matter of routine. They are especially important, however, in determining corrosion reactions with process chemicals and corrosion prevention measures. Some properties, and their effects, are:

- thermal expansion (especially differences in expansion of different components; e.g., vessel and cladding)
- melting point or range (affects weldability, hot-forming; e.g., hot-short cracks may become focal points for corrosive attack and mechanical failure).
- acid–base resistance
- resistance to solvents
- susceptibility to various types of corrosion
- response to corrosion control techniques. Frequently alloying elements such as chromium, nickel, or molybdenum are added to reduce interaction between the metal and process environments.
- reactivity to oxygen
- compatibility with connecting piping (to avoid problems such as galvanic corrosion and differences in pressure ratings).
- reaction with process fluids
  —leaching of constituents by process fluids (dealloying)
  —embrittlement
  —constituent in material (e.g., nickel) may catalyze a reaction in the process fluid, causing thermal effects.

Properties such as the following determine routine mechanical working and joining operations:

- tensile strength
- yield strength
- ductility and notch-sensitivity
- toughness and impact strength
- fabrication characteristics
- hardness
- creep strength
- fatigue strength

These factors are normally addressed in routine design. However, for the materials engineer to select appropriate materials, the process engineer must accurately specify all process conditions and potential excursions.

Metals and alloys are often subjected to heat treatment to improve mechanical properties and corrosion resistance or to bring about thermal stress relief. Examples of heat treatment processes are normalizing, tempering, annealing, quenching and stress relieving. Heat treatment can be done before fabrication to get better mechanical properties (e.g., increase ductility and impact strength) and corrosion resistance, or done after cold/hot work to reduce the residual stress. More than one heat treatment may be used in the sequence of fabrication. The performance of many alloys, such as high nickel alloys and high alloyed stainless steels, critically depends on heat treatment. Both the materials engineer and the process engineer should be alert to avoid causing a new problem while solving an old one: heat treatments, particularly to welds, to improve mechanical properties may actually worsen corrosion.

The scope of these *Guidelines* does not include discussion of the extensive variety of materials available, both metallic and nonmetallic, and the many proprietary variations (in alloys, ceramics and various plastics, particularly); therefore, several general references are suggested:

- *Metals Handbook*, American Society for Metals
- *How to Select Materials*, by Kirby
- *Mechanical Engineer's Handbook*, by Baumeister.

In addition, numerous publications are available from the National Association of Corrosion Engineers and the Materials Technology Institute of the Chemical Process Industries, Inc. on design, materials and coatings.

Mechanical failures are generally more predictable than those due to corrosion and are addressed by routine design criteria of pressure and temperature, as discussed in the references listed above. These failures include:

- brittle fracture
- mechanical fatigue
- thermal fatigue
- creep
- thermal runaway beyond design temperature and pressure.
- stress rupture
- catastrophic oxidation
- carburization

The focus in this chapter is the interaction between materials of construction and the environment.

5.1.2 Corrosive Process Environments

Process conditions are normally specified by the process engineer. Corrosive process environments may include:

- inorganic acids
- organic acids
- hydrogen sulfide
- chlorine
- alkaline environment
- ammonia and its compounds
- amines
- hydrogen service
- water—freshwater, seawater, sewage
- metal ions

In addition to the references listed previously, there are several good sources of information on types of materials and the environments for which they are suitable:

- *Metals Handbook*, ASM, Volume 13, Corrosion
- *Corrosion Data Survey—Metals Section*, edited by D. L. Graver
- *Corrosion Data Survey—Non-Metals Section*, edited by N. E. Hamner
- *Corrosion Control in the Chemical Process Industries*, by Dillon
- *Corrosion Engineering*, by Fontana
- *Fundamentals of Designing: A Corrosion Aid for the Designer for Corrosion Control*, by Landrum

If the range of process conditions are accurately specified by the process engineer, the materials engineer can generally select suitable materials of construction without additional testing. However, upsets and impurities, trace elements and contaminants are likely to cause most of the problems; therefore, any potential contact with impurities, in all process fluids, ambient environment, utilities, etc., and for *all* operating scenarios, must be identified to the materials engineer.

5.1.3 Material–Environment Interaction

Both the external (ambient) and internal (process) conditions in contact with materials need to be examined.

The external environment, that is, the ambient conditions in the plant, may be corrosive. Atmospheric pollutants include corrosive species as well as those which may have adverse catalytic effects on other pollutants (e.g., coal dust). See Chapter 8, Thermal Insulation, for discussion of the effect of chlorine.

The internal environment is defined by the process, its chemistry, and its conditions. The process engineer should provide the materials engineer with sufficient information about the process, ambient conditions and utilities, for start-up and shut-down as well as routine operations, to ensure adequate selection, especially for corrosive service. Preliminary materials selection is usually based on process conditions, such as:

- Process chemicals, including the major and minor constituents of each process stream, trace contaminants, pH, and oxidizing or reducing agents and water content. For example, styrene will leach copper; thus materials in contact with styrene are generally specified to not contain copper.
- Operating conditions, including temperature, pressure, velocity.
- Process Variations. Potential operational excursions in process chemistry, temperature, or pressure; excursions associated with start-up or shut-down conditions. The order in which the conditions occur can be important (Hurst 1986), e.g., purging/cleaning with steam may constitute a temperature excursion.

- Contaminants in feedstock, process intermediate, product, or utility.
- Catalysts. Metal ions in the material may affect either the chemistry of the process itself or the product quality. For example, nickel is known to catalyze many synthesis reactions and its inclusion can result in unwanted side reactions.
- Utilities, including trace elements in cooling water, hydrotest water, steam, etc.

The probable behavior of the material under consideration must be determined either from references, by appropriate corrosion test(s), or a pilot plant.

5.1.4 Pitfalls in Material Selection

The process design (see Chapter 3) establishes the type, size, and number of various types of equipment, and can affect the physical layout of the units. Process criteria often determine materials of construction for pressure vessels, heat exchangers, valves, piping, pumps, tanks, and instrumentation. These requirements must be adequately documented in complete equipment or instrument data sheets, process flow diagrams (PFDs) or in the case of piping, on the piping and instrumentation diagrams (P&IDs). Fabrication and corrosion control techniques should also be specified.

The PFDs, P&IDs, equipment data sheets, and specifications must be complete and must adequately define the specified requirements to purchasing agents vendors, fabricators, subcontractors, and inspectors. Detailed fabrication specifications, such as weld quality and finish, are required, especially for equipment to be internally coated. Procedures for preservice chemical or physical cleaning of equipment must be established. Detailed quality control techniques in industrial practice are outlined by Landrum (1989).

Specific types of process equipment have characteristic corrosion problems. Bimetallic heat exchangers are frequently subject to corrosion, particularly where the two metals are in contact. Distillation or extraction columns have corrosion problems associated with the presence of distinctly different environments at different locations in the same vessel. Pumps, some piping configurations, and valves are subject to a higher incidence of velocity effects (erosion).

If corrosion testing is performed to provide a basis for material selection or fabrication techniques, the test conditions must be as close as possible to the actual (design) service environment. Velocity of process fluids, for example, may be overlooked, but it is just as important to test as composition, concentration, temperature, pressure, and time factors.

If operating conditions differ from design conditions, the original material selection may be invalidated. Design bases must be fully and clearly documented and communicated to the operators (through procedures, training, etc.); inadequate documentation frequently causes confusion and can invalidate any management of change procedure.

Requirements may be imposed upon the manufacturer and the supplier to ensure that the materials are accurately represented. A big problem is traceability of materials. Manufacturers may be required to attest that the material is in accordance with the material specification. Materials certification or a Certificate of Conformance may be required to provide the "pedigree," that is, paperwork certifying the materials are as specified. If further work is done on the material, the manufacturer may also have to provide a certified material test report, verifying the quality of welding or other treatments. Some means of identification, for example, lot number, weld number or heat number is required to trace the material to the manufacturer. Consult the ASME Boiler and Pressure Vessel Code for guidance in material segregation and traceability. Also vitally important is alloy verification.

5.2 CORROSION

Corrosion is chemical attack on a metal. Corrosion may occur at a uniform, predictable rate, or it may be localized, on the surface, or as a subsurface phenomenon. The following discussion of corrosion, although normally thought of in terms of the internal (i.e., process) environment, also applies to external surfaces of equipment and piping.

5.2.1 General Corrosion and Metallurgical Changes

General corrosion means the entire surface loses metal uniformly due to attack by chemical or electrochemical reaction. Reaction with gases present in the process will cause catastrophic oxidation, sulfidation, reactions with halogens and hydrohalides, and various other types of corrosion. The corrosion rate is predictable, based on previous experience and can be compensated for by adding a corrosion allowance to the wall thickness of piping and equipment. For example, for carbon steel 1/16 inch or more is added for typical project life. The National Board Inspection Code (NBIC) provides an explanation and formula for determining corrosion allowance. Decarburization and carburization are other metallurgical changes, although there is no metal loss or surface change.

5.2.2 Stress-Related Corrosion

5.2.2.1 Stress Corrosion Cracking

Every alloy is subject to stress corrosion cracking (SCC) in some environment; however, chloride stress corrosion cracking is commonly associated with stainless steel. The majority of SCC problems are associated with stainless steels and aqueous chloride salts, but both sulfide and chloride stress cracking are common in the process industry. It occurs when material has been under tensile stress in an environment containing sulfide compounds or chloride salts for a period of time.

A 1973 survey by DuPont (Table 5-1) shows that SCC accounts for 24% of corrosion failures and is a major problem in petroleum and chemical industries. These failures may occur without warning and hence can be quite hazardous and expensive. The sources of chloride are often overlooked: hydrotest water, cooling water, ambient air, vinyl stickers, and marking pens. The materials engineer should be made aware of any potential trace ions in the environment because they might affect material selection.

Table 5-1 Metal Failure Frequency for Various Forms of Corrosion[a]

Forms of Corrosion Failure	Occurrences (%)
General	31
Stress Corrosion Cracking	24
Pitting	10
Intergranular Corrosion	8
Erosion–Corrosion	7
Weld Corrosion	5
Temperature (cold wall, high temperature, and hot wall)	4
Corrosion Fatigue	2
Hydrogen-induced attack (grooving, blistering)	2
Crevice	2
Galvanic	2
Dealloying or Parting	1
End Grain Attack	1
Fretting	1
TOTAL	100

[a] Collins and Monark 1973

The best solutions to SCC are to coat the metal, modify the environment, or select a different material. The design options to consider are:

- Use a protective coating to avoid SCC attack under insulation.
- Reduce the operating temperature.
- Reduce chloride concentration in water and be aware of potential concentration mechanisms.
- Use a chloride SCC-resistant material such as duplex or ferritic stainless steels or nickel alloys (Inconel, Incoloy 800, Incoloy 825, Hastelloy C-276, Hastelloy G-3, or Carpenter 20Cb3).
- Lower the internal stress by solution annealing or stress relief where appropriate. Consider operation induced stress.
- Use cathodic protection if possible when SCC is positively known to be a risk.
- Add an inhibitor to delay the initiation of cracking.
- Consider creating compressive stresses by shot-peening (shot-blasting) to improve resistance to SCC.
- Application of zinc on stainless steels under high temperature potentials.

Regular inspection and nondestructive testing should in most cases detect SCC.

Nitrate stress corrosion cracking results from a certain combination of conditions which favor concentration of nitrates. Nitrate SCC caused the crack in the No. 5 Reactor at Flixborough (Lees 1980). Fortunately nitrate cracking is not common, outside of plants handling nitrates and nitric acid.

5.2.2.2 Corrosion Fatigue

Corrosion fatigue can be defined as a combination of normal fatigue and corrosion that causes failure at stress levels far below the design endurance limit of the metal involved. Corrosion fatigue resistance is remarkably decreased by an increase in the stress cycle frequency, even in the low frequency ranges. Compressive stresses will not cause corrosion fatigue. Environmental factors such as temperature, pH, oxygen content, and composition of process fluids, and mechanical factors, such as vibration, influence corrosion fatigue.

In a corrosive environment, material will continuously lose its resistance to fatigue. Use of high strength material and stress relief may help to prevent corrosion fatigue; however, using more resistant materials is more effective. Corrosion fatigue failure can happen suddenly and unpredictably. As a result, corrosion fatigue can cause catastrophic failures resulting in explosion, fire, toxic release, etc.

Design options to reduce failure caused by corrosion fatigue may include:

- Conducting the corrosion test under conditions identical to those in use before selecting the material.

- Specifying a more resistant material; do not use a high strength material.
- Changing the design to dampen or stop the stress cycling.
- Specifying butt welds instead of fillet welds.
- Specifying stress relief when required, but without decarburization.
- Using shot-peening to create compressive stresses and balance out the tensile stress which causes the corrosion fatigue.
- Using a metallic coating (electro or electroless). Plating techniques are preferred since they will not impose tensile stress onto the materials. Cracked metallic plating can act as a good fatigue crack initiation site.

5.2.3 Pitting

Pitting "results from electrochemical potential set up by differences in oxygen concentration inside and outside the pit" (Lees 1980). Pitting is also used as a generic term to refer to other types of localized corrosion.

Because of its localized and deeply penetrating nature, pitting is one of the more damaging types of corrosion in the process industry. Pits can extend through the material within a short period of time. Pitting is difficult to detect by on-line monitoring. Addition of corrosion inhibitors (e.g., oxygen scavengers) can prevent this type of corrosion. Pitting often occurs or is accelerated when vessels/piping are opened for inspection or other reasons.

5.2.4 Intergranular Corrosion

Intergranular corrosion (IGC) is a severe corrosion problem for austenitic tainless steels. IGC is caused by impurities (in the case of nickel alloys) or alloying elements (for stainless steels) that migrate from the surrounding areas to the grain boundaries and then precipitate between the grains. These precipitated materials have a different corrosion potential than adjacent grains and become either cathodic or anodic. If the precipitate is anodic, it will be corroded. If the precipitate is cathodic, a narrow zone next to the grain boundary will be corroded. Then a fine crack will form along the grain boundary and degrade the mechanical properties of the metal. Many unstablized austenitic steels are susceptible to IGC.

Intergranular corrosion in austenitic stainless steels occurs at the grain boundary regions due to chromium depletion which is caused by sensitization or chromium carbide precipitation. Low carbon grade or stabilized austenitic stainless steel were developed to fight IGC. Solution-annealing and not post-weld heat treating (when allowed by code) will significantly reverse the sensitization of austenitic stainless steels. Weld production tests, such as ferrite check of potential carbon dilution at the weld and heat affected zone, will help control IGC.

The following design solutions should be considered to avoid IGC:

- Select a metal that resists IGC in the process being considered. Specify stabilized or low carbon grade stainless steel for material, welding rods, or filler metals.
- Specify 65% boiling nitric acid test or the electrolytic oxalic acid etch test for austenitic stainless steels being used in a critically corrosive service.
- Specify solution annealed condition austenitic stainless steel.
- Avoid stress relief of austenitic stainless steels if code permits. When stress relief is required, avoid heat treatment temperature in the carbide precipitation range (900 to 1400°F or 480 to 760°C).
- Eliminate sharp angular intersections and crevices.

5.2.5 Galvanic Corrosion

Accelerated corrosion may occur when two dissimilar metals are joined. The metal with the lower position in the galvanic series may be corroded. Proper electrical isolation can protect the metal from galvanic corrosion. Also, coating the cathodic member of the couple can be effective in reducing galvanic corrosion.

5.2.6 Hydrogen Induced Attack

Some of the problems associated with use of hydrogen in chemical and refining processes are discussed below and in API RP 941, Steels for Hydrogen Service at Elevated Temperatures and Pressures in Petroleum Refineries and Petrochemical Plants, commonly known as the "Nelson Curves." Hydrogen is commonly encountered in process environments, for example, in hydrocarbon reforming operations and hydrogenation and dehydrogenation reactions.

Hydrogen Blistering. Hydrogen blistering is caused by atomic hydrogen diffusing into the steel, forming molecules and getting trapped in the internal voidage. Pressure of the hydrogen increases as more hydrogen molecules are trapped and the temperature continues to rise. Eventually internal hydrogen pressure warps the metal, forming blisters. Normalized, killed, fine-grain steels are often selected to avoid hydrogen blistering; coatings or cladding may be used to protect materials.

Hydrogen Embrittlement. Hydrogen embrittlement is caused by penetration of atomic hydrogen into a metal matrix, which results in a loss of ductility and tensile strength. More resistant materials or vented linings of low permeation rate metals may be used to avoid the problem.

Hydrogen Induced Cracking. Sulfide stress cracking is a common type of hydrogen induced cracking in the petrochemical industry. The cracking occurs when the metal is under stress. The metallurgist may specify design alternatives to reduce hydrogen induced cracking including:

- Specify A-193 B7M in place of A-193 B7 for bolting materials.
- Whenever feasible, use alloys with 35% or greater nickel content.
- Specify heating after electroplating or pickling steel to bake out the hydrogen and prevent it from diffusing into the metal matrix.
- Anodic protection. Never specify cathodic protection since hydrogen occurs at the cathode and hence accelerates cracking.
- Consider the use of HIC resistant steels and HIC tested steels.

Decarburization at Elevated Temperatures. In high temperature service, hydrogen reacts with the carbon in steel and the steel lose ductility, toughness, and strength. Low alloy (Cr–Mo) steels have better resistance to decarburization.

5.2.7 *Liquid Metal Cracking*

Certain metals with high tensile stresses are cracked by liquid metal. Removal of metallic coatings on steel and stainless steels before welding by acid cleaning or machining, but not grinding, will help avoid liquid metal cracking. Avoid galvanized steel items in contact with stainless steels to prevent liquid metal cracking in a fire. Avoid secondary contamination of stainless steels and Inconel.

5.2.8 *Erosion*

Erosion is a mechanical effect and therefore not technically within the scope of this section, but it is a significant factor in material selection. Erosion is wearing away of a material by mechanical energy. Erosion occurs by impingement of solid particles or liquid drops on the surface. Erosion is seen very frequently in high velocity slurry and pneumatic solids transport services, but it can also occur in more common scenarios, such as particles in steam, bubbles in a vapor, or where restrictions in flow exist. Erosion can typically be found at inlet and outlet nozzles, on internal piping, on grid or tray sections, on vessel walls opposite inlet nozzles, on internal support beams, on piping elbows and on impingement baffles. Impingement protection, smoother curvature, and higher corrosion allowances are generally used to combat this corrosion. Velocity limits must be considered when selecting the material. Erosion is also the result of cavitation in a flowing fluid, usually in or downstream of throttling service.

Erosion–corrosion results when a passive film or a corrosion product film formed on a metal is stripped off by erosion, resulting in more exposure of the metal to corrosion.

5.2.9 Metal Dusting

Although not strictly a corrosion problem, metal dusting occurs in high temperature environments with oxygen present in various forms.

5.3 DESIGN CONSIDERATIONS

5.3.1 Crevice Corrosion

Corrosion often occurs where corrosive fluids are trapped in a cavity, such as a gasket surface or welded lap joint. The following considerations may help minimize this type of corrosion:

- Minimize the use of threaded joints.
- Minimize flanged connections and try to use welded joints. A double butt joint is preferred. Do not use a permanent backing strip if using a single butt joint.
- Specify "solid" nonabsorbent gaskets.
- Use continuous seal welds in corrosive environments.
- Seal weld the tube to tube sheet joint in heat exchangers when practical.
- Use a full weld around the top side of tray support rings in vessel.

5.3.2 Temperature

Hot Wall Effect. The heating medium should elevate the heat transfer surface temperature uniformly. However, in cases of poor design, local hot spots, due to film boiling or nucleate boiling, can develop. The hot spots will have a higher corrosion rate due to their higher surface temperature. Proper design ensures a good circulation rate for convective boiling or provides for the heat transfer surface to be submerged at all times in the fluid being heated.

Since heater tube failure is a common problem, critical heater instrumentation should be provided for detection of failure and emergency shutdown. Heater tube failure is detected by low flowrate, low pressure or high temperature readings on a heater pass effluent.

Cold Areas. In acid gas service (such as H_2S, CO_2, SO_2, or SO_3), free water condensation must be avoided. The acid gases will dissolve in the condensate forming strong acids that cause severe corrosion. Even ambient conditions *not* considered severe, condensation of chlorine, for example, may cause corrosion under thermal insulation. Heat tracing may be required to eliminate this problem on lines and equipment exposed to ambient temperatures (see Chapter 8). All process and surface temperatures must be maintained above the dewpoint to prevent condensation. Convective sections of fired heaters present a particular problem. Both bulk and heat transfer surfaces must be designed to be comfortably above the dewpoint of the flue gas.

5.3.3 Trapped Liquids

Providing free drainage (via a sloped floor under storage tanks, proper drain line for pressure vessels, sloped tube for condensers, point drain for piping systems, etc.) will eliminate the possibility of liquid trapped inside a tank, equipment or piping and thus avoid the aggressive corrosion caused by concentrated fluid in dead pockets.

5.3.4 Corrosion under Wet Insulation

Various types of corrosion may occur hidden under insulation, including general corrosion pitting, crevice corrosion and external stress-corrosion cracking. Coating the metal surface will help prevent this corrosion attack. Ultrasonic scanning through the insulation has been used to periodically check wall thickness; this technique will give an early alert to this type of corrosion. Refer to Chapter 8, Thermal Insulation, for further discussion.

5.3.5 Corrosion under Plastic Lining

The plastic lining of steel pipe may be stripped off or cracked by swelling, dissolution, bond rupture due to oxidation and heat erosion, or aggressive environments. Corrosive process fluid will penetrate the lining and attack the base metal, causing premature failure of the vessel or pipe. Resistance to temperature, thermal shock, concentration and velocity should be considered when specifying the plastic lining materials.

5.4 FABRICATION AND INSTALLATION

Many corrosion problems are related to the welding process. Weld cracking causes a large percentage of equipment and piping failures. The welding procedures should be well defined and included in material specifications. The ASME code, Section IX, and the American Welding Society Handbook should be consulted. Selection criteria for welding procedures include:

a. Process service and alloy report. Use of an inert gas shield and low hydrogen electrode may be required.
b. A double groove butt weld joint is preferred for seam welds. For nozzle joints or other connections, a full penetration weld should be used to avoid porosity and formation of a crevice.
c. The chemical composition of the filler metal should match the base metal if possible. Overmatched filler metal may be required for some situations.

d. A permanent backing strip should not be used for pressure joints. A temporary (consumable) backing strip should be the same material as the parent material and removed after welding. Backing strips and backing rings are often the only way of assuring a full penetration weld.

e. Preheat and interpass temperature should be specified to equalize welding shrinkage, to control hardness and to expel the hydrogen from the weld. No preheat is required for austenitic stainless steels to reduce the sensitization and carbide precipitation; in fact, pre-heat would make it worse.

f. A seal welded tube-to-tube-sheet joint in heat exchanger may be used to avoid crevice corrosion.

g. Rod size, welding speed, and heat input can also affect the quality of the weld.

Quality assurance for welding may include:

- nondestructive examination such as radiography (RT), ultrasonic testing (UT), magnetic particle testing (MT), and liquid penetrant (PT)
- hardness test at weld and heat affected zone.
- chemical analysis of production weld.
- destructive test of production weld such as tensile tests, fatigue test, shear test, etc.
- welding qualification tests, procedure and performance.

Postweld heat treatments, such as stress relief or solution annealing, are used for different purposes and applied to different metals. Procedures for these treatments that specify heating rate, temperature, holding time and cooling rate should be well defined for each individual material to preserve its mechanical properties and corrosion resistance. It is critical that treatments to improve mechanical strength do not inadvertently reduce corrosion resistance.

5.5 CORROSION MONITORING AND CONTROL TECHNIQUES

Corrosion control often affects materials selection. One must be familiar with the control measures that are required for particular materials. Aside from simply accepting some reasonable rate of corrosion (which is the most practical approach in some cases), corrosion control may involve any or all of the following major approaches:

- a change of materials
- a change of process environment (e.g., process conditions, inhibitors)
- use of barrier linings or coatings
- application of electrochemical techniques (e.g., cathodic protection)

5.5.1 Corrosion Monitoring

A corrosion monitoring program can predict the corrosion rate, identify local corrosion, and estimate remaining service life. This information can be maintained in a computer database as part of the maintenance program.

During scheduled plant shutdown or turnaround, operating personnel can conduct extensive equipment inspection of critical equipment in aggressively corrosive areas. Internal inspection of pressure vessels, heat exchangers, compressors, etc, should be done to check for localized corrosion, cracking, distortion or collapse of internal components, and scale build-up inside and outside of tubes.

During plant operation, nondestructive inspection techniques, such as radiography, ultrasonic, magnetic particle, and liquid penetrant testing, can be used. On-line monitoring of corrosion coupons and corrosion probes may be used. An infrared radiation thermometer may be used to detect hot spots in a furnace, heater, boiler or electric transformer.

5.5.2 Change of Process Environment

Changing the process environment is a useful way to deal with corrosion, especially if resistant materials are not available or replacement is expensive. A strongly corrosive atmosphere can be changed by controlling pH, decreasing temperature, reducing concentration of process fluids, or adding an oxygen scavenger. Oxygen scavenging by sulfite or hydrazine in boiler feedwater is a typical example. Caustic injection to raise pH and avoid a corrosive, highly acidic condition is another.

5.5.3 Inhibitors

Sometimes a small amount of corrosion inhibitor is added to the process fluid to reduce the corrosion rate. Inhibitors are classified by mechanism of action (Table 5-2). Selection of an inhibitor is quite complex. Note that not only the inhibitor's effect on corrosion, but also its effects on the process chemistry and product specification need to be carefully considered.

5.5.4 Barrier Coatings

Selecting a coating to resist corrosion requires definition of service conditions, surface preparation and application methods, subject to regulatory and safety restraints.

5.5.4.1 Linings

Clad or Weld Overlay—Cladding is the process of bonding a thin layer of more resistant metal to substrate metal (usually less expensive) by weld overlay, hot rolling, brazing, or explosive bonding. Corrosion resistant clad or weld over-

Table 5-2 Corrosion Inhibitors

Inhibitor	Method of Action	Example
Absorption-type	Suppresses metal dissolution and reduction reactions	Organic amines
Hydrogen-evolution poison	Retards hydrogen evolution, but it does it by accelerating the permeation of H^+ into the metal, which can lead to hydrogen embrittlement	Arsenic ion
Oxygen scavenger	Removes oxygen from water or aqueous solutions	Sodium sulfite, Hydrazine
Oxidizer	Inhibits corrosion of metals and alloys that demonstrate active–passive transition	Chromate, nitrate, and ferric salts
Vapor-phase	Is used as blanket gas for machinery during shipment or for tightly enclosed atmospheric equipment such as switchboxes	Nitrogen blanket

lay on substrate materials is used for pressure vessels or heat exchangers at elevated design pressure. Welded overlay can be stress relieved; this method may be preferred to cladding for hydrogen service. Both explosion cladding and current roll cladding techniques produce better bonds than weld overlay. *Unbonded (Loose) Lining*—Unlike clad or weld overlay, loose lining has very weak bonding or no bonding at all to the substrate material. Teflon or plastic lining of pipes and valves and lead lining of storage tanks are very common examples. Loose lining should not be used in hydrogen service, high temperature, or vacuum service. Polytetrafluorothylene (PTFE) and perfluoro (alkoxyalkane) copolymer (PFA) withstand the widest fluid-temperature range and provide good chemical resistance (Jones 1990). The linings in plastic-lined products are generally thicker than coatings.

5.5.4.2 Coatings

External coatings, such as paint or plastic film, sometimes serve as a means of corrosion control for low temperature and moderately corrosive process environments. Coatings are classified as metallic or organic and are further classified by method of application. All coatings require rigorous surface preparation. Blasting (abrasive grit) or acid etching is normally used to provide the cleanliness and rough surface required for good bonding.

Electroplating or electrodeposition—A hard chromium plating on a shaft or valve seat, for example, provides very good resistance to erosion–corrosion and abrasion.

Electroless Nickel Plating is used for chemical resistant linings

Galvanizing—Zinc coated hot-dipped galvanized steel is widely used for structural steel bolts and nuts, and sometimes tube bundles for wet surface condensers.

Thermoplastic resins—A coating is applied in the services that require resistance to chemicals, abrasion, or high temperatures. The surface must be blasted to obtain good mechanical bonding. The three basic methods of application are: fluidized bed, electrostatic spray, and thermal spray (in which the powdered resin is melted on its way to the part to be coated) (McCallion 1989). Examples are PVDF (polyvinylidene fluoride), FEP (fluorinated ethylene propylene) and EAA (ethylene acrylic acid).

Vapor Deposition—The coating metal is vaporized by heating electrically in a high vacuum chamber and is deposited on the substrate. Compared to other coating methods, vapor deposition is relatively expensive.

Diffusion Coating or Surface Alloying—Heat treatment is used to cause alloy formation by diffusion from one metal to another. Alonized^R steels, for example, have excellent corrosion resistance to air and sulfur gases at high temperature.

Chemical Conversion Coating is produced by deliberately corroding the metal surface to form a protective coating. Inorganic zinc silicates protect by a galvanic mechanism (Foscante 1990).

Laser Surface Alloying—Treating the substrate with directed energy beams reduces general corrosion in hydrochloric acid.

Organic Coatings—Selection of the organic coating material and surface preparations are equally important. Surface preparation cleans the surface and provides roughness for good mechanical bonding of the coating. Methods include grit-blasting, sand blasting, solvent or vapor degreasing, steam and water cleaning, flame cleaning, pickling and wire brushing. Application techniques also affect the quality (that is, uniformity and thickness) of the coating. Epoxies and polyurethanes are common classes of coatings.

5.5.5 Electrochemical Techniques (Cathodic Protection and Anodic Protection)

There are two types of galvanic protection: cathodic and anodic. Cathodic protection is a process in which electrons are transferred from an external source to the metal, suppressing dissolution of the metal. Cathodic protection supplies electrons from an external power supply or a sacrificial anode. Cathodic protection is only good for moderately corrosive environments. This method is widely used in oil field, cooling water service, and for underground piping or structures (Figure 5-1).

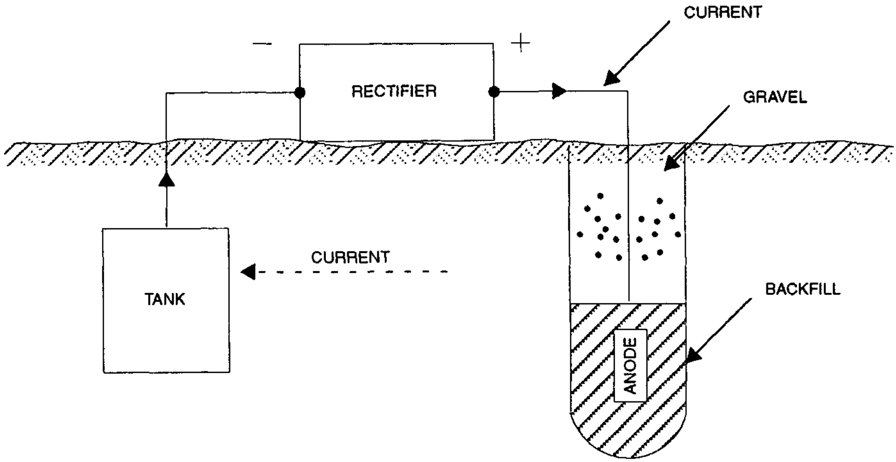

Figure 5-1. Cathodic protection of an underground tank using impressed currents.

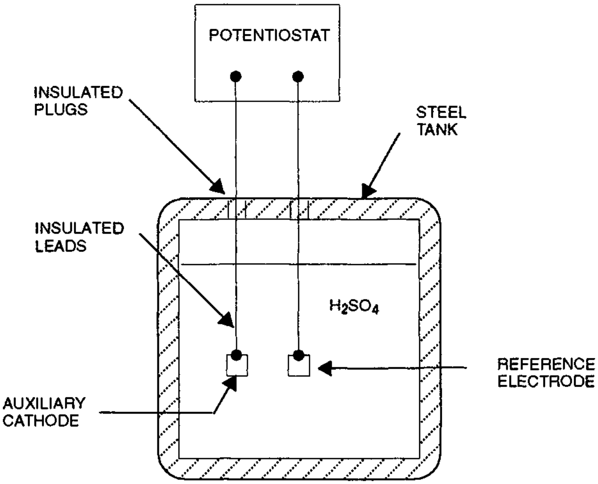

Figure 5-2. Anodic protection of a steel tank containing sulfuric acid

Anodic protection is based on formation of a protective film on a metal by externally applied anodic currents. Thus, the anodic protection can be applied to passive metal only. Anodic protection of a sulfuric acid storage tank is illustrated in Figure 5-2.

5.5.6 Corrosion Allowance

Although technically not a way to control corrosion, use of a corrosion allowance is a commonly used method to address the problem of general (uniform) corrosion. A corrosion allowance is added to the wall thickness based on the general corrosion rate predicted by previous experience and the design life of the equipment or piping. Corrosion allowance cannot be used to compensate for pitting or localized corrosion. Periodic inspection and wall thickness determinations must be made and monitored to determine when the equipment or piping must be derated or replaced.

5.6 REFERENCES

5.6.1 Regulations, Codes of Practice and Industry Standards

The editions that were in effect when these *Guidelines* were written are indicated below. Because standards and codes are subject to revision, users are encouraged to apply only the most recent edition.

ASME B31.1. *Power Piping*. American Society of Mechanical Engineers, New York.

ASME B31.3. *Chemical Plant and Petroleum Refining Piping*. American Society of Mechanical Engineers, New York.

APFA (American Pipe Fittings Association). *Guidelines for Selection-Installation–Operation of Plastic-Lined and Fitting Systems.* American Pipe Fittings Association, Springfield, Virginia.

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Other industry organizations that may provide specifications and technical standards for materials:

American Concrete Institute (ACI)
American Iron and Steel Institute (AISI)
American Society for Nondestructive Testing (ASNT)
American Society for Testing and Materials (ASTM)
International Standards Organization (ISO)
National Board Inspection Code (NBIC)
Society of Automotive Engineers, Inc. (SAE)
Steel Structures Painting Council (SSPC)

5.6.2 Specific References

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11

SOURCES OF IGNITION

11.1 INTRODUCTION

All potential ignition sources must be identified, although some may be difficult to analyze or control. Therefore, it is common practice to minimize the occurrence of such sources while taking all necessary steps to protect the equipment should such a source be present. These steps are described in Chapter 17 and may involve control to protect against flammable atmospheres, design to contain any explosion within the equipment, or incorporation of devices to intercept, suppress, or vent a flame reaction zone. Even if all internal ignition sources were eliminated within the process equipment, an external pool fire or impingement flame might still damage the equipment or initiate an uncontrolled internal reaction. Therefore, external fire protection measures such as thermal insulation and sprinkler systems may be used in addition to prudent design and layout to minimize the probability and severity of external fire.

In addition to protecting equipment, measures should be taken to minimize the probability of a flash fire or vapor cloud explosion should a leak occur. Many ignition sources are obvious, such as flares, burn pits, furnaces, and other flame sources. Less obvious ignition sources include internal combustion engines, atmospheric static charges, and equipment that might not be recognized as "fixed" ignition sources on a site plan.

The principal objective of this chapter is to provide information and literature references for ignition sources that are not obvious and might go undetected for years. Often, such sources are insidious. For example, a poorly designed liquid transfer system might regularly give rise to static sparks but not cause ignition because the vapor is outside its flammable range. Any change in the vapor concentration might quickly give rise to an explosion. As another example, after years of uneventful operation, a fire might develop in a spray dryer due to accumulation of an unusually thick powder layer which spontaneously ignites. This fire might in turn ignite a powder suspension in the dryer causing an explosion. Measures to avoid ignition sources must often be taken at the design stage. However, to do this it is necessary to gather appropriate information on the ignition behavior of the materials concerned. Discovery of this behavior once a unit is operational means costly retrofit, redesign, or add on safety measures.

11.2 TYPES OF IGNITION SOURCE

Apart from obvious ignition sources such as flames, several disparate groups of sources can be considered. These are:

- Moderate temperature sources that may give rise to spontaneous ignition.
- Electrical sources such as powered equipment, electrostatic accumulation, stray currents, radiofrequency pick-up, and lightning.
- Physical sources such as compression energy, heat of adsorption, friction, and impact.
- Chemical sources such as catalytic materials, pyrophoric materials, and unstable species formed in the system.

Ignition sources are often considered only in the context of the "fire triangle," whose sides comprise a fuel, an oxidant, and an ignition source (the three essential ingredients for most fires). However it is important to recognize that some materials can be "ignited" in the absence of an oxidant. Examples include acetylene and ethylene oxide (decomposition flames), and some metal dusts (reaction with nitrogen). Also, under process conditions, some materials may be "ignited" in the absence of oxidant even though at ambient conditions they may have a significant limiting oxidant concentration (LOC). An example is ethylene at elevated temperature and pressure, which may be ignited by many of the mechanisms discussed in this chapter (Britton et al. 1986).

Useful general reading for this chapter may be found in Lees (1980), Kuchta (1985) and Medard (1989). Lees' two-volume book is a well-known reference work. The manual by Kuchta reviews extensive ignition and flammability studies by the U.S. Bureau of Mines in the context of accident investigations. Medard's two-volume book provides a unique review of chemical instability in addition to coverage of conventional combustion science.

11.3 IGNITION BY FLAMES

This section considers both obvious ignition sources such as fired heaters and less obvious ignition sources such as internal combustion engines. An important feature of flames, as opposed to sparks and other brief ignition sources, is that they can readily ignite flammable or combustible materials of high ignition energy. Specifically, flammable mixtures can be ignited throughout their flammable ranges, since flames are at least equivalent to the ignition sources used to establish these ranges.

Some liquids, such as trichloroethane and anhydrous ammonia, have no conventional flashpoint but nevertheless have flammable limits (ASTM is developing a new flashpoint test to resolve this problem, with emphasis on halogenated hydrocarbons). The NFPA flammability hazard rating is typically

"1" based on the flashpoint test result. However, given a large ignition source (such as a flame) their vapors may ignite at ambient temperature. Production of a flammable mixture is frequently aided by some degree of confinement. This has led to accidents in confined spaces when welding in the presence of halocarbon degreaser vapors; a contributing factor in such accidents may well be oxygen enrichment due to excess oxygen used in the torch.

11.3.1 Flares, Burn Pits, Furnaces

Flares are considered in Chapter 15 both as an "open air" ignition source and as a source of ignition internal to the process should flashback occur. Location of unavoidable ignition sources must be considered in relation to storage of fuel sources and trajectory of possible vapor clouds (see Chapter 3).

11.3.2 Hot Work: Welding, Cutting

These ignition sources are handled administratively by the use of permits and training to ensure compliance. Before starting hot work, it must be ensured by gas analysis/freeing or inspection that no flammable or combustible material can be ignited. As an example, during welding of a label onto a brand new 55 gallon drum, the drum exploded and was propelled at the welder, fracturing his legs (Britton and Smith 1988). No regard had been given to the possibility of a flammable mixture in the unused drum, but in this case the manufacturer had wiped it clean with methyl ethyl ketone prior to shipment. It is important to recognize that flammable atmospheres may be established rapidly in the presence of small quantities of flammable liquid. Even after a thorough air sweep, a flammable atmosphere may be reestablished should liquid be trapped in a dead space. In powder handling systems, ignition of a powder layer could result in a smoldering ignition source that could later ignite a powder suspension in the system. Before using fuel–oxygen cutting equipment in confined spaces, the hazard of oxygen enrichment should be evaluated. Should this occur, clothing and other combustible materials will readily catch fire.

11.3.3 Safety Valves and Vents

Rupture disks, deflagration vents, and other devices such as the flashback decoupler are frequently employed to relieve combustion and decomposition events involving flames, as described in Chapter 17. When such devices operate, jet flames or fireballs are produced that may extend from a few feet to about 100 feet in length, depending on the type of facility being protected. It is essential that the flame be directed to a safe location away from personnel and equipment at risk from flame impingement. A vented flame may heat thin-walled equipment (such as neighboring silos) igniting the material inside. Flames impinging on unstable material lines might produce internal decomposition events. Where rupture disks have associated ducting, the latter should not be combustible (such as fiber reinforced plastic) since hot gases or flames may lead to melting/charring and formation of secondary fires outside the duct.

11.3.4 Internal Combustion Engines

Internal combustion engine ignition sources comprise electrical, exhaust, and intake systems. In the latter cases, flammable gas or vapor can ignite and backfire either through exhaust or intake lines. For fixed engines such as diesel generators or pumps and gas turbines, consideration should be given to location of these lines. A particular problem with diesel engines is "runaway" should a flammable gas enter via the intake, since fuel cutoff control may be lost. Where fitted, catalytic converters may produce sufficient temperature for ignition.

11.3.5 Vacuum Trucks

The vacuum truck offers several potential ignition sources comprising hot surfaces, backfires, mechanical sparks, and electrical sparks. Most vacuum trucks are made for use in water service such as sewage, sludge, etc., and might not be suitable for flammable or combustible liquid service. Hoses normally supplied are nonconductive and the vacuum pump usually discharges at grade (Sommer 1976). While most liquid pick-ups are usually highly contaminated with water, dirt, etc., and have a high electrical conductivity, precautions should be taken if flammable or combustible liquids might be picked up, particularly if the liquids might be nonconductive and water-immiscible. This might allow accumulation of static electricity. A "static" incident is described by Pratt (1992).

Of 12 vacuum truck fires considered, the tank truck engines were usually the cause of ignition owing to the truck being located too close to the spill pick-up point (Sommer 1976). One or two cases were probably due to exhaust backfires or sparks, and two cases were possibly caused by vacuum pumps discharging at grade near the engine. Concerns existed that ignitions might be caused by pick-up of rocks (flint-type sparks) and other sparking objects, or whipping of discharge hoses during unloading. One unloading accident might have been caused by an impact or static spark from a coupling on the end of an unloading hose dropped into a storage tank.

Lightfoot et al. (1978) concluded that the use of bonding cables and venting above the truck through a safety venturi will eliminate most fires. The following recommendations were made:

- Power the vacuum drive from the truck engine power take-off rather than a separate engine. Engine exhaust stack should be vertical and not under the truck. No catalytic converter or excessively hot attachment to be present.
- Discharge vapors through a safety venturi 20 feet above the truck. The venturi will dilute vapors below lower flammable limit (although vapors may become flammable during last 1–3 minutes of loading). The design should prevent accumulation of vapors under or near the truck at grade while loading on vacuum.
- Discharge flammable liquids by gravity flow or regular pump rather than by air pressure (note that air pressure discharge is a general unsafe practice for flammable liquids).
- Equip each truck with a combustible gas detector. Tests should be made on a calm day before pick-up of a flammable liquid, whenever the truck is downwind of the pick-up point.
- Check the safety valve routinely and schedule annual check and service of valve.
- Bond truck to source and ground source whenever flammable liquids are loaded or discharged (exception: remote flammable liquid spill).
- Use a minimum 30–40 feet of hose for loading purposes to keep the truck a safe distance from a flammable liquid spill.
- Position the truck upwind of the flammable liquid pick-up if possible, otherwise crosswind, and downwind only if gas detectors show no flammable vapor present. If little or no wind is blowing do not pick up flammable liquids unless gas detectors show no flammable vapor is present. Keep truck at least 30–40 feet away from spill area.

To the above could be added specific precautions when handling relatively pure nonconductive products such as hydrocarbons. These would be similar to those for tank trucks and include the use of conductive or semiconductive hose, with bonded end-connectors. Several other recommendations by Lightfoot et al. (1978), such as chemical compatibility and fire protection, should also be considered.

11.4 SPONTANEOUS IGNITION (AUTOIGNITION)

Spontaneous ignition is defined as the ignition and sustained combustion of a substance, whether gas, liquid or solid, without introduction of any apparent ignition source such as a spark or flame. It is synonymous with "autoignition" and "self-ignition." Ignition is the result of self-reaction from any initial condition (temperature, pressure, volume) at which the rate of heat gain exceeds the rate of heat loss from the reacting system.

Liquid phase self-heating due to chemical reaction in the absence of oxidant is usually considered separately from spontaneous ignition. Chapter 14 describes such runaway reactions which can be hazardous even if ignition does not subsequently occur. Spontaneous ignition of liquids is considered in the context of misting or flashing and subsequent autoignition, or via slow auto-oxidation in absorbent material. Some reactive liquids may self-heat and ignite in the absence of oxidant. These are classed either as explosives (such as nitroglycerine) or autodecomposible liquids (such as ethylene oxide) as discussed in Section 11.6.

11.4.1 Gas Phase Autoignition

The most common example of autoignition is the Diesel engine, since this operates on the principle of ignition by heat of compression. In the Diesel engine, fuels that readily self-ignite are desirable. Converse behavior is found in the spark-ignition engine, where self-ignition causes engine "knock." In this case, fuels that resist prespark ignition reactions are desirable instead. The autoignition behavior of gases and mists is highly complex, especially when related to the dynamic conditions in an engine. Similarly, dynamic conditions in process equipment containing possible sources of hot spot autoignition, such as a hot bearing, defy quantitative analysis. Often, the concept of "autoignition temperature" (AIT) is used to determine whether a hot surface will ignite a stagnant gas pocket. This approach is conservative if the AIT is known at the prevailing pressure and gas volume involved, since the assumed reaction time is very long.

At ambient pressure, standard AIT values can be used to help select equipment to be used in classified areas. Bartheld (1978) discusses the application of AIT in assessing motor surface temperatures in hazardous areas. Gosda et al. (1989) and Bothe and Steen (1989) compare AITs with gas and vapor ignition temperatures measured for hot surfaces. Chapter 12 and the National Electrical Code (NFPA 70) contain further information. The commonly listed AIT (see NFPA 497M) refers to the ambient pressure value measured in open-necked glass flasks. The current test method is ASTM E 659 (500 ml flask) which in 1976 replaced ASTM D 2155 (200 ml flask). Owing to differences in these ASTM test methods, AITs differing by at least 20°C are to be expected.

Although AITs have been tabulated for many materials, the test results must be considered only as a "snapshot" of what might happen under different conditions. For example, increased test volume and pressure will usually lower the AIT, and container surface effects might be important. Figure 11-1 shows schematically the behavior of a material (such as an ether) that exhibits cool flames. At atmospheric pressure, only slow combustion (no explosion) is found up to the AIT, although a cool flame region is traversed as temperature is increased. In this case, the lowest "cool flame temperature"

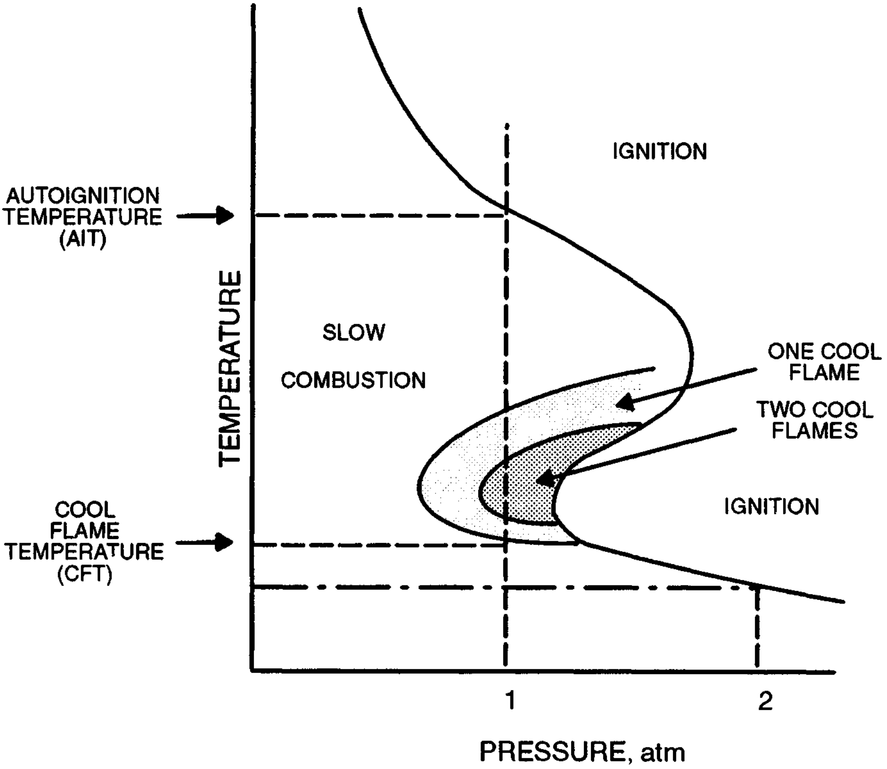

Figure 11-1 Schematic autoignition temperature–pressure diagram (courtesy of L. G. Britton).

(CFT) is much lower than the AIT. At some higher initial pressure, it is possible to enter the ignition region at a temperature even lower than the ambient pressure CFT. Thus, pressure effects can be very significant.

With the exception of ASTM D 2883, standard AIT test methods do not allow initial pressure to be varied. Tabulated values refer to atmospheric pressure tests. With reference to Figure 11-1, if the cool flame region were entered in a closed test vessel initially at 1 atmosphere, the increased temperature and pressure from the cool flame could shift the entire system into the ignition region. Single cool flames often cause temperature increases of about 150°C. Transition from slow combustion to hot flame ignition may occur under certain conditions in process equipment, where large volumes and nonuniform temperatures can further complicate any evaluation. In process equipment, elevated temperatures and pressures are common. In some cases, autoignition is prevented by limited reaction time, and loss of flow may lead to detectable self-heating of process streams or hot reactor head spaces (Britton et al. 1986). In distillation columns and other vacuum equipment, sudden ingress of air due to a leak or vacuum break might cause an explosion. Possible occurrences, test methods and the significance of cool flames are discussed by Coffee (1980) and D'Onofrio (1980). Snee (1988) describes pilot scale experiments to investigate the cause of several autoignitions during resin manufacture; vapor autoignitions occurred due to sudden admittance of air during opening of manholes or when the final product was discharged from the reactor. Richardson et al. (1990) discuss autoignition via heat of rapid compression as a possible cause of a major accident on a North Sea oil platform. Autoignition in chemical processes is poorly understood and the subject requires study under realistic conditions.

11.4.2 *Spontaneous Ignition of Liquids in Absorbent Solids*

Absorbent solids containing combustible liquids and exposed to air experience slow oxidation (often referred to as auto-oxidation). If the ambient temperature and size of the pile of material is sufficient, heat from the slow oxidation will accumulate rather than be lost to the surroundings. The accumulation of heat raises the temperature and this accelerates the oxidation rate until true combustion begins. The fire may take seconds or days to develop. A study of insulation fires and related phenomena, including a review of test methods, is described by Britton (1991). Other examples include piles of oil soaked rags, oily filter elements and spill control materials such as vermiculite soaked with a combustible liquid. Sufficiently large masses of contaminated absorbent may ignite at ambient temperature in many cases, particularly where the absorbent has good thermal insulating properties. The phenomenon occurs not only from initial temperatures below the liquid autoignition temperature, but in many cases from initial temperatures below the liquid flashpoint.

A special case is spontaneous ignition in distillation column packings, which are not truly "absorbent," but which may accumulate heavy material such as paraffin waxes and polymers. The large surface area and relatively low heat capacity may allow self heating to take place. In an unpublished incident an amine polymer is believed responsible for blackening and scorching of a gauze packing, which was estimated to have locally attained 1040–1400°C during the event. A causal factor appears to have been opening of the column to air while steam remained on the reboiler, since the burned material was found in an extended zone above the reboiler outlet. Other incidents are discussed by Strofer and Nickel (1989).

11.4.3 *Spontaneous Ignition of Powders (and Other Solids)*

Combustible powders spontaneously ignite at a sufficiently high temperature. This temperature depends primarily on the size and geometry of the powder accumulation. It also depends on factors such as moisture, particle size, ambient oxidant concentration and the presence of any antioxidant added to the powder. Unstable materials may undergo self-heating due to decomposition rather than combustion, as discussed in Section 11.6.

The two general cases usually encountered are powder layer ignition and bulk powder ignition. The essential difference is that the spontaneous ignition temperature (SIT) of powders stored in bulk can be less than atmospheric temperature, and special scaling methods must usually be used to estimate the SIT. Powder layer SIT can be determined experimentally without any need to extrapolate the results.

Ignition of powder layers is a relatively simple problem normally involving heating on one side such as by a light fixture or hot motor casing. Hot plate tests as described by Beever and Thorne (1982) and by Nagy and Verakis (1983) may be used to determine the SIT and ignition delay time. It is important to recognize that the SIT can change very rapidly with changes in layer thickness, so the experiment should closely simulate the worst-case plant situation. Where layers are heated on both sides, such as inside hot equipment, isothermal testing as done for bulk solids should be considered.

Ignition of bulk powders may occur during processing, storage, or transportation, where the initial temperature is equal to or less than that of the surroundings. "Ignition temperatures" based on small-scale hot plate or furnace tests such as ASTM D 1929 are meaningless for such cases. Isothermal test methods described by Beever and Thorne (1982) may be used to determine the SITs of powder contained in mesh baskets of different sizes. Provided the geometry is held constant, a simple scaling model can be used to extrapolate the data to larger sizes and other geometries. The method as applied to investigation of spontaneous ignition of activated carbon stowed in ships' holds is described by Bowes and Cameron (1971). The method has also been successfully applied to SITs of agricultural products in large silos, to blocks of polyurethane foam, and to plastic powders in production facilities. The estimation of ignition delay time is usually less accurate. Where ignition is predictable the options include reduction of hold-up time of the hot powder, addition of antioxidant, exclusion of air, or reducing the representative thickness to increase heat loss rate to the surroundings. The solution to the activated carbon fire problem was simply to include a suitable polyethylene liner in the bags to exclude air.

A special and more difficult case is that of "hot-spot" ignition, where powder is added hot to a cooler container or a mass of powder is heated only locally. Griffiths and Kordylewski (1992) show how to predict ignition temperatures for "hot stacked" process materials. In many cases expert consultation is required to address this type of problem.

11.5 ELECTRICAL SOURCES

This section emphasizes electrical sources of ignition not covered elsewhere in this book or for which literature sources are not readily available. Recently, several excellent articles and a new standard on static electricity have appeared and thus the reader is referred to these. Some areas, such as radiofrequency (RF) stray currents, may be unfamiliar and the coverage reflects this fact rather than the importance of the phenomenon.

Electrical sources are the easiest to categorize in terms of energy, since sparks are used to establish minimum ignition energies of flammable mixtures. Figure 11-2 shows the minimum stored spark energies (mJ) to ignite a series of optimum flammable mixtures in air. Effective energy ranges for various types of ignition source are also shown. Owing to the great ignition energy dependence of dusts and mists on their particle size distributions (Britton 1992), only lycopodium spore is used as an example material. This has an approximately uniform particle size and is frequently used as a "standard" dust in explosibility testing. Figure 11-2 has obvious limitations owing to the overlap of effective energies of disparate ignition sources, but nevertheless is a useful illustration.

11.5.1 Static Electricity

Discharge of static electricity is a potential ignition source. Many operations on liquid hydrocarbons and organics in chemical plants such as pumping, mixing, pouring, filtering, and agitating cause static charge buildup that may lead to an incendive static spark. Transfer and processing of powders, pellets, and bulk solids also present static discharge hazards. If such an event takes place in a flammable vapor–air mixture an ignition or explosion may result. A similar situation arises when flowing gas contaminated with metallic oxides is directed against an ungrounded conductive object which then becomes gradually charged until a static spark occurs. Therefore it is crucial to prevent the simultaneous occurrence of a flammable mixture and static spark.

Static electricity is generated by a change in relative position of contacting surfaces and may be found throughout industry in the following situations:

- Product flow in piping.
- Mixers blending solids into liquids in a partially filled tank or vessel constructed of a nonmetallic material or lined with a nonconducting material.
- Particulates passing through chutes or pneumatic conveyors.
- Container splash filling operations.
- Steam, air, or gas flowing from any opening in a pipe or hose, when the stream is wet or the air or gas stream contains particulate matter.

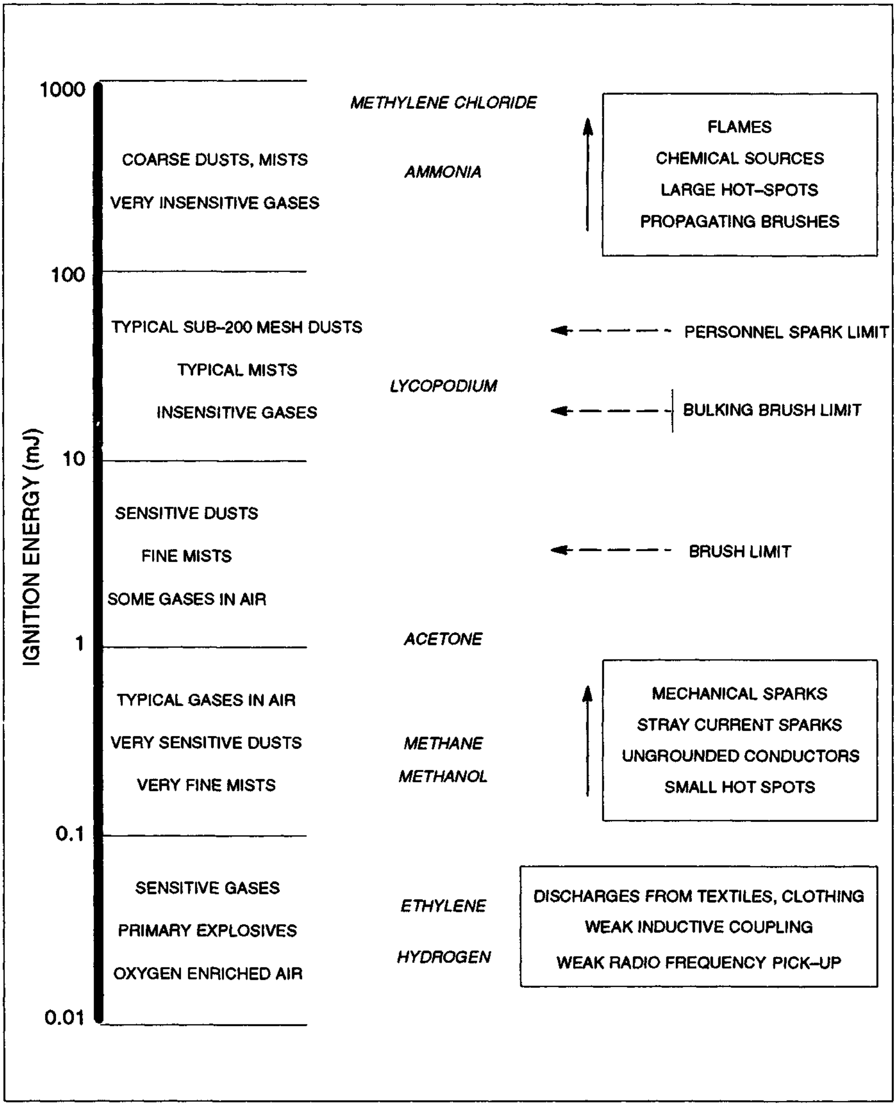

Figure 11-2 Illustration of ignition energy ranges (courtesy of L. G. Britton).

- Nonconductive belts in motion.
- Personnel wearing nonconductive shoes.

Until the British Standards Institution published BS 5958 in the early 1980s, specific recommendations for various industrial handling situations were not available, and practices were developed by individual companies or trade associations. Broad recommended practices such as NFPA 77 and API RP 2003 addressed mainly grounding procedures plus other precautions based on petroleum industry experience. Other documents published in the U.S., such as NPCA Bulletin 603 for solvent handling, gave more specific recommendations. In 1991, a revised BS 5958 was published giving specific recommendations for most industrial situations based on current knowledge. This standard covers liquids, solids, and mixed phase handling. Plastic containers (including intermediate bulk bags), personnel grounding, and other issues are addressed.

11.5.1.1 Personnel Grounding

BS 5958 gives recommendations on when personnel should be grounded. Britton and Smith (1988) discuss the basis for selecting "conductive" versus "antistatic" footwear with reference to electric shock hazards. In practice, use of conductive or antistatic shoes is only one of several alternatives. Where mobility is not critical, such as at fume hoods, grounding bracelets may be more suitable. A second alternative is the use of removable conductive straps fitted around regular shoe heels and connected to the ankle. This has several advantages over footwear issued specifically to one operator. The devices can all be specified to have a minimum resistance of about 1 Mohm to avoid electric shock hazard. All devices used for grounding the foot have the same shortcoming, namely, that both the device and the floor must give the expected continuity. Accumulation of nonconductive resin or lacquer can defeat the system. Regular testing and housekeeping are required. Area continuity testers are commercially available for both the device and the floor. A question often raised is where to use personnel grounding. The answer is that this should be carried out in the same way that an area is electrically classified, assuming that the operator is a source of ignition. For example, the immediate area around a manual drumming operation can readily be equipped with a conductive floor (such as a grounded, conductive rubber mat) and other areas defined for through traffic.

11.5.1.2 Liquid Handling

A practical monograph has been published based on the experience and internal practice of the Shell Company (Walmsley 1992). This closely follows the recommendations of BS 5958 with some simplification and discussion. A special issue of *Plant/Operations Progress* devoted to static electricity (January 1988) includes the recommendations of a Swiss Expert Commission, based largely on Ciba–Geigy's internal practice (ESCIS 1988). A common theme of more recent publications is that static hazards are experienced not only with petroleum products and other liquids of "low conductivity" (nominally less than 50 pS/m).

Hazards may occur with conductive liquids such as alcohols handled in plastic equipment, where grounding can be impractical. Even in grounded equipment, liquids with a conductivity of at least 1000 pS/m may accumulate static in stirred slurries. Static may also accumulate in plastic lined pipes and hoses, and in microfilters. Liquids with elevated dielectric constants such as esters relax charge slower than hydrocarbons, and under the same conditions the conductivity may need to be increased to about 10,000 pS/m to prevent significant static accumulation.

To assess static ignition hazard during liquid handling one must consider the ignition energy of the vapor, the conductivity of the liquid, and the operation involved. If a flammable vapor or mist is present under the handling conditions, the liquid conductivity and type of operation must be considered to determine if static can accumulate. Britton (1992) presents an extensive listing of liquid conductivities and ignition energies that may be used in conjunction with recommended practices. In many cases, such as liquid mixtures, the conductivity will be unknown and must be measured.

Owing to improved catalysts and production techniques, the conductivities of many commercial-quality liquid products has decreased owing to higher purity. This may involve, for example, decreased levels of water, acids, and other trace impurities. In cold weather, the conductivity will be further depressed (Britton 1992). Thus, liquids previously considered "conductive" in published listings may enter the "semiconductive" category with a conductivity less than 10,000 pS/m. Under such conditions static problems have been experienced in rubber hoses and in end-of-line bag filters.

In addition to common grounding practices, it is important to eliminate brush discharges from nonconductive charged surfaces. These discharges have limited energy but can ignite many vapor–air mixtures and even fine mists (Britton and Smith 1988). They can be produced both from plastic surfaces and from liquid surfaces, even from liquids contained in fully grounded equipment such as unlined metal tanks. Typical measures are to limit transfer rates, avoid splash filling, and to place filters a sufficient distance upstream for charge to dissipate. Other measures are necessary when two phases are present, such as water–oil mixtures or stirred slurries. These measures are described in BS 5958 and by Walmsley (1992). As discussed by Britton and Smith (1988) a very energetic "propagating brush" discharge can occur when high charge densities deposit on nonconductive surfaces that can act as capacitors. The discharges have been observed in plastic pipes downstream of filters in low-conductivity liquid service. The phenomenon also occurs in plastic-lined pipes and hoses, and glass-lined vessels, leading to pinhole puncture of the lining. In lined pipes and hoses, an ignition hazard may exist as liquid drains out admitting air. The phenomenon in glass-lined reactors is a particularly difficult problem. During stirring, the discharge may occur partly in the vapor space and represent an ignition hazard. Also, the pinhole can later expand leading to iron contamination and possibly even to catalysis and runaway reaction.

11.5.1.3 Solids Handling

One of the most important yet poorly recognized facts about powder handling is the effect of particle size on the ignition energy of the suspension. Ignition energy varies inversely with the second or third power of particle size (Britton 1988, 1992), meaning that the ignition probability of a suspension is largely determined by the concentration of the smallest particles present. Ignition probability depends on numerous factors such as container size, powder resistivity, mass flow rate, transfer velocity, and surfaces contacted. It can be influenced by the accumulation of additives (Britton 1988) in addition to the overall particle size distribution (Glor 1988).

Experiments have indicated that powders (with the exception of explosives) are not ignited by ordinary brush discharges (Britton 1988). However, over the past 15 years it has become apparent that many powder ignitions have been due to the appearance of energetic discharges on the powder surface during powder bulking in large containers. These have been termed "bulking brush," "wall-to-cone," "conical pile" or "Maurer" discharges, of which the first is the most common term. They are described by Britton (1988) and Bartknecht (1989), and appear as bright radial discharges on the powder bed that can be several feet long. Although the ignition energy of a powder suspension is difficult to determine (Britton 1992) it is generally accepted that these discharges have a maximum effective energy in the range 10–25 mJ. This is based on analyses of ignitions that have occurred in properly grounded equipment.

The actual value depends on the test method used to establish ignition energies, plus the inevitable assumption that samples taken for ignition energy testing after the event are representative of the material that initially ignited. A survey of the ignition energy test methods used indicates that in qualitative (but practical) terms, the maximum effective energy of bulking brush discharges compares with (or is less than) that of lycopodium spore. Lycopodium can be considered a "standard" dust owing to its relatively uniform particle size. It is implicit therefore that when these discharges are produced, and there is fine dust having a minimum ignition energy (MIE) less than 10–25 mJ present, there will exist a certain ignition probability even in properly grounded equipment. If there is also a flammable vapor present, such as in bins containing resin that has not been fully purged, the ignition probability of the "hybrid mixture" so produced increases rapidly with the vapor concentration. Ignition via "ordinary" brush discharges may be possible, even at vapor concentrations below the vapor LFL.

Bulking brush discharges could in principle be controlled by ionizing techniques, but these have not yet been proven for large pneumatic transfer systems. Accepting that the discharge will occur, design alternatives are inerting or avoiding vapor and fine particles. In many resin systems, not only is thorough degassing carried out prior to air transfer, but one basis for catalyst and process selection is the particle size distribution of the product. In addition, additives such as antioxidants are selected on the basis of their measured MIEs and the systems are equipped with deflagration vents.

Since there is no evidence for powder ignition by "ordinary" brush discharges, not only are conductive filter bags unnecessary but they can be dangerous spark sources should they contain isolated conductive patches, or should they fall into the bin. Provided no flammable vapor is present, nonconductive bags should be selected. It is important however to ensure that bag cages are properly grounded (not isolated from the tubesheet by the folded bag) and cannot fall down into the bin, where they can be both a spark hazard and a menace to the rotary valve.

Glor (1988) and Bartknecht (1989) describe the propagating brush discharges possible in powder handling systems when plastic surfaces are contacted and become charged. These can certainly ignite powder suspensions and are also a personnel shock hazard. They have been observed during pneumatic transfer through plastic pipes and during the filling of large plastic containers with resin pellets (Britton 1988). Glor (1988) gives criteria for avoiding these discharges in systems containing nonconductive linings. This basically states that the discharges do not occur if the breakdown voltage of the lining is less than 4 kV. The same criterion has been proposed for designing flexible intermediate bulk containers (FIBCs), where the discharge may occur across the wall during filling or the spout during unloading. It should be noted that conductive plastic vacuum hoses are available and should be used both to prevent personnel shock and ignition risk for ignitable powder.

General handling recommendations are given in BS 5958 and in the articles by ESCIS (1988) and Walmsley (1992). An important fact of powder handling is that vapor ignition when adding powders to flammable liquids is all too common. During manual addition of powder, various ignition sources may exist such as sparks from ungrounded equipment, the operator, or nearby electrical equipment such as a fan or forklift truck, or brush discharges from a bag, plastic liner, or other nonconductive element. In some cases, powder ignition can occur in the absence of flammable vapor. For example, a fine powder suspension may be ignited by a spark from an ungrounded operator who has become charged by the act of manual pouring.

11.5.2 Lightning

Standard and recommended practices are given in NFPA 78, API RP 2003, Army TM 5-811-3 and LPI-175. A short overview of lightning protection for plant is given by Frydenlund (1990). Further information is given in Chapter 12.

Special bonding and grounding procedures are necessary for certain equipment such as floating roof tanks, but pipelines are electrically continuous across flanges due to bolt contact. Star washers are sometimes used for coated flanges or Teflon coated bolts. Oxygen lines may have additional protection (such as Kirk cells) against lightning to avoid internal arcing and ignition. These devices switch from high to low ground resistance during a lightning transient. Certain items such as "sandwich" valves, swivel joints and other breaks in electrical continuity may require jumper cables.

It should be emphasized that proper grounding relies on the ground contact itself. Dry ground terminals may be ineffective. Also, water pipes may contain sections of plastic pipe and be effectively isolated from ground.

11.5.3 Stray Currents

A stray current is defined in API RP 2003 as any electrical current flowing in paths other than those deliberately provided for it. Such other paths include the earth, pipelines, and other metallic objects or structures in contact with the earth. A stray current may be continuous or intermittent, unidirectional, or alternating, and is usually distributed among a number of available parallel paths in inverse proportion to their individual resistances.

In this section we consider stray currents picked up from radiofrequency transmitters, overhead high voltage lines, sources of electrochemical currents and cathodic protection systems. Additional examples and precautions are given in API RP 2003.

11.5.3.1 Radiofrequency Stray Currents

Excell (1984) gave a technical and historical background showing that close to high power radio or radar transmitters there is a real possibility that sparks can be produced at discontinuities in metal structures. In these cases the metal structures act as adventitious antennas. Examples include metal cranes (spark gap from hook to load) and bonded fuelling hoses which might constitute loop antennas during make/break contact.

Richards and Rosenfeld (1987) gave a more recent review of the problem in relation to gas ignition, electro-explosive devices, personnel burns and computer/process control systems. Historical examples include personnel injuries (burns) in Honolulu Container Terminal and measurement of up to 1 kV relative to the ground on large jib cranes in Hamburg docks, this latter case being due to a 300 kW broadcast transmitter some 7 km away. An undocumented incident involved a road tanker explosion at a U.S. gas station caused by a radio transmission from a police officer reporting in.

The effectiveness of an antenna depends on its size and shape plus the radiofrequency. Below 30 MHz, loop structures such as cranes, tanker loading loops and loops formed by columns and pipes are most effective. Richards and Rosenfeld (1987) show how to calculate the inner perimeter *P* for typical loop antennas. The efficiency of such antennas varies with the ratio of perimeter to wavelength.

Rusty surfaces appear to increase the incendivity of sparks created in this way, and ignition may occur for voltages less than 300 V. The power thresholds for ignition vary with the impedance of the structure. To assess the hazard, RF field strength analysis is recommended in conjunction with worst-case antenna assumptions. Comparison is then made with a nomograph showing field thresholds at different frequencies for different gas ignition sensitivities (methane or hydrogen) and antenna inner perimeters. Vulnerable distances of 20 km or more might apply especially for vertically polarized 1–2 MHz signals, assuming an output power of 150 kW feeding an antenna with gain of 7. Remedial actions short of relocation include RF screens, reduction of transmitter power, or structural redesign. Hand-portable radios are not considered a significant hazard except in special cases involving electro-explosive devices. However, they should be banned from computer suites and control rooms since external RF protection is totally defeated by their proximity to the electronic systems (Richards and Rosenfeld 1987).

11.5.3.2 Overhead High Voltage Transmission Lines

Objects close to ground level with overhead UHV transmission lines are situated in an electric field which may be of the order 5 kV/m. Isolated objects or people might give rise to sparks when they contact a ground path. The maximum energy released can be effectively related for an alternating field by the object's capacitance to ground and its open circuit voltage. Deno (1974) applied Norton's Equivalent Current Source Theorem to simplify the analysis of an object at grade in a known electric field. Examples were given of a well-insulated wire fence (dry fenceposts) and an automobile. Practical measurements supported the analytical method used. While the analysis was directed at personnel shock thresholds, the same principles could be used for ignition hazard analysis. An experimental vapor ignition study using 50-Hz sparks was reported by Fiumara and Avella (1983). Using capacitances typical of people and vehicles, hydrocarbon or alcohol vapors were ignited only at peak voltages above 4 kV, which was higher than induced voltages reported in the literature. Very intense fields and/or more easily ignited mixtures would be required for ignition to occur via this mechanism.

11.5.3.3 Galvanic and Cathodic Protection Stray Currents

Low voltage sparks capable of igniting gas mixtures may be produced by Galvanic currents associated with contact and separation of dissimilar metals. Two cases discussed by Medard (1989) involved sampling and gauging of tanks containing an electrolyte (acid, base, or salt solution). In the first, an aluminum dipstick produced 1.5 V at 1.6 A in contact with the manway on a cast iron nitrator. Pale sparks were observed. The energy in this case was low

(0.013 mJ) owing to the low circuit inductance of 0.01 mH. In a second case where a flask was lowered into an acid tanker via a stainless steel wire, a low order hydrogen–air explosion occurred. The recommendation was only to introduce metal objects made of the same metal as the tank.

Electrical potentials may exist between vessels and mooring structures due particularly to electrical or chemical cathodic protection. Significant currents can be generated when electrical contact is interrupted and this might represent an ignition hazard. Harrison et al. (1981) made a literature review and practical study of this problem for the U.S. Coast Guard in relation to tanker/terminal operations. It was shown that significant stray currents could be produced when opening the loading circuit, in one case even with two bonding cables and a connected loading arm present. To avoid sparking or arcing in loading circuits, insulating flanges are commercially available to prevent short-circuits (see API RP 2003 and ISGOTT). Nonconductive hose (an alternative to the insulating flange) might be hazardous in this application due to possible static discharges from charged nonconductive liquid flow (particularly downstream of filters) or external tribocharging of the plastic hose carcass.

In addition to ship-to-shore loading lines and analogous systems where such stray currents may be encountered, vapor recovery systems subject to U.S. Coast Guard regulations require use of insulating flanges. A practical difficulty with insulating flanges (particularly in loading and unloading lines) is that since there is no international uniformity of use (despite the ISGOTT recommendation), they may or may not be installed at terminal facilities. There is an obvious hazard in incorporating a permanent insulating flange on the ship itself, since if there is a second flange on shore the hose will be ungrounded between them and possibly be a static spark risk. A dilemma occurred in South America when two major companies offloading from the same ship wanted (per their internal procedures) to respectively bond the ship to shore and isolate it from shore using an insulating flange. The latter practice was agreed on after reference to ISGOTT, breaking the procedural deadlock.

11.6 PHYSICAL SOURCES

In this section we consider ignition resulting from miscellaneous energy sources. Those considered are heat of compression, mechanical effects and physical adsorption.

11.6.1 Compression Ignition

Compression ignition can sometimes occur in systems containing flammable vapor or mist plus air. Ethylene decomposition during pipeline compression and in compressors is discussed by Britton et al. (1986); sudden isentropic compression ignited trapped ethylene in the presence of air which had not been properly purged. Since air is a diatomic gas it has a higher ratio of specific heats than most fuel gases and this greatly increases the final temperature attained by compression. The oxygen content of air also facilitates reaction, so there is far less hazard when only nitrogen is present, even though the final temperature due to compression is the same as with air. Owing to the high transmission pressure of ethylene (>1000 psig), large compression ratios of the order 100 or greater are commonly available in major pipeline systems, so proper purging of air and slow pressurization of lines are very important in preventing ethylene decomposition.

Fires can occur when pressuring oxygen cylinder-valve lines, where ignition of valves and tubing is possible with some materials of construction such as Monel or stainless steel (in such cases, impact of particulate material is often the assumed cause of ignition). Several accidents have also occurred with cylinders containing flammable gas.

Medard (1989) describes the unusual case of nitromethane transportation in rail cars, where on separate occasions the liquid detonated during shunting. The ignition mechanism was believed to involve sudden compression of air pockets by energetic waves of liquid moving along the surface. While nitromethane is no longer transported in this manner, analogous situations during liquid transfer are addressed by procedures described by Medard.

11.6.2 Mechanical: Sparks, Friction, Impact, and Vibration

Impact may cause fracture or stretching of metal, possibly with the formation of metal sparks. Glancing friction may also cause "streaking" resulting in relatively large areas of hot metal. The ignition process is highly complex and may be further complicated by the presence of surface contamination such as rust or protective coatings which could produce catalysis or thermite reactions (see Section 11.7). The impact may also involve nonmetals such as rock or concrete.

Hot surface ignition is discussed in Section 11.3. In all but the simplest cases, no analytical solutions are possible (see, for example, Laurendeau 1982). An excellent practical review of friction and impact ignition studies is given by Powell (1969).

Affens and Lange (1976) concluded that the temperatures developed by metal fracture during tanker collisions (or by analogy, shrapnel impact on a storage tank) would not be sufficient to ignite a flammable hydrocarbon–air mixture. Ignition would more likely be associated with friction and in particular with frictional sparks. Medard (1989) takes the view that the high temperatures associated with metal thinning during penetrating impact or bursting of pressure vessels are likely to result in ignition. Since the probability of ignition will depend critically both on impact conditions and the properties of the flammable mixture, either outcome is credible. With regard to shrapnel impact on storage tanks, the debris might include pipework and other equipment containing burning material, rendering the question of impact ignition academic.

Mechanical sparks have been studied by Bartknecht (1989) and their incendivities related to properties of the flammable vapor or powder involved. Data are presented showing the range of propane concentrations in air that are susceptible to flintstone friction sparks; for lean mixtures, the effective energy of such sparks can attain about 5 J relative to electrical sparks. Unfortunately, since neither of the powder ignition parameters used (minimum ignition energy and cloud ignition temperature) is based on a standard U.S. test, the data presented for powders are difficult to apply.

A study of petroleum vapor ignition during grit blasting is given by Singleton (1976). The study concluded that grit blasting of rusty steel may be safely undertaken in flammable atmospheres typical of the petroleum products involved.

"Nonsparking" alloys are somewhat of a controversial issue, since in principle there is no such thing. This is because impact sparking depends on what is being struck. Studies such as Bernstein and Young (1957) and reviews such as by Powell (1969) conclude that there is no benefit of beryllium bronze and other "nonsparking" tools in flammable atmospheres, since ignition by hand tools was only significant when rock or concrete was struck. However, the observations do not apply to hydrogen and other gases of low ignition energy, where "nonsparking" materials may have valid application.

Forced vibration of certain elastomers results in internal heat accumulation, and unlike cyclical bending of metals, the heat can sometimes result in spontaneous ignition. This has occurred with a rubber seal under which compressed air was escaping and whistling. In a bizarre but repeatable incident, a cotton–rubber composite fire hose caught fire when discharging cold water (Medard 1989).

11.6.3 Heat of Adsorption

Physisorption is an exothermic process which can occur on adsorbents such as activated carbon, silica gel and molecular sieve. If preloading is not carefully done, large exotherms can be produced. There is also the possibility of exothermic chemisorption and catalyzed polymerization or surface reaction, for example with chemisorbed oxygen. In several incidents involving ethylene purification, runaway reaction has occurred leading to decomposition. The physical and chemical heat sources can "bootstrap" in such cases (Britton et al. 1986). Medard (1989) discusses adsorption hazards of acetylene over activated carbon.

11.7 CHEMICAL REACTIONS

There are numerous possible routes to ignition via local chemical reactions which cannot occur in the system as a whole. Examples include:

- catalysis
- reaction with powerful oxidants
- thermite reactions
- formation of unstable species (for example, peroxides, acetylides, nitro compounds)
- formation of pyrophoric materials (for example, iron sulfides)

In addition to these broad groups, ignition may result from "quantitative" bulk chemical reactions such as those between unrecognized oxidizing agents and reducing agents. However, these are the result of poor process chemistry and do not class as ignition sources. An extensive data base on physical properties of chemicals is being compiled by DIPPR, the Design Institute for Physical Property Data (see Daubert and Danner 1989). A recent article by A. S. West (1993) provides molecular structure tables on high energy hyperbolic ignition.

11.7.1 Catalysis

Catalysis is primarily a problem in reactive chemical systems and can occur due to materials of construction, migration of catalyst from elsewhere in the system, or catalyzed reaction with either a contaminant or a secondary reactant present at abnormal levels. This chapter is not concerned with catalyzed bulk reactions such as liquid phase runaways, which are covered in Chapter 14. Instead, the catalysts represent local sources of heat. For example, an iron–constantan thermocouple might glow red hot should iron be a specific system catalyst.

Decomposition of hot, reactive chemicals such as acetylene, ethylene oxide and ethylene can be catalyzed by a wide range of high surface area solids such as powdered rust, silica gel, charcoal, alumina and other metals/metal oxides.

Many examples of catalysis are to be found in ethylene systems. In the high pressure polyethylene process, numerous decompositions have been assigned to catalyst migration from the reactor. In ethylene purification systems, catalysis can occur in conjunction with exotherms due to adsorption (Britton et al. 1986). Unexpected catalysis has also occurred due to the presence of abnormal levels of hydrogen. Separate examples are given by Britton et al. (1986) and by Halle and Vadekar (1991). In the first a decomposition flame was initiated by the catalytic reaction of ethylene and hydrogen in a purification bed. In the second, a runaway hydrogenation reaction was believed initiated by an accumulation of rust.

Exothermic vapor phase reactions of ethylene oxide may be catalyzed by high surface area iron oxides under certain conditions. This may occur either in the presence or absence of air (Britton 1990b). A recent ethylene oxide distillation column explosion was caused by such a catalytic reaction in a hot reboiler tube, leading to a vapor phase ethylene oxide decomposition. While the reaction would normally be moderated by liquid wetting during column operation, low liquid levels in this case allowed hot vapor phase reaction to occur in the reboiler after full liquid thermosiphon through the tubes was lost. This incident was discussed in three papers at the 1993 Loss Prevention Symposium (Ream and Simpson 1993; Simpson and Minton 1993; Viera and Wadia, 1993).

11.7.2 Reaction with Powerful Oxidants

It is well known that ignition is aided by increased ambient oxidant concentration. Small traces of solid oxidant can in some cases cause fuels to ignite at room temperature. A familiar example is a mixture of glycerol with potassium permanganate, which ignites after some delay. Traces of heat transfer salt (containing nitrates) caused liquid dichlorosilane to immediately explode upon contact (Britton 1990a). Liquid oxygen (or air) can be condensed by very cold equipment such as in liquid nitrogen or helium service. This can be a hazard outside the equipment if liquid air condenses and mixes with a combustible material. Inside equipment, a hazard can result from traces of oxygen in an inert stream should this condense out. Strong oxidants in contact with any fuel, including wood and grass, should be evaluated for ignition potential. Recommendations for oxidant storage and handling are given in NFPA 43.

11.7.3 Reactions of Metals with Halocarbons

There have been numerous explosions involving primarily aluminum under high load contact with halocarbons such as refrigerants, solvents and lubricants. However, one must also consider reactions with barium, lithium, magnesium, beryllium and titanium. Schwab (1971) describes a compressor explosion involving aluminum and Freon 12. A minor explosion occurred when an operator tried to screw a seized aluminum bolt, lubricated with "Fluorolube" into an aluminum block; Teflon-type lubricants were considered safe to use (MCA Case History 1449). Metal–halocarbon reactions may be hazardous in themselves or provide sources of ignition.

11.7.4 Thermite Reactions

Mechanical sparks usually have low incendivity except at high impact velocities. Exceptions from common experience include sparks of special materials used as "flints" in gas lighters, where the hot fragments become incandescent upon reaction with air. Another exception occurs when the contacting surfaces react together. The most common of these is reaction between aluminum and oxides such as iron rust or red lead, where the "thermite" reaction may occur. In the classic thermite reaction, aluminum is oxidized and ferric oxide is reduced, releasing a great amount of heat. Analogous reactions can occur in other systems of metals and metal oxides. It is important to recognize that thermite reactions can be hazardous ignition sources even if the metal oxide is present only superficially. The ignition of methane by aluminum alloy–rusty surface impact has been studied by the Bureau of Mines (Desy et al. 1975).

11.7.5 Thermally Unstable Materials

In addition to those materials that can spontaneously ignite in the presence of air, numerous materials may ignite due to inherent thermal or shock instability. Examples include many organic peroxides and explosives. Such materials are beyond the scope of this chapter, since the reactions may be considered quantitative. However, traces of unstable materials with the same general properties may accumulate in some systems and represent sources of ignition.

11.7.6 Accumulation of Unstable Materials

Unstable species may form and accumulate unexpectedly under certain process conditions. The species may be thermally unstable or sensitive to shock. In some cases they may detonate. The most common example is the group known as peroxides (for example as compiled in ASTM 394). The risk of accumulation depends on air ingress (therefore to some degree on the volatility of the liquid involved), and also on the solubility and stability of the peroxide. Of materials that form peroxides, only some are significant hazards. Apart from peroxides' enhancement of monomer polymerization rate, certain peroxides are insoluble in their organic precursors (such as butadiene polyperoxides in butadiene) and may be an explosion hazard upon formation (in the case of butadiene, formation of its highly explosive peroxide is believed to require the presence of aldehydes). Some other peroxides must be concentrated by evaporation and are therefore not normally a storage hazard even if air is present. Other peroxides are too unstable to concentrate. At high oxygen partial pressures, peroxide formation can be rapid. For example, several ignitions have occurred while making up calibration mixtures of aldehydes in air. Ignition occurred as liquid evaporated, possibly with rust catalysis in the cylinders used. The general subject is complex and grouping into "hazard classes" has limited application. A thorough process evaluation may be required for hazard assessment. A monograph on peroxides is given by Medard (1989).

Thomas (1991) theorized a possible cause of a major storage facility fire involving accumulation of an unstable material in a vapor recovery system. The system contained acrylonitrile and methyl methacrylate vapors which had left their less volatile inhibitors behind, enabling polymer formation to occur in the pipework or activated carbon beds. Owing to the excess air present, this polymerization was accompanied by unstable polyperoxide formation. It is theorized that the unstable mass accumulated until spontaneous ignition was possible during carbon bed regeneration. This ignition source then ignited the gas phase in the vapor feed line. Alternative scenarios, such as simple spontaneous ignition of monomer in the carbon bed (or even of the bed itself) also deserve consideration.

Medard (1989) discusses various broad groups of unstable materials. The following require thorough evaluation whenever the precursors may be present:

- In systems containing even traces of acetylene and other alkynes, unstable acetylides can form on metals such as copper or silver.
- In systems containing NO_x or ammonia, various unstable nitrides, amides, imides or nitro-compounds may form.
- In cold boxes, a serious problem has been formation of unstable gums caused by reaction of NO_x with alkenes and dienes, especially those with conjugated double bonds. The problem is compounded by the oxidizing properties and instability of liquified NO_x.
- In the presence of chlorine, hypochlorites, or other chlorinating agent, ammonia and its salts may form the sensitive explosive nitrogen trichloride. These chemicals must be kept apart since they might inadvertently mix in drains or other situations.

A final example is a fire in a nearly empty storage tank believed caused by reaction of monoethanolamine with iron to form the thermally unstable complex trisethanolamino–iron. This thermally unstable material is believed to have accumulated and subsequently decomposed on steam coils in the temperature range 130–160°C (Dixon and Williams 1950). Often, anticipated hazardous reactions of this type are noted on material safety data sheets. NFPA 491M and compilations such as Bretherick (1990) are further resources for identifying hazardous binary reactions.

11.7.7 *Pyrophoric Materials*

A pyrophoric material ignites upon short exposure to air under ordinary atmospheric conditions (author's definition). This definition excludes materials that spontaneously ignite in bulk after long exposure times (such as freshly won coal). It also excludes materials that autoignite at relatively low temperature but greater than ambient temperature (such as carbon disulfide). To be pyrophoric, reaction with air must be fast. Some materials such as metal alkyls, Raney nickel and silane are well-known pyrophoric materials and are handled accordingly. Pyrophoric materials may also accumulate unexpectedly in a system. Examples are iron sulfides and finely divided metals.

Pyrophoric iron sulfides (FeS and Fe_2S_3) may form in anaerobic atmospheres in the presence of hydrogen sulfide. They can produce a hot-spot ignition source upon sudden exposure to air. Finely divided metals such as iron can also ignite upon sudden exposure to air as a result of their large reactive surface area. Ignition of reduced oxides such as ferrous oxide may be possible. Other examples are given by Medard (1989).

It is difficult to create a completely satisfactory definition for "pyrophoric," particularly one which cites some ignition temperature criterion. Britton (1990a) discussed the problem of silane, a pyrophoric gas (whose ignition temperature has been measured as about –100°C) which nevertheless can accumulate at room temperature if it escapes at high velocity. Under such conditions an ignition source such as an electrical spark may cause an explosion. Also discussed was dichlorosilane, which autoignites above 40°C and whose pyrophoricity is moot. Certainly, in neither case would the low autoignition temperature be a safety feature since accumulation of an explosive gas cloud could not be ruled out. The principal significance is that "pyrophoric" materials have no electrical classification, since ignition may occur whether electrical equipment is present or not. Other problems of definition occur with metal alkyl solutions, whose pyrophoricity is determined by solvent evaporation and other factors.

The definition adopted by OSHA 1910.1200 is "a chemical that will ignite spontaneously in air at a temperature of 130°F (54.4°C) or below." The absence of any reference to volume, ignition delay or other test condition means that nonpyrophoric materials such as animal feedstuff (which may spontaneously ignite after long periods of bulk storage) are not excluded. Adoption of OSHA's definition would exclude many hazardous materials from the electrical equipment provisions of the National Electrical Code. Since 130°F is much greater than normal ambient temperatures, materials with ignition temperatures well above ambient could be mistakenly identified as "pyrophoric" and unsuitable electrical equipment provided in the belief that such potential ignition sources are irrelevant. Dichlorosilane (a sensitive gas used in the electronics industry) provides a particularly vivid example, since its explosion is more severe than that of hydrogen (Britton 1990a).

There are situations where many nonpyrophoric materials may autoignite at room temperature or less, and these must be excluded by the definition of "pyrophoric." A survey by the White Oak Weapons Center (Kayser and Boyars 1975) gives a wide selection of materials, from ferrous oxide to fish scraps, that are subject to spontaneous ignition at ordinary temperatures, given the appropriate conditions. These conditions may include the presence of moisture, dispersion in air or on rags, or a large pile of material standing for an extensive period of time (see Section 11.3 for a discussion of autoignition). Hence the Kayser and Boyars survey should be used in conjunction with the original citations given.

11.8 DESIGN ALTERNATIVES

In some cases ignition is predictable and avoidable at the design stage. For example, knowing the ignition characteristics of bulk powder, the container temperature, size, geometry or hold-up time may be designed to avoid spontaneous ignition. To assess such alternatives, it is essential to conduct appropriate material tests prior to design. This can avoid primary reliance on more active control measures such as inertion and flame mitigation.

A common shortcoming in solid-phase systems subject to self-heating is provision of inadequate temperature monitoring. Examples include purification beds, catalyst beds and storage containers. Thermocouples, especially when mounted in heavy thermowells, may fail to respond to exotherms occurring elsewhere in the system. Thermocouples mounted in the gas outlet will tend to average out any exotherm in the solid phase. Large volumes should be monitored by many thermocouples or by commercially available temperature profiling systems. For purification beds such as molecular sieve or activated carbon, special attention should be paid to exothermic activity during and after regeneration and preloading.

NFPA 69 gives recommendations on the following alternatives either to minimize the probability of ignition or to mitigate an ignition event inside equipment:

- reduce oxidant concentration
- reduce combustible concentration
- detect and extinguish sparks
- chemically suppress the incipient flame
- isolate the section of equipment containing the flame event
- construct equipment to contain the flame event

Further alternatives, such as deflagration venting, are described in Chapter 17. It is often important to determine the most probable site for ignition in a system. This might be a fan motor or absorbent bed, for example. The ignition site can determine the severity of any flame event, since in pipes and other equipment of large length-to-diameter ratio, run up to a detonation might occur in the available flame acceleration space. The ignition site can also influence the effectiveness of flame arresters under deflagrative conditions (Chapter 13). In deflagration venting of enclosures, the ignition site influences the amount of unburned material that will be vented ahead of the flame and therefore the severity of explosions external to the equipment (this can be significant especially when the unburned material is vented into a partially confined space).

The information in this chapter, while far from comprehensive, should alert the reader to the wide variety of potential ignition sources. In reactive chemical systems in particular, every effort should be made to identify and evaluate the cause of unexpected observations, such as solid deposits in equipment. Simple observations, such as mild electric shocks experienced by personnel, should be seriously assessed in any area that might contain flammable gas or powder suspensions. Years of uneventful operation usually occur before a hazardous condition is recognized. A major objective is to recognize this condition before it becomes only too obvious. The ideal solution is to recognize and eliminate the potential at the design stage.

11.9 REFERENCES

11.9. 1 Regulations, Codes of Practice and Industry Standards

The editions that were in effect when these *Guidelines* were written are indicated below. Because standards and codes are subject to revision, users are encouraged to apply only the most recent edition.

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11. 9. 2 Specific References

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7

HEAT TRANSFER FLUID SYSTEMS

In 1986 a chemical plant fire occurred in a vaporizer containing a commonly used heat transfer fluid; there was considerable property damage and lost production (Bowman and Perkins 1990). This same fluid has been implicated in hydrocarbon mist explosions (Vincent and Howard 1976). Subsequent investigation of the fire and other vaporizer incidents uncovered pluggages caused by build-up of degradation products. Ironically the pluggage itself may seal off the tube and prevent leakage of the heat transfer fluid before tube rupture occurs.

7.1 INTRODUCTION

Heat transfer fluids have wide application in the chemical, petroleum, and solar energy fields. Their operating temperature range makes them suitable for heat transfer both for heating and cooling over a broader range than is easily attainable with steam or water. Heat transfer fluids are used to optimize heat transfer in a number of applications where high temperatures are required, where temperature variations must be precisely controlled, or where it is essential to prevent water (or steam) from contacting process chemicals. Examples of such processes include reaction vessels for organic chemicals, pharmaceuticals, resins, and plastics; reboilers for regenerating amines and glycol; dies and molds for injecting and extruding plastics, and regeneration gas for solid desiccants; typical industrial users are listed in Table 7-1.

These systems have the potential for great destruction, as they involve the pumping of hot flammable liquids in conjunction with one or more unfavorable factors, such as: the heat transfer fluid is above its flashpoint; systems have large hold-ups and high flow rates; piping and user equipment are located throughout the plant; and piping and user equipment are adjacent to other important equipment or nearby combustibles (FMEC 1992). Although heat transfer fluids provide better heat transfer control than other fluids, leakage (even minor) can have serious results.

This chapter discusses the general design and operating guidelines for heat transfer systems, as well as emphasizing related safety issues, including thermal exposure, loss of containment, and other concerns. Manufacturers' literature should be consulted for final selection and application of heat transfer fluids.

Table 7-1 Typical Industrial Uses of Heat Transfer Fluids[a]

- Pharmaceuticals manufacture reactor heating or cooling
- Petroleum refining
- Chemical process heating/cooling
- Waste heat recovery
- Offshore oil and gas platform heating (used for regeneration of glycol used in moisture scrubbing systems on offshore natural gas processing platform)
- Tanker and barge heating
- Rubber, plastic and paper process heating
- Metal treating: Annealing, stress-relieving welds and castings heaters
- Synthetic fiber production and finishing process heating
- Surface coatings, curing and commercial baking ovens
- Converters: calendering, crimping, hot presses
- Brine liquor concentration and distillation
- Bituminous materials heating
- Alkyd paint and resin kettle heating

[a] Adapted from Monsanto, Publ. 9093

7.2 GENERAL DESCRIPTION OF HEAT TRANSFER FLUIDS

The heat transfer fluids discussed here are intended for indirect heating or cooling of a process stream. The following are typical characteristics of heat transfer fluids:

- The fluids have a high specific heat, high thermal conductivity, low viscosity, and low density, which makes them efficient heat transfer agents.
- The majority of these fluids have a low vapor pressure and high boiling temperature. Thus, they do not require significant pressurization even at their maximum operating temperature.
- At temperatures above their maximum limits, the fluids decompose forming lower and higher boiling point components. Therefore, care must be taken not to expose the fluid film at the heat transfer surface to temperatures higher than the recommended maximum. (Skin temperature is a more important limit for decomposition than bulk temperature.)
- The fluids are chemically and thermally stable within a defined application range. They resist chemical degradation and changes in physical properties at temperatures below their maximum bulk temperature operating limits.
- Degradation by moisture, contact with other process materials, or heat stress may shorten their service life. Some fluids are subject to oxidation when exposed to air atmosphere; silicone-based fluids do not oxidize, but form more volatile components over time at elevated temperatures.

7.2.1 Classification of Heat Transfer Fluids

Heat transfer fluid systems are liquid phase, vapor phase, or both. The liquid phase systems transfer sensible heat without phase change. The vapor–liquid systems transfer latent heat of vaporization via a boiling-condensing cycle characteristic of the applied fluid.

7.2.1.1 Liquid Phase Heat Transfer Fluids (Liquid Systems)

Most commercial heat transfer fluids are hydrocarbons (mainly multi-ring aromatics), although some are silicone-based. Table 7-2 lists typical composition and properties of some commercially available heat transfer fluids. The commercial fluids are classified by operating temperature.

Table 7-2 Commercially Available Heat Transfer Fluids

Fluid and Supplier	Chemical Composition	Temperature Range (°F)		Vapor pressure (psia)^{a}	Pour point (°F)	Flash point (°F)	Fire point (°F)	Autoignition temp.
		Min	Max.					
Chemtherm 550, Coastal	Paraffinic Oil	100	600	2	15	390	430	670
Dowtherm G, Dow	Aryl Ethers	20	700	43	–30	285	295	1083
Dowtherm HT, Dow	Hydrogenated Polyphenyl	25	650	15	–15	355	375	662
Dowtherm LF, Dow	Alkylated Aromatic	–40	650	47	—	240	275	873
Hitec, Coastal	Nitrates, Nitrite	500	1000	—	288^{b}	—	—	—
Mobiltherm 603, Mobil	Paraffinic Oil	100	600	—	25	340	—	670
Multitherm IG-2, Multitherm	Paraffinic Oil	150	600	1	0	440	500	700
Multitherm PG-1, Multitherm	Paraffinic Oil	150	550	15	–40	340	385	980
Syltherm 800 Dow Corning	Alkyl Siloxane Polymer	0	750	197	–40	350	380	725
Syltherm XLT, Dow Corning	Polydimethylsiloxane	-100	500	76	–168	130	148	662
Syntrol 350, Exxon	Diaryl Alkane	0	700	19	–34	380	405	770
Thermalane 550, Coastal	Synthetic Paraffin	0	550	1	–40	430	385	720
Thermalane 600, Coastal	Synthetic Paraffin	0	575	1	–90	464	520	710
Thermalane 800, Coastal	Synthetic Paraffin	0	625	21	–100	445	495	710

Table 7-2 *Continued*

Fluid and Supplier	Chemical Composition	Temperature Range (°F)		Vapor pressure (psia)[a]	Pour point (°F)	Flash point (°F)	Fire point (°F)	Autoignition temp.
		Min	Max.					
Thermalane FG-1, Coastal	Paraffinic Oil	100	550	9	-40	340	385	980
Thermalane L, Coastal	Synthetic Paraffin	-50	500	13	-120	330	360	630
Therminol 55, Monsanto	Alkylated Aromatic	0	600	7	-40	350	410	675
Therminol 59, Monsanto	Alkylated Aromatic	-50	600	15	-90	302	335	770
Therminol 60, Monsanto	Alkyl Polyphenyl	-60	600	22	-90	310	320	835
Therminol 66, Monsanto	Hydrogenated Polyphenyl	15	650	15	-15	350	380	705
Therminol 75, Monsanto	Alkyl Polyphenyls	160	750	19	120[b]	390	440	1000
VAPOR-LIQUID PHASE								
Dowtherm A, Dow	Diphenyl-Diphenyl Oxide	100	750	152	54[b]	255	275	1139
Dowtherm J, Dow	Alkylated Aromatic	-100	600	175	-100	135	155	788
Thermex, Coastal	Diphenyl-Diphenyl Oxide	100	750	155	54[b]	245	260	1180
Therminol LT, Monsanto	Alkylated Aromatic	-100	600	206	-104	134	150	805
Therminol VP-1, Monsanto	Diphenyl-Diphenyl Oxide	100	750	155	54[b]	255	260	1150

[a] Vapor pressures are the maximum of temperature range.
[b] Melting point
Adapted from: Ballard and Manning 1990; additional data from Mol 1992; Dow Corning n.d.; Dow Chemical 1991.

Low- and Medium-Temperature Fluids. Heat transfer fluids are normally used at low pressure and medium temperatures of 150 to 300°C (approximately 300 to 550°F). Many are refined mineral oils. For low temperature applications, calcium chloride brine, methanol and glycol-water are generally used; Dowtherm J and Syltherm can also be used.

Glycol-Water Heat Transfer Fluids. Glycol-water (ethylene glycol or propylene glycol) solutions are widely used for secondary cooling and heating applications in vessel jackets and pipeline tracing systems. The glycol-based fluids cover the temperature range from -50 to 180°C (-60 to 350°F) depending on the type of glycol used, and the inhibitor compounds contained in the glycol (Dow, n.d.). The specially formulated industrial inhibitors included with the glycols help prevent corrosion to the equipment in contact with the fluid. Details regarding the design and operation of glycol–water heat transfer fluid systems can be obtained from the manufacturers of these materials, and only the potential hazards associated with these materials will be discussed further.

Glycol–water mixtures are generally not flammable because they have no measurable flash point in concentrations up to 80 volume percent glycol. However, undiluted glycols have a flash point ranging from 100 to 122°C (214 to 252°F) depending on the type of glycol and the corrosion inhibitor compounds. It is therefore possible to ignite the pure glycol as received from the manufacturer or if the water is vaporized and the concentration of glycol increases to greater than 80 volume percent.

Steel, ductile iron, copper, brass and bronze are generally acceptable for glycol systems. Using dissimilar metals in a system is not recommended because galvanic corrosion may result. The operating temperature of the heat transfer fluid system has a significant effect on the corrosion rate. Glycol heat transfer fluid systems can tolerate brief temperature excursions up to 100°F above the manufacturer's maximum recommended operating temperatures. However, extended exposure of the fluid to temperatures in excess of 50°F above the recommended maximum temperature will result in accelerated degradation of the glycol and inhibitor systems. At temperatures above 65°C (150°F), the system must be closed and preferably inerted with nitrogen to avoid rapid oxidation of the glycol, inhibitor depletion, and subsequent increased corrosion. Corrosion can be especially significant in heat exchangers and copper tubing used for tracing, resulting in loss of containment of the fluid.

Ethylene glycol and propylene glycol differ in viscosity and toxicity. Ethylene glycol-based fluids are less viscous than propylene glycol-based fluids, and, therefore, provide better heat transfer efficiency and better low temperature performance. However, in applications where toxicity is a concern, propylene glycol fluids should be used due to their low acute oral toxicity versus the moderate toxicity of ethylene glycol. An example would be food processing applications. Also, spills of one pound or more of ethylene glycol currently require reporting to the Environmental Protection Agency (EPA) under the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA). Both glycols are biodegradable and should not concentrate in common water systems. The possibility of spills into lakes or rivers should be avoided, since rapid oxygen depletion may have harmful effects on aquatic organisms.

Examples of other low temperature fluids are the fluorinated hydrocarbons, ammonia, ethylene and propylene. These fluids, commonly called refrigerants, are not covered in this chapter.

High Temperature Fluids. Several different kinds of fluids are used at both low and high pressure, and at temperatures between 275 and 375°C (550 and 700°F), although applications above 330°C (630°F) are rare. Some of the major fluids are: synthetic paraffin, diaryl alkane, polyphenyl derivatives, aryl ethers, and dimethyl siloxane polymer; dimethyl siloxane polymer is often used under high pressure.

For high-temperature applications, inorganic salts are an alternative. One type is a mixture of sodium nitrate, potassium nitrite, and sodium nitrite. Inorganic salt mixtures differ from organic liquids in that they are nonflammable, have no appreciable vapor pressure and are thermally stable up to 538°C (1000°F), which is about 300°F above the temperature limits of the other fluids. Minimum temperature at which salt mixtures are typically molten is 200°C (400°F). The main problem with salt mixtures is corrosivity. Since they are infrequently used, they are not discussed further in these *Guidelines*. Refer to Singh's book (1985) for further information on inorganic salts.

7.2.1.2 *Vapor Phase–Liquid Phase Heat Transfer Fluids (Vapor–Liquid Systems)*

These systems transfer heat with heat of vaporization. The alkylated aromatics are essentially pure compounds that can be used at very low temperatures close to their respective freezing points. Other vapor–liquid systems include eutectic mixtures of diphenyl and diphenyl oxide, which are fairly stable up to 400°C (750°F). Vapor phase–liquid phase fluids can also be used in liquid systems, but pressurization is needed above the normal boiling points.

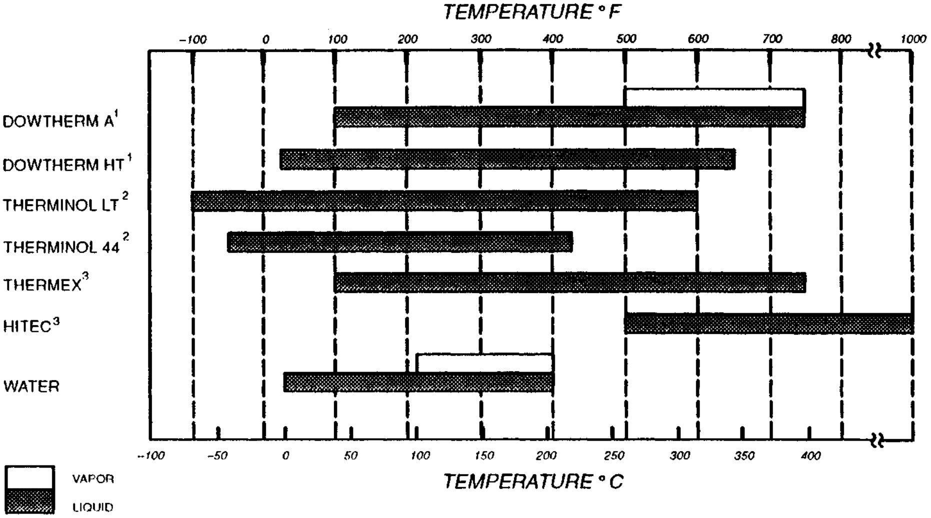
7.2.2 *Comparison of Heat Transfer Fluids with Other Heating Media*

7.2.2.1 *Advantages of Steam Heating Media*

Steam heating media are generally used when the required temperature is consistent with normally available process steam. For temperature ranges common to heat transfer fluids, steam is frequently more economical and has the advantages of having high latent heat, no flammability, no toxicity and no sludge formation. Operating ranges of several heat transfer fluids are compared to water in Figure 7-1.

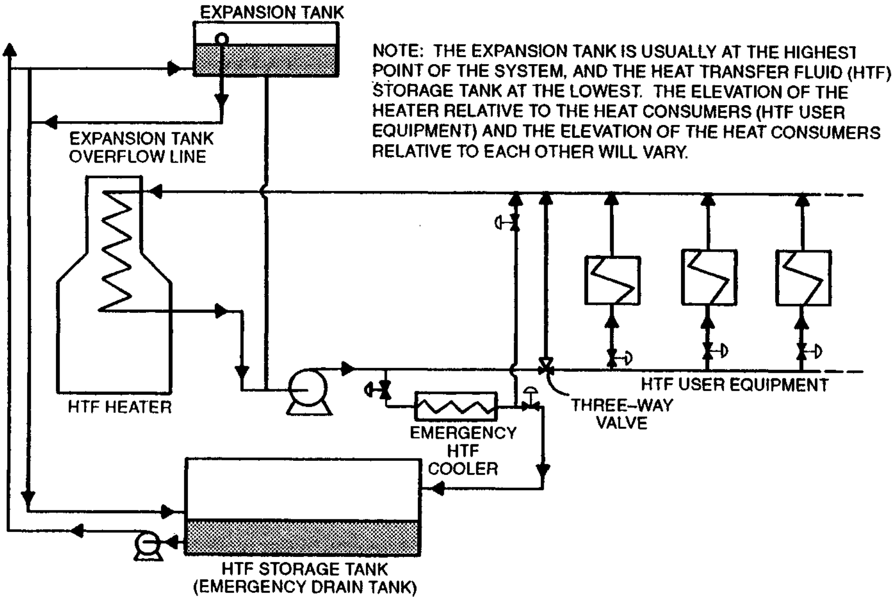
7.2.2.2 *Advantages of Heat Transfer Fluid Systems*

These systems can be used at higher temperatures than steam or hot water (Figure 7-2). Heating via heat transfer systems avoids hot spots which may develop in fired heaters. The heat transfer fluid generally is heated in a fired furnace. This heating can be accomplished at a more remote and safer location than with a fired heater used to heat the process stream directly. In batch systems, where both heating and cooling are required, these systems offer temperature control and flexibility of operation beyond that of steam.



NOTES: 1 = REGISTERED TRADEMARK OF DOW CORNING CORP.
2 = REGISTERED TRADEMARK OF MONSANTO COMPANY
3 = REGISTERED TRADEMARK OF COASTAL CHEMICAL COMPANY

Figure 7-1. Operating temperature ranges for heat transfer fluids compared to water. (Based on data from Ballard and Manning 1990, Dow 1991, Mol 1992, Monsanto n.d.)



NOTE: THE EXPANSION TANK IS USUALLY AT THE HIGHEST POINT OF THE SYSTEM, AND THE HEAT TRANSFER FLUID (HTF) STORAGE TANK AT THE LOWEST. THE ELEVATION OF THE HEATER RELATIVE TO THE HEAT CONSUMERS (HTF USER EQUIPMENT) AND THE ELEVATION OF THE HEAT CONSUMERS RELATIVE TO EACH OTHER WILL VARY.

Figure 7-2. Typical liquid phase heating scheme for heat transfer fluid (HTF) system. (FMEC 1992)

Advantages of Liquid Phase Systems. Liquid phase systems may be considered where a high pressure system (e.g., steam) is undesirable or for common heating applications where other media are unavailable. Liquid phase systems should be considered when service requires accurate process temperature controls in heating service, uniform heat delivery, and quick response to heating or cooling demands. This is particularly important for heat-sensitive process materials.

Following are some of the advantages of liquid phase systems over conventional steam media and the vapor–liquid systems:

- Because there is no phase change in liquid phase fluids application, problems associated with conventional steam condensate handling are eliminated (that is, there is no need for condensate traps, a collection system, etc.). This factor becomes important when multiple users are operating from the same supply and return headers but at different operating temperatures.
- One liquid phase system may be used for both heating and cooling purposes, thus providing a means of indirectly transferring heat between hot and cold process services.
- The liquid phase fluid maintains the same temperature throughout an adequately insulated supply line. Pressure variation (drop) does not significantly affect the temperature of the fluid as would occur with a vapor system.
- Provided that the fluid is not subjected to excessively high temperatures and no decomposition occurs, minimum venting is required.
- Liquid phase fluids operate at low pressure and thus avoid costly high pressure piping and equipment required by high pressure steam systems.
- The heat transfer coefficient can be maintained high by controlling the velocity of the fluid over the heat transfer surfaces. Liquid phase fluids may impact the system size, by eliminating large diameter vapor lines, vents, flash drums, and control devices typically used with steam as the heating medium.

Advantages of Vapor Phase–Liquid Phase Systems. Following are some of the advantages of vapor phase–liquid phase heat transfer systems over the liquid phase systems:

- The vapor phase provides much more heat transfer capability per pound of fluid than the liquid phase.
- No pumps are needed when a gravity return condensate system is used with natural circulation (thermosiphon) circuits.
- The vapor phase system requires less inventory of fluid since the supply line is filled with vapor rather than liquid.

7.2.2.3 *Disadvantages of Heat Transfer Fluid Systems*

Heat transfer fluids have been limited in application primarily due to the following reasons:

- The fluids frequently operate near or above the flash point or fire point. Some are capable of operating above their autoignition temperature. This makes them a significant fire hazard; therefore, precautions against ignition sources or fire must be of utmost concern.
- Decomposition products from some of the aromatic fluids, e.g., substituted benzene and diphenyls, contain benzene and benzene derivatives or other hazardous compounds.
- Thermal degradation reduces heat transfer efficiency and the service life of the fluid. The degradation of the fluid may cause system fouling and increase maintenance and downtime.
- Fluid pumpability (high viscosity) problems exist for some fluids at the lower end of the operating temperature range (typically 2° [35°]). This is especially troublesome during startup of the system at low ambient temperatures. The system may require costly heat tracing to maintain temperatures sufficient for good pumping rates.
- Heat transfer fluids may cause severe burns and eye, skin, and respiratory tract irritations. Care must be taken to minimize worker exposure to the fluid.

7.3 SYSTEM DESIGN CONSIDERATIONS

Design of the heat transfer fluid system is determined by process design, for example batch versus continuous process; philosophy of process control, etc. Temperature ranges, peak temperature, and peak loads are factors influencing choice of heat transfer fluid. Available steam or other utility temperature should be considered. Prevention of leaks and temperature regulation are critical design criteria. Other factors are included in the list in Table 7-3. Manufacturer's literature should be consulted for final application of heat transfer fluids.

7.3.1 *Instrumentation and Controls*

Instrumentation and controls applicable to heat transfer fluids systems are comparable to conventional process control systems. Most instrument systems are intended to control the heating or cooling mechanism at both the heater or vaporizer and the energy using units. The heater controls are required to regulate the firing in proportion to either the fluid flow or the outlet temperature. In certain situations the controls are simplified to an

Table 7-3 Factors in Design of Heat Transfer Fluid Systems

- Batch process or continuous operation
- Temperature ranges and peak temperature
- Available steam or other utility
- Process control
- Auxiliary equipment sizes
- Safety review of the process (Hazard and Operability Study)
- Peak load requirements
- Turndown requirement particularly if some uses are nonroutine or intermittent
- Loss of heat from the piping configuration at ambient temperature
- Requirements for future expansion
- Personnel, property and environmental protection controls
- Choices of fluids or manufacturers
- Manufacturer's literature

on-off or high-low mechanism depending upon the degree of accuracy required by the process. However, since the most critical variable in the operation of the heat transfer fluid is temperature, it is generally recommended that units be equipped with modulating temperature controllers. Proper energy delivery is further achieved by installing individual temperature controls at each user. Manufacturer's literature should also be consulted.

7.3.2 Materials of Construction

The designer should refer to materials engineering specialists and heat transfer fluid manufacturers. The materials of construction are generally selected on the basis of their compatibility with the fluid and the system operating pressure and temperature ranges.

Manufacturers' literature on the heat transfer fluids typically recommend the use of mild carbon steel throughout the system, but materials must have brittle-ductile properties to be suitable for low temperatures where appropriate. The use of aluminum, bronze and brass alloys should be kept to a minimum, because of their lower mechanical strength at higher temperatures. Copper and copper alloys should not be used in heat transfer systems with a hydrocarbon fluid unless air is excluded (FMEC 1992). Nonmetallic materials such as plastics and elastomers are not recommended for this service other than as packing or seals within material temperature limitations. Austenitic stainless steel, 300 Series, should not be used where fluids may contain trace chlorides and/or where water contamination is likely or normal. Refer to discussion of the individual components (Section 7.4) for more specific materials requirements.

7.3.3 Monitoring, Analysis, and Replacement of Fluid

As the fluid degrades, generally flash point, fire point and autoignition temperature of the fluid decrease; this increases the hazard. As discussed by Ballard and Manning (1990) regular analysis of the fluid is important. One manufacturer recommends the analyses listed in Table 7-4 be run quarterly during the first year and semi-annually thereafter. For other heat transfer fluids, consult the manufacturer for specific analysis. Automatic sampling devices should be considered. To establish a degradation curve for each specific system, testing is conducted more frequently at first. Essentially, fluid changeout must be determined on a case by case basis. Continued operation with degraded fluid can be disastrous, for example, irreparable fouling of the heat transfer surfaces. On the other hand, discarding usable fluid is wasteful. Knowing how fast the heater performance is deteriorating and the extent of the fluid degradation are key factors in deciding when to change the fluid.

Table 7-4 Analysis of Heat Transfer Fluids[a]

Viscosity increases impair the heat-transfer and flow properties of the fluid while viscosity decreases improve the heat-transfer and flow performance. A viscosity increase warns that there are high boilers in the fluid and a decrease in viscosity denotes the presence of low boilers; viscosity measurements can therefore indicate fluid degradation. The viscosities of polyphenyl fluids and mineral oils increase while those of synthetic paraffins decrease.

Total acid number indicates the extent to which the fluid has hydrolyzed and/or oxidized into acids. Values up to 4.0 mg potassium hydroxide (KOH) per gram of fluid are acceptable for paraffins. For polyphenyls, which form more corrosive acids, 1.0 mg KOH per gram may be too high.

Acetone insolubles measure the amount of char (carbon) and solids in the fluid as well as any scale loosened from the heat transfer surfaces. The suggested upper limit to avoid erosion problems is 50 mg/100 mL of fluid.

Water contributes to the low boilers. It also indicates the susceptibility for further acid formation in the fluid. A safe limit for synthetic paraffins is 2,000 ppm. Using aromatic fluids with water content above 400 ppm is not recommended.

Low boilers indicate fluid degradation. Values above 5% indicate that it is time to check the flash, fire, and autoignition temperatures. Some fluids operate satisfactorily with up to 15% low boilers.

High boilers also indicate fluid degradation, especially the amount of sludge present. The danger level for forming coke deposits is above 10%.

Flammability. Flash, fire, and autoignition temperatures all decrease with use. Some companies establish minimum levels when the fluid must be replaced. Usually there are no significant decreases until the low boiler content reaches 10%.

[a] Ballard and Manning 1990

7.3.4 Deinventorying the System

No matter how long the system is designed to operate, it will have to be deinventoried (emptied) and hydrocarbon freed (cleaned) occasionally for normal maintenance and inspection. The system should be designed so that the "normal" equipment, especially circulating pumps, can also be used for deinventorying. However, some components of the system, notably filters and the circulating pumps, will have to be deinventoried more frequently, while the balance of the system continues to operate. These pieces of equipment may require special considerations for emptying and cleaning, in addition to those which apply to the entire system.

When emptying "normal" items of equipment, it is common to have a source of compatible vapor at a high enough pressure to be able to "blow" the liquid inventory to a suitable point in the system. As most of these systems are liquid systems, there will be no vapor available for this purpose. In fact, even the liquid–vapor systems may be designed to run normally at such a low pressure that the vapor may not be at sufficiently high pressure to allow it to be used as a motive force to deinventory. In this case, an extraneous pressured vapor (usually nitrogen) will have to be made available to blow liquid inventory from these items. Steam is also a possibility, but, depending on where the liquid is to be blown, it may be a bad choice, resulting in contamination of inventory with condensed steam.

Assuming nitrogen is to be used, these "normal" items of equipment (pumps and filters, including any piping components within the isolation valves) should have a design pressure specified which is compatible with the design pressure of the nitrogen (or other pressuring gas) system. Additionally, the "sink" for the liquid (usually the expansion tank, possibly the inventory tank) should have sufficient vapor venting capacity to vent the maximum rate of pressuring gas that the system will allow, as it would be normal to blow the vapor through the system (to deinventory the drain line also).

Deinventorying should be performed as soon as the item is taken off line (while hot) to allow the maximum recovery of these relatively expensive fluids. After blowing out, the system should be isolated from the pressuring gas and vented to a suitable low pressure destination for "steam-out" of the equipment. Steam is the usual fluid of choice for this operation as even low pressure steam headers in a plant usually have a significant amount of superheat which is necessary for complete hydrocarbon removal. The very low vapor pressure of these heat transfer fluids at ambient temperature would make a "cold" purge (e.g., with nitrogen) expensive and time consuming.

7.3.5 Insulation

Nonabsorbent insulation should be selected and applied after leakage and pressure tests have been completed. Where leaks are likely to occur, use either no insulation, nonabsorbing insulation, a spray shield, or insulation treated to prevent penetration by heat transfer fluids.

7.3.6 Shielding

To help prevent a spray release, shielding should be provided around seals, flanges, valve packing and other potential leakage points. If these points are insulated, a metal covering should be used over the insulation. The low points should be provided with drain holes.

7.4 HEAT TRANSFER FLUID SYSTEM COMPONENTS

7.4.1 Liquid Phase System Components

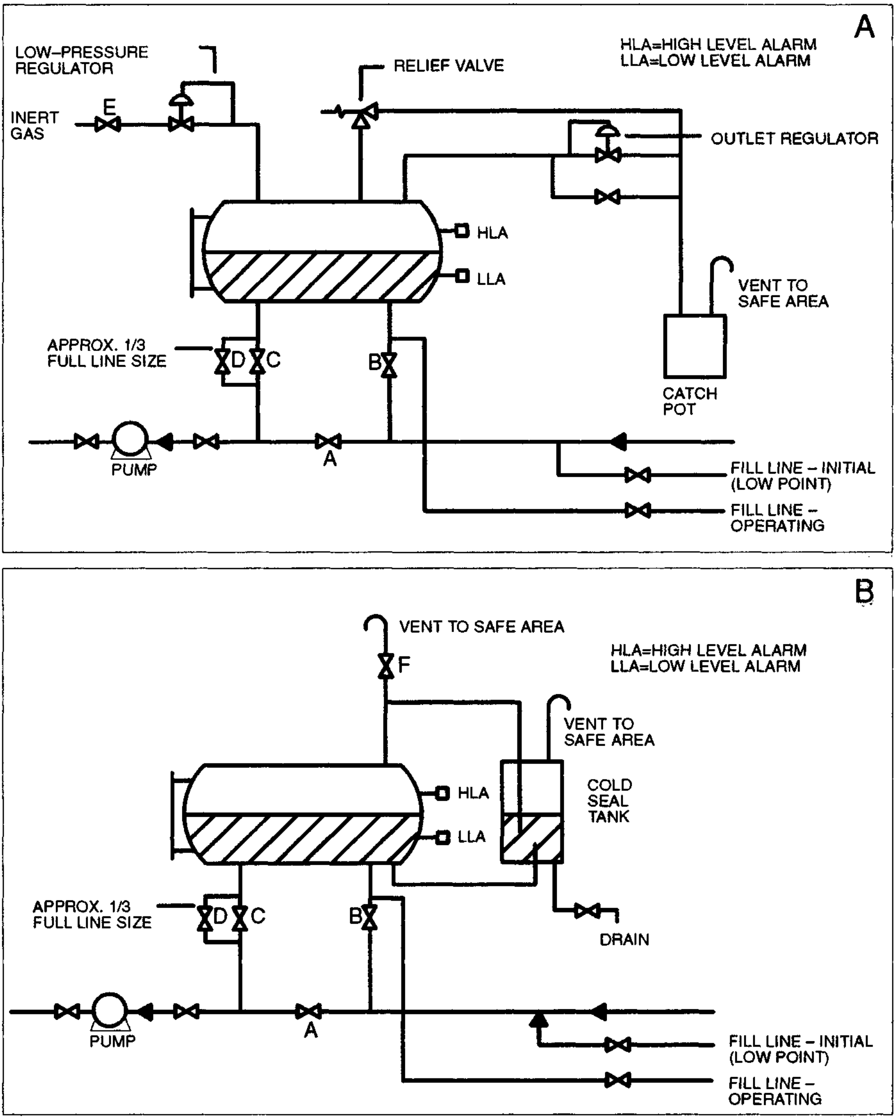
The major components of a liquid phase system are heaters, pumps, expansion tanks, filters, piping system, and valves. Figure 7-3 shows a typical expansion tank.

7.4.1.1 Heater

The heater must be designed to provide a consistent temperature to all users without degrading the quality of the heat transfer fluid by exposure to excessive temperature. The heater can be either electrical (for small units only) or fuel fired. Normally, the heat transfer fluid should be at sufficient velocities over the heating surfaces so that no area of the fluid is subject to hot spots caused by stagnation. This can be accomplished by ensuring turbulent flow over the heating surface to avoid excessive film temperatures that may be detrimental to both the heat transfer surfaces and the fluids. Attention to the safe control and operation of the heater is critical. Since heating in a fired heater is not uniform, the maximum heat fluid conditions must be used in evaluating what film temperatures will be encountered.

7.4.1.2 Pumps

The pumps and fluid handling piping must be designed with sufficient pressure head and flowrate capacity to maintain the required heat transfer rate at all downstream users and ensure adequate system circulation. Most heat transfer fluid vendors advise that pumps must conform to ANSI B73.1 or to API Standard 610, which are both suitable for high temperature service. Sealless pumps are now generally used for this service. Magnetic drive pumps have no seal around the driver shaft and therefore avoid seal leakage problems, but bearing failure can cause the "can" to rupture. Care must be taken to ensure that flashing of the fluid does not occur at the bearing, causing cavitation. Manufacturers also recommend the use of fluid-cooled bearings



NOTE: FOR STARTUP OR VENTING OPERATIONS, VALVES B, C, D AND F ARE OPENED. VALVE A CAN BE THROTTLED TO ASSUME FLUID FLOW THROUGH THE EXPANSION TANK. VALVE E SHOULD BE THROTTLED TO LIMIT THE INERT GAS FLOW THROUGH THE EXPANSION TANK.

FOR NORMAL OPERATION, VALVES B, C AND F ARE CLOSED, AND VALVES A, D, AND E ARE OPEN. THIS ARRANGEMENT PROVIDES NORMAL RETURN FLOW TO PUMP SUCTION WITH AN OPEN STATIC HEAD LINE FROM TANK TO PUMP. BYPASS LINE THROUGH VALVE D MINIMIZES THERMAL SIPHON TO EXPANSION TANK.

Figure 7-3. Typical expansion tank. (A) Suggested inert gas arrangement for expansion tank. (B) Suggested cold seal trap arrangement for expansion tank. (Monsanto, Publ. 9128, ed. A) and seals to extend the service life of the pumps and tandem seals. Mechanical seals or ring-shaped flexible graphite packing gives the best service for pumps. Installation of a temporary strainer at the suction to the pump is recommended for start-up and a drip pan below the pump is recommended. The fluid collected in the pan should not be returned to the system unless analyzed. Adding oxidized, corrosive, or contaminated fluid can be dangerous (see Section 7.3.3, Monitoring, Analysis, and Replacement of Fluid).

7.4.1.3 *Expansion Tank*

The expansion tank must be designed to provide adequate space for heat transfer fluid expansion at maximum operating temperatures, to vent moisture and low boiling components (decomposition products), and to provide sufficient positive suction head for the pump. Because of these requirements, expansion tanks are usually, but not necessarily, installed at the highest point in the system. Most manufacturers recommend the use of double drop leg piping arrangement from the bottom of the tank to the pump (Figure 7-3); this provides uninterrupted flow of fluid and improves the venting capability of the system (Monsanto, Publ. 9093).

Depending on the type of fluid, the expansion tank should be sized for one-fourth full capacity at ambient temperatures and three-fourths full at maximum operating system temperature. Expansion volume needs to take into account the full system volume, including exchangers, piping, and other equipment volumes. Some fluids expand 30% or more from ambient temperature to an operating temperature of 288°C (550°F). A level control device should be provided to allow the operator to monitor the tank level and shut off the heater at minimum level. The expansion tank must also be closed at the top to avoid contamination with air and moisture which cause fluid degradation. An inert gas (nitrogen) blanket or sweep gas can be used to prevent potential contamination. The tank must also be provided with a pressure relief device. Vents from the tank must be routed to a safe location or to a pressure relief header. Secondary containment should be provided by diking or other arrangement.

7.4.1.4 *Filters*

Filter manufacturers can be contacted to determine whether filtering will remove solid particles such as scale or the very fine solids (such as coke and sludge) formed when fluids degrade. Changeout of the filters is difficult, since the filter cartridges contain hot fluid, which usually has a disagreeable odor and may be toxic. However, strainers may be temporarily installed at the pump suction to remove debris typically associated with initial startups. A side stream filter to remove impurities, scale or corrosion products generated during normal operation may be considered, but it in turn creates additional safety issues, particularly when deinventorying the system.

7.4.1.5 *Piping System*

As with every hydraulic system in process service, the piping system must be designed to provide the normal flow rate at the most economical pressure drop. Because the system undergoes temperature changes, adequate flexibility must be built into the design of the piping to relieve thermal expansion and contraction stresses (Magner 1988).

Because these fluids are flammable, it is critical to avoid leaks. Welded pipe connections are preferred throughout. Heat transfer fluids tend to leak through joints and fittings (due to very low viscosity and surface tension at operating temperatures) and soak the insulation; this can present a fire hazard (see Chapter 8). Flanged joints should be held to a minimum, and in some cases be left uninsulated. Where access is necessary, raised-face flanges with weldneck joints are often recommended. Insulation that resists saturation (closed cell type) should be used to reduce spontaneous ignition.

Spiral-wound type flange gaskets are often used for high temperature heat transfer fluids (Fuhr 1992); properly installed, these leak less than other gaskets. Standard materials of construction for these gaskets are 304 stainless steel with flexible graphite filler.

7.4.1.6 *Valves*

A designer generally refers to specialists for selection of the valves in this service. The following are some guidelines which must be confirmed before final selection:

- Valve materials should be cast or forged steel with 13-chrome trim.
- Globe valves should have outside screws for tight sealing of fluids.
- Gate valves are acceptable and preferred, but must not be relied upon to provide tight shutoff.
- To minimize leaking, use of metal reinforced stem seals is recommended. Generally, a minimum of five rings of packing with spring loading is specified on valve stems to assure a reasonable seal.
- Temperature limitations of nonmetallic seat and seal materials generally restrict valve selection.
- Installation should be with stems in horizontal position so any leaking fluid will drain away from the insulation.

7.4.2 Vapor Phase–Liquid Phase System Components

Because the properties of a vapor–liquid system differ from those of a single phase (liquid) system, the components differ slightly. Figure 7-4 shows a typical vapor–liquid fluid heating system.

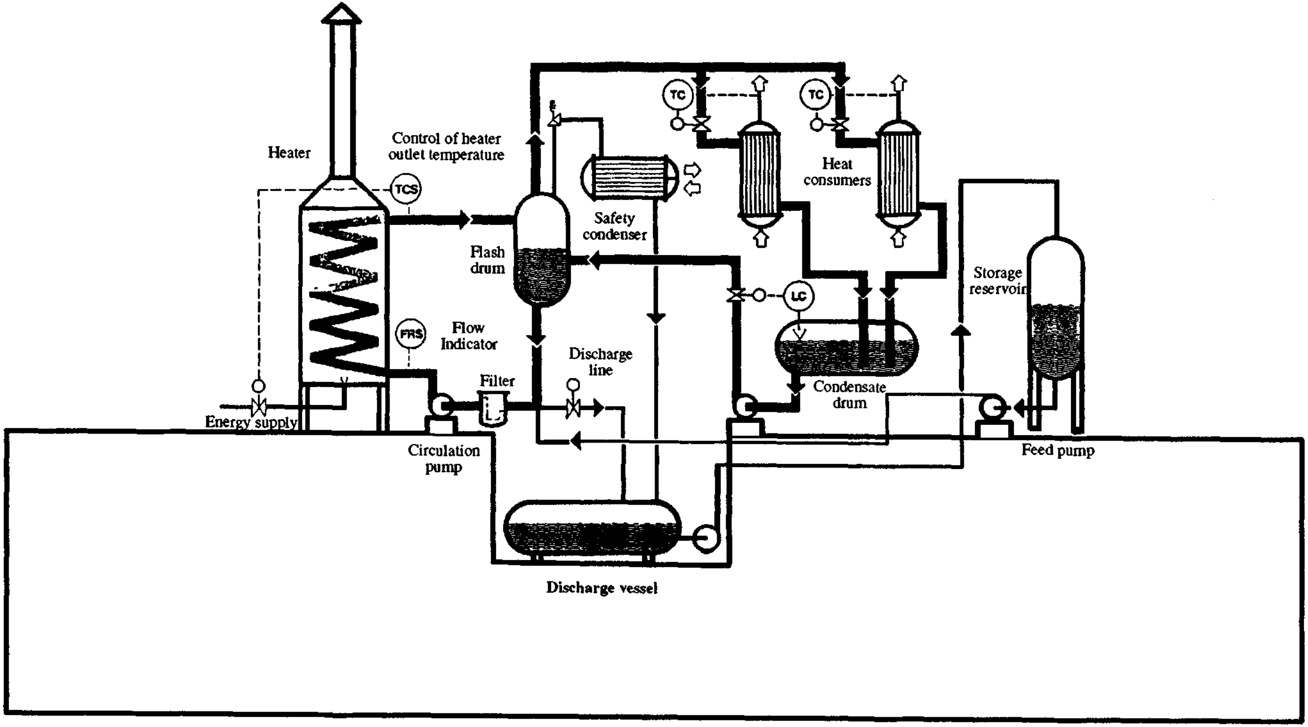


Figure 7-4. Heat transfer system using the heat-transfer medium in the vapor phase.

7.4.2.1 Vaporizer (Heater)

The vaporizer must provide a consistent temperature to all users without degrading the quality of the heat transfer fluid. The vaporizer can be either electrical or fuel fired, although electrical vaporizers are generally used only for very small systems. Since these fluids have a tendency to decompose at high temperatures, the heat transfer fluid velocities through the vaporizer should be sufficiently high to ensure turbulent flow and thus minimize boundary layer effects and film temperatures. To provide these high circulation rates, some manufacturers of heat transfer fluids recommend using a forced-draft circulation heater (pumparound loop) and flash tank; others recommend the use of low flow alarms.

Fluid vapor pressure is a good measure of fluid purity or contamination by low boiling components. The vaporizer instrumentation should include both pressure and temperature measurement devices. Any discrepancy in temperature or pressure, compared to the expected vapor pressure for the fluid, is an indication that the fluid contains contaminants or decomposition products.

Degradation of the heat transfer fluid occurs at high temperatures. The presence of water, rust or oxygen may accelerate degradation. The degradation products are low and high boilers and solid carbon.

Low boilers (for example, water and benzene) are compounds that boil at a lower temperature than the heat transfer fluid. Low boilers usually pass through the vaporizer rapidly without affecting its pressure–temperature relationship. They collect at high points of the heat exchanger system and in the vapor space of condensate receivers. Problems result from condensation and refluxing of low boiler constituents in dead-end (no flow) high points of the system. Low boilers such as chlorine (and perhaps phenols) are corrosive to pipe walls. Corrosion may result in pipe failure and leakage of hot heat transfer fluids into the insulation. This in turn may lead to:

- Autoignition of the vapor-soaked insulation.
- Formation of plume and potential fire, if the flow breaks through the insulation and the condensing plume reaches an ignition source.
- Soaked insulation and potential fire hazard when the vapor condenses in the insulation.
- Blocked safety valve nozzles. The low boilers (particles composed mostly of carbon and iron rust) accumulate at the dead-end nozzles at the tops of vessels and eventually plug the safety valve inlets.

Recommended remedial actions are to remove as many of the low boilers as possible by venting them from the system continuously or at frequent intervals and to inspect vessels in this service as needed to assure safety valve nozzles are unrestricted.

High boilers are higher molecular weight compounds that boil at higher temperatures than the heat transfer fluid. They are normally retained in the fluid in the vaporizer, although there is some sublimation into the vapor distribution system. Since the fluid is exposed to its highest temperature within the vaporizer, the high boilers are generated and concentrate in it. As the concentration of the high boilers increases, the degradation rate of the heat transfer fluid also increases. The viscosity of the high boilers is usually greater than that of the standard fluid.

The heat transfer coefficient in the vaporizer is adversely affected by the physical properties of the high boilers, especially their higher viscosity. These circumstances can lead to further localized degradation of the high boiler–fluid mixture into solid carbon on the vaporizer tubes, which impedes circulation and further aggravates the degradation cycle.

7.4.2.2 *Reboilers*

Reboilers, heated by primary heat transfer vapor from the flash tank, are an alternative to using self-contained, electrically heated vaporizers. These units are normally of the shell and tube design: process fluid to be reboiled on the tube side and condensing heat transfer fluid vapor on shell side.

7.4.2.3 *Pumps*

Heavy-duty cast steel centrifugal pumps constructed in accordance with American Petroleum Institute (API) standards are recommended for the vapor phase system. Some vendors provide pumps in condensate service with a water-cooled stuffing box. In addition, for operation over 260°C (500°F), pumps should also be equipped with water-cooled bearings. Reciprocating pumps are generally not suitable. These pumps should not be of the positive displacement type; one option is the sealless type previously discussed. Vacuum pumps should be positive displacement types with liquid seal.

7.4.2.4 *Pipes and Gaskets*

The vapor–liquid systems are susceptible to leakage. Therefore, the piping system as well as all other equipment and components require unusually high criteria for proper sealing.

7.4.2.5 *Auxiliary Equipment*

Charge System. A charge system has three functions: to introduce the initial charge of heat transfer fluid, to supply make-up fluid to heating loops, and to provide storage capacity for fresh charges. A charge system can be common to more than one vaporizer or reboiler loop.

Drain System. A dedicated vessel should be provided to receive fluids drained during maintenance of heat transfer fluid loops. Draining is normally carried out by pressurizing the equipment with inert gas. Connection options for proper disposal or recycle of drained fluids should be addressed.

Vacuum System. A vacuum system has four functions: to evacuate the heating system before startup, to collect noncondensables during operation, to empty individual users prior to maintenance, and to take off any excess fluid from a heating loop that is overcharged. The vacuum header should be sloped toward the condenser so any liquid that collects at low points will drain off.

7.5 SAFETY ISSUES

The primary consideration is to make sure the system is tight to prevent leaks that could cause ignition and fire. Many heat transfer fluids autoignite in air. The potential for autoignition is increased by the high process temperatures and lower autoignition temperature of the fluid selected. Spontaneous ignition can occur if combustible heat transfer fluids are absorbed into hot, porous insulation (Britton 1991; Green and Dressel 1989). Leakage of the system may result in vapor and mist explosions or insulation fires. Even a well-designed system may leak (Vincent and Howard 1976). Vapor leaks may form a fog of combustible liquid; combustion of the fog–air mixture can result in an explosion; this possibility should not be ignored, no matter how remote.

A leak detection device has recently been developed ("Monitoring" 1992) that uses photoionization-detection technology. This hand-held analyzer may be used to check for leaks around valves, pumps, gasketed flanges, or sightglasses.

A common cause of fire following release of heat transfer fluid is an improperly located discharge outlet from a safety valve or breather vent (FMEC 1992). These components frequently discharge directly into plant areas. In another study of accident protection in heat transfer fluid systems, Albrecht and Seifert (1969) found that many fires involving heat transfer fluids result from tube failure, followed by leaking of fluid into the heater firebox. Tube failure is generally attributed to coking or mechanical failure. In the incident described at the beginning of this chapter, and illustrated in Figure 7-5, Bowman and Perkins (1990) concluded that fluid degradation resulted in carbon formation that plugged the tubes.

7.5.1 Fire Protection

Fire protection is critical due to the hazardous nature of the fluids. Chapter 16, Fire Protection, includes general fire protection considerations. Heat transfer fluids manufacturers recommend the following general guidelines:

- Fired heaters and equipment should adhere to the spacing guidelines set forth by and included in Chapter 3 of these *Guidelines* as Tables 3-7, 3-8, and 3-9).

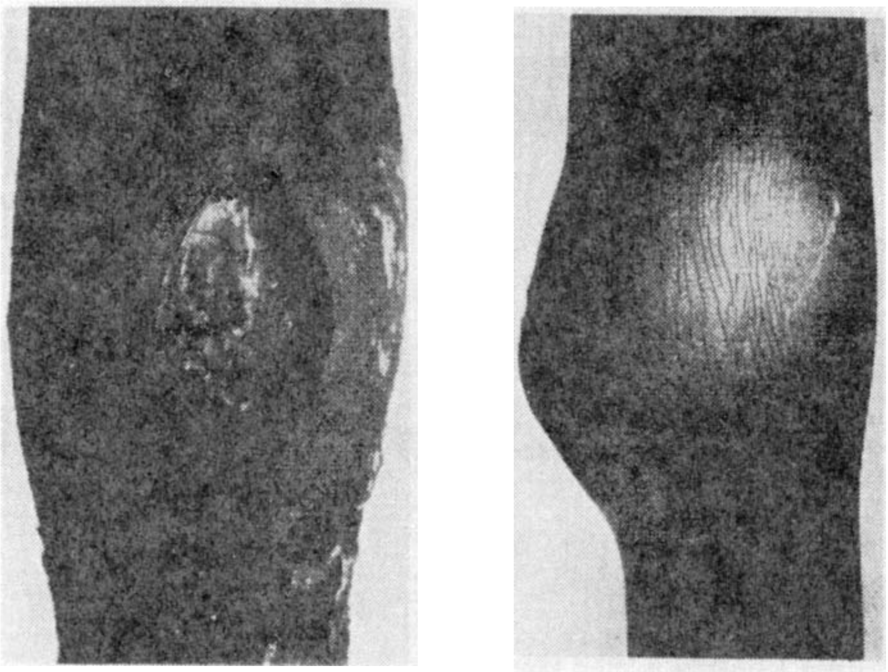


Figure 7-5. Views of failed tube showing bulging and plug.

- Heat transfer equipment should not be installed in closed structures. If installed in closed structures, explosion- (deflagration-) relief panels and ventilation should be considered (see Chapter 17).
- Automatic and remotely operated valves and pump shutoffs should be used to prevent the possibility of feeding the fire in case of a tube rupture or break in the distribution piping.
- Automatic sprinklers should be considered for part of the system, typically for expansion tank, vaporizer, pumps (if with a mechanical seal) and sometimes the heater.
- For fired heaters:
  - —Provide automatic sprinkler protection and supplemental fire hydrants or hose connections.
  - —Provide Class B fire extinguishers.
  - —Slope grade so spills or leaks are routed away from equipment.
  - —Provide facilities for extinguishing a fire in the fire box (usually steam snuffing or water spray) (Vincent and Howard 1976, Vincent et al 1976). Include fire detection (high stack temperature).
  - —Provide remote operation of valves on key equipment, with manual backup of automated controls.

—Electrical equipment should be designed to prevent ingress of heat transfer fluid mist and vapors.
—Provide adequate firefighting foam capabilities to handle the largest anticipated heat transfer fluid liquid spill fire.
—Specifically for a vaporizer, the area should be protected by an automatic fire suppression system, such as an automatic deluge sprinkler system.
—Exposed cable trays, control equipment, pipelines, etc., should be protected by fire-resistant insulation, rated for a minimum of two hours, or automatic water spray.

7.5.2 Thermal Insulation

As discussed earlier, leakage of heat transfer fluids from joints and fittings may soak insulation layers and increase the hazards of fire at the temperatures normally encountered in these systems. Material that reduces this hazard should be selected (see Chapter 8). Cellular glass resists saturation due to its closed-cell nature. To ensure leak-free piping and reduce the risk of fire, fabrication, installation and maintenance procedures include:

- Minimizing the number of flanges and mechanical joints.
- Using manufacturer's or code recommended piping specifications.
- Installing valve stems horizontally or in downward position so that leaking fluid will not enter the insulation.
- Removing the insulation if a leak develops and containing the fluid until the leak is repaired.
- Using cellular glass or metal-shielded insulation on sections of lines where leaks are more likely to occur (where control valves or instrument fittings are attached).

7.5.3 Fluid Degradation

At high temperatures, heat transfer fluid degrades, forming low and high boilers and solid carbon. Fluid degradation occurs by high temperature, by oxidation, and by the presence of water and/or rust. The solid particulates, composed mostly of carbon, accumulate in the upper vapor space of the condensate receivers, blocking the safety valve nozzles (Bowman and Perkins 1990). The low boilers may be vented from the system continuously or at frequent intervals; inspection may be needed more frequently in this service.

Degradation of the fluid in the vaporizer may lead to formation and deposit of carbon on the tube wall. Bowman and Perkins (1990) report full pluggage of tubes in the vaporizer furnace: "In most cases, the pluggage has resulted in a rupture of the tube. However the pluggage itself has sealed off the tube on both ends of the rupture and prevented . . . leakage" of the heat transfer fluid. Operating procedures may need to specifically prohibit service conditions that encourage fluid degradation.

7.5.4 Monitoring and Control Features

Personnel and plant safety should be the primary concern in the design and operation of any process unit. Several features must be built into the design to assure proper response under any emergency, including the automatic activation of controls or prompt operator intervention. Heat transfer fluid manufacturers can provide additional guidance on proper safety controls. The following are some of the safety control features that could be incorporated into a heat transfer fluid system design:

- Expansion tank high-level alarm in case of process leakage into the heat transfer fluid.
- Expansion tank low-level alarm in case of heat transfer fluid loss.
- Pressure relief valves on heater outlet, expansion tank, and system users (if appropriate); route effluent for safe disposal.
- Fail-safe design of control valves and critical instrumentation in case of utilities failure such as loss of power or instrument air.
- Proper electrical classification and minimization of potential ignition sources, recognizing that the heat transfer fluids typically operate above their normal flash points.
- Fire-safe or automatic fire shut-off valves on connections below liquid level of expansion tank and liquid storage tanks, depending on size.

For vapor–liquid systems, consider:

- Vent accumulation temperature indicators.
- Pressure indicator near the vaporizer (to register vacuum as well as positive pressure).
- High and low pressure alarms in each heating loop.
- Level indicators in vaporizers, condensate collectors and liquid preheaters
- Low level alarm and low level power cutoff on vaporizer.

For heat transfer heaters, on vaporizing systems, controls should be provided to shut off the heat input automatically and sound an alarm on low vaporizer liquid level or high vapor pressure or temperature. On liquid systems, controls should be provided to shut off the heat input automatically on high liquid temperature or low circulation rate. Shutdown devices should be provided on each pass of multi-pass units.

Combustion safeguards and fuel safety shutoff valves approved by an applicable agency for protection against fuel explosions resulting from flame failure should be provided on gas and oil fired burners. In addition master fuel trips should be provided for the following operating conditions:

- Low combustion air flow (mechanical draft units)
- Low fuel pressure trips (trips fuel oil and/or gas only)

- High fuel pressure (trips fuel gas only)
- Loss of atomizing medium (trips fuel oil only)
- Loss of forced draft fan or induced draft fan (where applicable)
- Loss of control power
- High furnace (fire box) pressure
- High fuel gas knockout pot level (for gaseous fuels which might contain liquids)
- Snuffing steam actuation
- Loss of flame
- Manual shutdown (remote and local)

7.5.5 Additional Safety Considerations for Design of Heat Transfer Systems

Some other features that may need to be considered are:

- Volatiles in the system. At startup, heat up should be slow to allow for volatiles (water, for example) to be vented.
- Compatibility–reactivity with process fluids. Welded tube sheets or other special design may be considered.
- Tracing with heat-transfer fluid circuits requires unique application techniques. Manufacturer's literature should be consulted.
- Heat transfer fluid circuits may fall under ASME Section 1 "Boiler Code," requiring additional pressure relief considerations.
- Ethylene (or propylene) glycol–water systems may have further design criteria because of the potential for corrosion of bundles to result in cross-contamination. Freeze protection may be required.
- Decomposition products may form deposits on metal heat transfer surfaces, causing localized overheating and failure of the metal.
- Consideration should be given to conducting special leakage testing in addition to a hydrostatic test (FMEC 1992). Consult the manufacturer for detailed testing procedures.

7.6 REFERENCES

7.6.1 Regulations, Codes of Practice, and Industry Standards

The editions that were in effect when these *Guidelines* were written are indicated below. Because standards and codes are subject to revision, users are encouraged to apply only the most recent edition.

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13

DEFLAGRATION AND DETONATION FLAME ARRESTERS

In the 1980s many deficiencies in the design and application of flame arresters were recognized. Test methods had generally not been sufficiently rigorous to address all flame propagation modes, and end users often had inadequate understanding of the problems involved in selecting and using arresters. For example, end-of-line (deflagration) arresters had in many instances been installed in-line where only a detonation flame arrester should have been used (Roussakis and Lapp 1991). Conversely, there have been a number of cases reported where in-line detonation flame arresters have failed to stop deflagrations. Numerous explosions caused by arrester "failure" might be better attributed to poor selection, application and/or maintenance.

Clean air legislation has inadvertently created a safety problem by requiring reductions in volatile organic compound (VOC) emissions. This is normally achieved by capturing VOC vapors and transporting them to suitable recovery, recycle, or destruction systems. This emission control requirement has led to the introduction of ignition risks, for example from a flare or via spontaneous combustion of an active carbon bed. Multiple connections to a flare header greatly increases the variability of the mixture composition and greatly increases the probability of entering the flammable range.

13.1 DEFINITIONS AND EXPLANATIONS OF TERMS

In the US Coast Guard standard (33 CFR 154), a deflagration flame arrester is classified either as "Type I" or "Type II" depending on whether it is placed end-of-line or in-line. Type I flame arresters are acceptable for end-of-line applications. Where a Type I arrester is provided with cowls, weatherhoods or deflectors, it shall be tested in each configuration. Type II flame arresters are acceptable for in-line applications. Type II arresters shall be specifically tested with the inclusion of all pipes, tees, bends, cowls, weather hoods, which may be fitted between the arrester and the atmosphere.

In the US Coast Guard standard, a detonation flame arrester is classified either as "Type I" or "Type II" depending on its performance during fire endurance testing. A Type I arrester is acceptable for applications where a stationary flame may rest on the device. Type II arresters are suitable for applications where stationary flames are unlikely to rest on the device and further methods are provided to prevent flame passage when a stationary flame occurs, such as a temperature monitor and automatic shutoff valve.

Deflagration is defined as a combustion wave propagating at a velocity that is less than the speed of sound as measured at the flame front (Figure 13-1) propagates via a process of heat transfer and species diffusion across the flame front, and the flame front is not coupled in time nor space with the preceding weak shock front. The pressure peak coincides with the flame front but a marked pressure rise precedes it. Typical maximum pressure ratios generated by deflagrations in pipes are in the range of 8–12. Maximum propagation velocities of 10–100 m/s are typical although up to several hundred meters per second may be observed.

For the purposes of arrester testing, a "low pressure" deflagration is defined as one whose overpressure divided by the initial absolute pressure of the unburned gas is less than one. A "high pressure" deflagration is one whose corresponding ratio is between one and ten.

Deflagration-to-Detonation Transition (DDT) is the transient phenomenon resulting from the acceleration of a deflagration flame to detonation via combustion-generated turbulent flow and compressive heating effects. At the instant of transition a volume of precompressed, turbulent gas ahead of the flame front detonates at unusually high velocity and overpressure. The overpressure depends on the degree of precompression due to deflagration before transition occurs and can be enhanced by shock wave reflections. During the DDT, the detonation wave is described as "overdriven."

Detonation is propagation of a combustion-driven shock wave at a velocity at or above the speed of sound as measured at the flame front (Figure 13-1). The wave is sustained by chemical energy released by shock compression and ignition of the unreacted medium. The flame front is coupled in time and space with the shock front, and there is no pressure increase significantly ahead of the shock–flame front. Propagation velocities in the range 1000–3500 m/s may be observed depending on the gas mixture, initial temperature and pressure, and type of detonation. Detonations may be initiated within limits of fuel concentration known as the "detonable limits," either directly using a detonating initiator or via DDT. The following detonation phenomena have been observed:

- **Galloping Detonation** is a detonation which periodically fails and reinitiates during propagation. This type of detonation is typically observed in near-limit mixtures. Since it reinitiates via DDT, a galloping detonation is periodically overdriven and results in large overpressures at periodic distances along a pipe.
- **Overdriven Detonation** is the condition that exists during a deflagration-to-detonation transition (DDT) before a state of stable detonation is reached. Transition occurs over the length of a few pipe diameters and

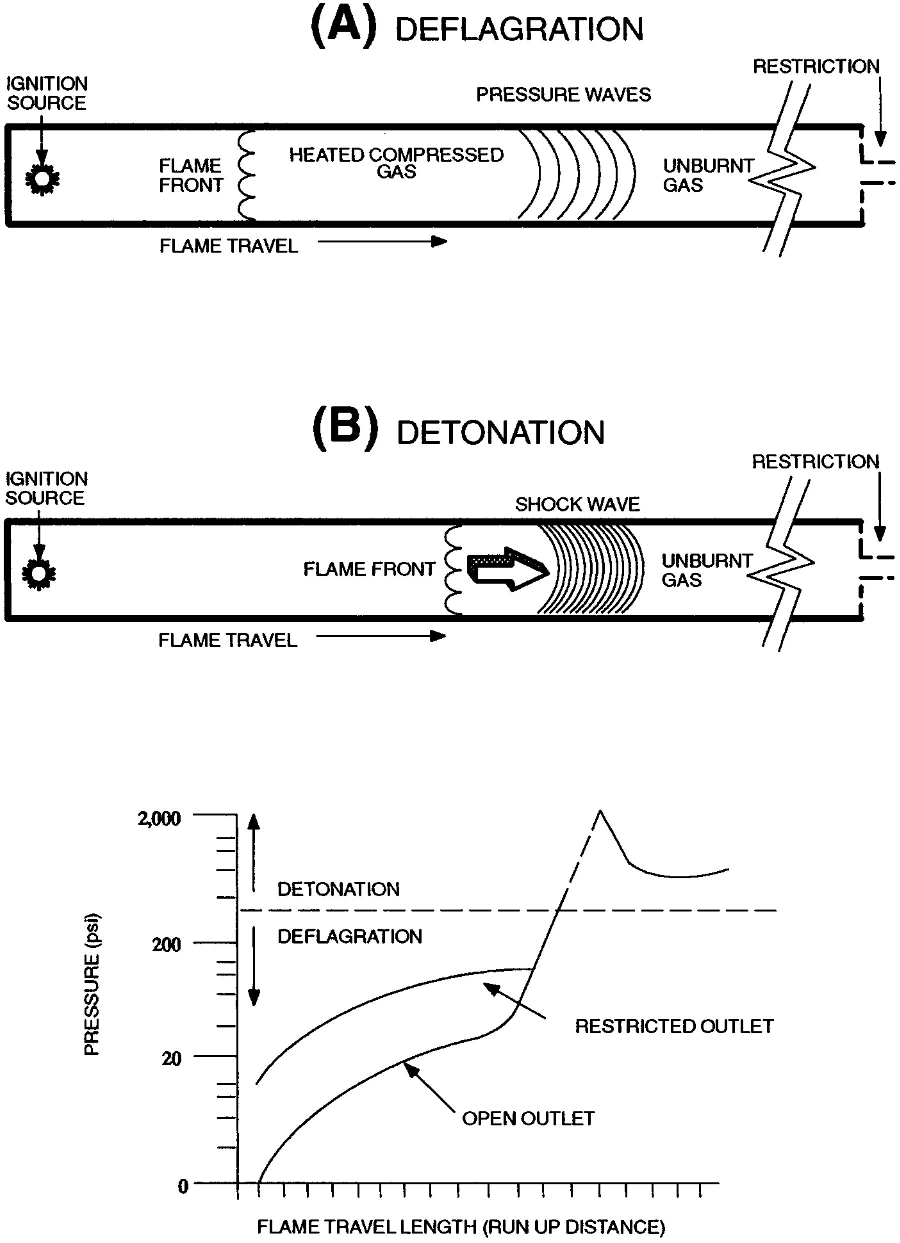

Figure 13-1 (A) Deflagration. (B) Detonation (Knittel 1992)

propagation velocities of up to 2600 m/s have been measured for hydrocarbons in air. This is greater than the speed of sound as measured at the flame front. Overdriven detonations are typically accompanied by side-on pressure ratios (at the pipe wall) in the range 50–100. A severe test for detonation arresters is to adjust the run-up distance so that DDT occurs at the arrester, subjecting the device to the overdriven detonation impulse.

- **Spin Detonation** is a detonation that propagates with a spiral trajectory along a pipe. This type of detonation may be observed over a relatively wide range of mixture compositions and pipe diameters at which the detonation cell size is larger than the pipe diameter (see Chapter 8). The trajectory results in a locally overdriven detonation front that constantly generates large overpressures and temperatures along the pipe wall.
- **Stable Detonation** is a fully developed detonation wave propagating at a constant velocity equal to the speed of sound. For hydrocarbons in air this velocity is typically in the range 1600–1900 m/s. Typical side-on pressure ratios (as seen at the pipe wall) are in the range 18–30, while face-on pressure ratios normal to the direction of propagation may greatly exceed 100 owing to momentum flow. The characteristics of stable detonations are predictable using Chapman–Jouguet theory as described in textbooks on detonations.

  Stable detonations that have propagated over large distances are referred to as "long run" stable detonations. They impart a large integrated flow of heat and momentum to the arrester.

Directionality refers to the direction of flame approach for which an arrester is designed to operate in a line. A "unidirectional" arrester is suitable for arresting deflagrations and detonations approaching from only one direction as tested. A "bidirectional" arrester is either symmetrically constructed or has been tested for deflagrations and detonations approaching from both directions.

Maximum Experimental Safe Gap (MESG) is defined in terms of the precise test method used, of which there are three variants (British, IEC Standard and Underwriters Laboratory). Each apparatus comprises a subdivided combustion chamber, the separate chambers being filled with the test mixture and connected by a gap of specified size and variable width. The MESG is the maximum gap size which prevents flame propagation between the chambers for all compositions of the test gas in air under the specified test conditions. The MESG is used under US regulations to compare gases for detonation flame arrester applications, under the assumption that flames of mixtures with smaller MESGs are harder to stop.

Operating Pressure (P_O) is the maximum absolute system operating pressure normally seen at the arrester location.

Restricted refers to an arrester test condition (also known as "restricted end") designed to simulate flow restrictions on the protected side of an arrester. In practice these may comprise tees, elbows, valves and other line obstructions. Such restrictions may reflect weak shock waves, preheating the unburned gas and creating the possibility of the flame encountering weak reflected shocks at the arrester. These and other detrimental effects can inhibit arrester performance. Test protocols address this effect with a restrictive orifice of prescribed dimensions for the pipe diameter being tested.

Run-Up Distance is the distance in the direction of flame propagation from the point of ignition to any point in a pipe system. Deflagration flames accelerate over this distance due to turbulence and precompression effects. Depending on pipe diameter, surface roughness and the presence of turbulence-producing obstacles (elbows, valves, etc.), this distance may be sufficient for DDT to occur. The following table illustrates the effect of run-up distance in a straight 3 inch diameter pipe, for a 4.3 vol% propane mixture in air initially at 23 psia. In each case initiation is at the closed end of a pipe with an arrester plus bursting disk at the other end. Overpressures are the maxima measured at the arrester location.

Run-up (ft)	Propagation Velocity (ft/s)	Detonation	Overpressure (psi)
1	15	No	6.9
6	250	No	16.1
19	400	No	48.3
24	7360	Yes	2044

Unrestricted describes an arrester test condition in which there is no restriction downstream of the arrester (relative to the flame approach direction) that could cause shock wave reflection coincident with flame arrival at the arrester and other detrimental effects. See also "restricted."

13.2 INTRODUCTION

In this chapter the reader is introduced to current concepts for arrester selection and placement. The following essentials are discussed:

- A flame arrester is a device permeable to gas flow but impermeable to any flame it may encounter under anticipated service conditions. It must both quench the flame and cool the products sufficiently to prevent reignition at the arrester outlet.

- Proper application of an arrester can help avoid catastrophic fire and explosion losses by providing a flame barrier between at-risk equipment and anticipated ignition sources.
- Arresters have often failed in practice. There have been significant advances in arrester technology over the last decade which explain many "failures" as due to misapplication. Plant inspections have shown that misapplication of flame arresters continues to be common.
- Arresters cannot be designed from first principles and can only be proven by tests simulating the conditions of use. The user should ensure that an arrester has been properly tested to meet the intended purpose, and should be prepared to stipulate the required performance standard or test protocol to be followed.
- In almost all cases, if an arrester is placed in-line rather than at (or close to) the open end, a detonation flame arrester is needed. Detonation flame arresters must be able to stop both detonations and deflagrations. They require extensive testing and mandatory testing protocols may apply.
- Unless flame arresters meet the requirements outlined in this chapter they should be replaced, relocated, or both. In some cases arrester performance and application are regulated.

All types of flame arresters feature a permeable barrier that removes heat and radicals from a flame front sufficiently fast both to quench the flame and to prevent reignition of hot gases exiting the arrester. The barrier is usually a permeable metallic matrix (element) but may comprise loose metal packings, tube bundles, parallel plates, or liquid seals. Arresters are used to prevent a flame propagating into a system from outside (such as via a tank vent) or from one part of a system to another (through connecting piping). They must offer an acceptable flow resistance in either one or both directions and must function under all process conditions. Although often considered passive devices, they must be designed for periodic maintenance including any associated pressure and temperature sensors, or ancillary equipment, for example, where a liquid seal must be maintained. Recent overviews of arresters are given by Piotrowski (1991), Roussakis and Lapp (1991), and Howard (1992).

Arresters such as the crimped ribbon type (see later) can be modeled as a bundle of narrow tubes or channels of specified diameter and length. As reviewed by Piotrowski (1991) the length required to arrest flames is approximately given by:

$$L = \frac{(S_t D_h^2)}{100v}$$

where S_t = Initial flame speed (cm/s); v = Kinematic viscosity (cm^2/s)
D_h = hydraulic diameter (cm) = (4 x Cross-sectional area)/Perimeter

The relationship shows that as flame speeds increase the length of the narrow tubes or channels must increase. Alternatively the effect may be offset by employing narrower tubes or channels. Usually, both methods are employed in detonation flame arresters of this type. An obvious application problem of the relationship is that the flame speed is not a fundamental or calculable quantity except in the case of stable detonations. For deflagrations in pipe systems, the flame speed is normally far higher than the fundamental burning velocity owing to the expansion factor of burned gas and the turbulent acceleration of the flame front. Thus, the flame speed is normally an experimentally derived quantity only. In practice, it is not possible to determine the required channel length or diameter except by experimental trial-and-error under test conditions closely simulating the eventual use of the arrester.

The most common flame arrester application is for mixtures of flammable gases or vapors with air. Special arresters may be required for use with other oxidants. Specific designs have been developed for unstable materials that propagate decomposition flames (Section 13.6.1).

The flame arresters described in this chapter cannot be used for flames of suspended dusts. Chapter 17 describes alternative devices for this service.

13.2.1 End-of-line and Deflagration Flame Arresters

A flame arrester designed to prevent propagation into a system from outside is placed close to the end of the line and is known as an "end-of-line" or "deflagration flame" arrester. These are commonly used in atmospheric tank vent systems involving open vent pipes and vent valves (Figure 13-2). Being close to the end of the line, there is insufficient "run-up" distance for deflagration-to-detonation transition (DDT) to develop in the piping (see "Definitions"). Such arresters are neither designed for nor suitable for stopping detonations.

For certain gases and vapors it can be established that DDT will not occur under the process conditions used. Examples include the decomposition flames of 100% ethylene oxide or ethylene oxide diluted with inert gas such as nitrogen. In such cases deflagration arresters may be used in-line as described in Section 13.6.1. However, for most fuel–oxidant systems, in-line use of a deflagration flame arrester would require either a very close tolerance on the mixture composition to ensure that operation is always outside the detonable range, or testing to actual pipe configuration to ensure that DDT cannot occur over the range of possible mixture compositions. In the latter case, no changes to the pipe configuration would be allowed without retesting.

In addition to avoidance of DDT, the deflagration arrester should not be used under conditions more severe than those it has been tested for. Deflagration flames may be accelerated by various turbulence-promoting pipe features

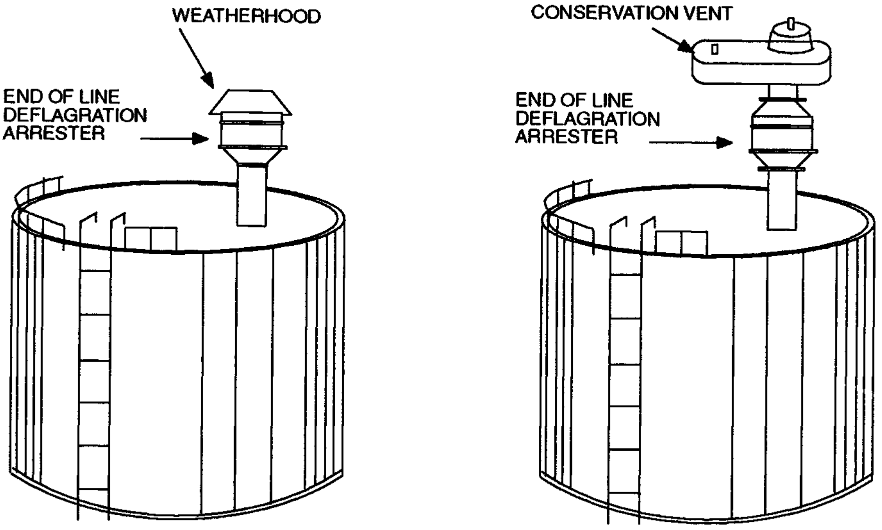

Figure 13-2 End-of-line flame arrester.

such as elbows, tees and valves. The test should anticipate and address the actual configuration to be used in practice.

13.2.2 In-line and Detonation Flame Arresters

If a flame arrester is not placed at the end of the line it is known as an "in-line" or "detonation flame" arrester. This type of arrester is used in all cases where sufficient "run-up" distance exists for a detonation to develop. If a deflagration is capable of transition to detonation before to reaching the arrester, a detonation flame arrester must be used. A detonation flame arrester must be able to stop both detonations and deflagrations, and must be carefully selected for this demanding service. Figure 13-3 shows typical locations for detonation flame arresters in a vapor collection and destruction system.

13.2.3 Recent Developments

When vapor recovery systems at marine terminals were mandated by state and local regulatory agencies, the implications of connecting tankers and refineries with long, large diameter vapor recovery lines containing potentially flammable mixtures concerned both vessel and shoreside facility operators as well as the U.S. Coast Guard (USCG). By the time industry facilities were under design to comply with the early start-up dates imposed by state and local mandates, arresters 12–18 inches or even larger diameter were being contemplated. However, no tests on such a scale had ever been reported, nor

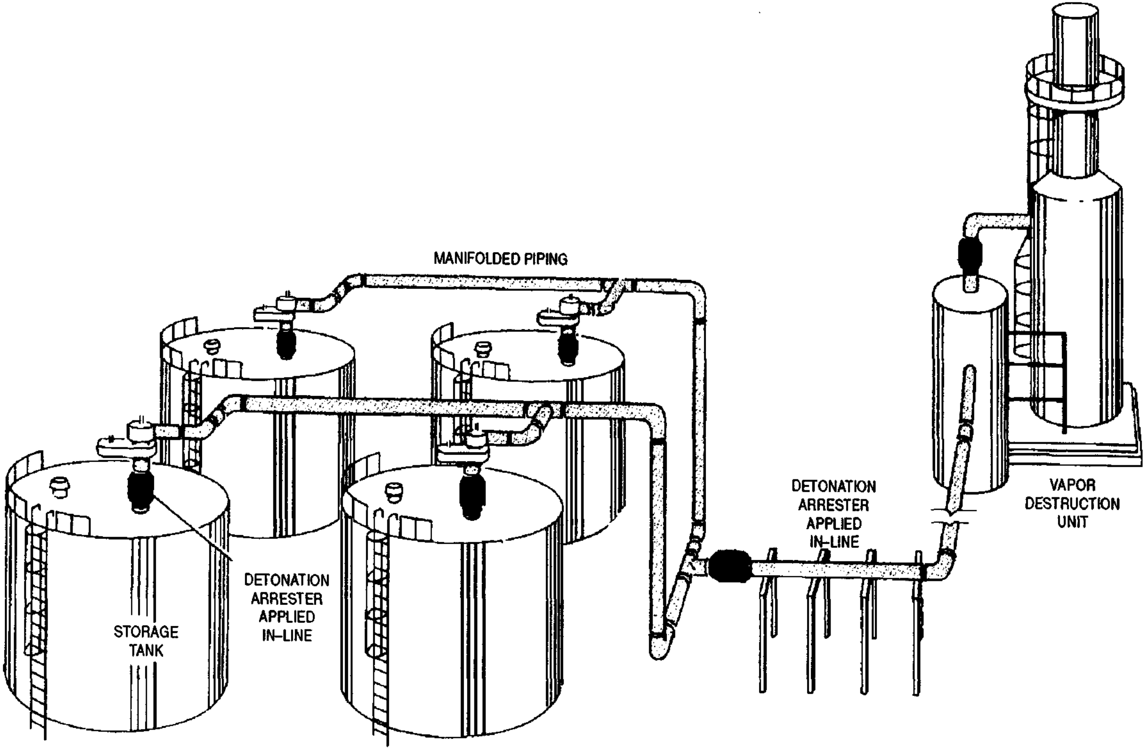

Figure 13-3 Vapor recovery system with detonation arresters applied (Protectoseal 1991).

were any planned (Capp and Seebold 1991). In 1989 steps to amend this deficiency were taken when the API formed the Detonation Arrester Oversight Task Force and contracted with the U.K. Health & Safety Executive to carry out detonation testing in 18 inch pipe according to a tentative U.S. Coast Guard test procedure. The results of this testing plus investigations at other research establishments eventually led to regulatory adoption of an amended USCG test protocol.

In 1991 Underwriters Laboratory issued a proposed 6th edition of UL 525. Deflagration flame arrester requirements are revised while detonation flame arresters requirements are entirely new. In addition, other standards have been issued or drafted by agencies such as the Canadian Standards Association. Where USCG certification is required, their test protocol takes precedence.

Effluent disposal system applications are discussed in Chapter 15. Testing and certification protocols are described and contrasted later in Section 13.4 of this chapter.

13.3 TYPES OF FLAME ARRESTERS

Although this is reiterated throughout the text, whatever flame arrester is considered, it must be proven suitable for the application by testing.

13.3.1 Deflagration Flame Arresters

As described in Section 13.1.1, deflagration flame arresters are normally located "end-of-line" to prevent externally initiated flames from entering a system. One end of the arrester is either open directly to the atmosphere or connected via a vent valve, cowl or a short length of open-ended straight pipe. This pipe is normally no longer than 15 to 35 feet for systems containing saturated hydrocarbons. The maximum length depends on pipe diameter and arrester vendor specifications.

It is essential that transition to detonation (DDT) does not occur in the piping between the atmosphere and the arrester. Hence, if any significant length of piping is involved it should not contain turbulence-promoting obstructions such as tees, elbows, valves or other flow restrictions unless realistic testing indicates that DDT will not occur.

The following types of deflagration flame arresters will be briefly described (see Figures 13-4 and 13-5):

1. Crimped Ribbon
2. Parallel Plate
3. Expanded Metal Cartridge

4. Hydraulic (Liquid Seal)
5. Packed Bed
6. Wire Gauze
7. Perforated Plate
8. Sintered Metal

In addition to these types, arresters using compressed wire wool elements and metal foam elements have been developed. The latter consists of polyurethane foam with an electroplated metal surface. Both have the possible drawback that quality control of the irregular matrices is difficult to assure.

Crimped ribbon and parallel plate types are the most commonly used vent flame arresters. Hydraulic types using a liquid seal are commonly used in flare applications and in corrosive service. Whichever arrester design is used, it is essential that it be properly tested under conditions that simulate the proposed service.

13.3.1.1 *Crimped Ribbon*

Crimped ribbon arresters are constructed by alternately wrapping layers of crimped and flat metal ribbons. This results in many small, triangular flame channels through the disk-shaped element (Figure 13-4a).

The main advantage of crimped ribbon arresters for end-of-line use is a relatively low fabrication cost. Since typically only 20% of the arrester face is obstructed, the flow resistance is relatively low and the arrester face area need not be much greater than the cross-sectional pipe area.

A drawback of the design is sensitivity to damage during handling. This should be considered critical during maintenance of the element. Damage may lead to enlarged channels allowing flame penetration or to channel collapse leading to increased pressure drop. The small channel size may make these arresters sensitive to fouling due to solids deposition, and regular maintenance is essential in service where this occurs.

13.3.1.2 *Parallel Plate*

These are constructed of unperforated metal plates or rings arranged edgewise to the gas flow and separated from each other by a small spacing (Figure 13-4b). They are relatively low in cost, robust and can be dismantled for cleaning. Their main disadvantages are weight and resistance to gas flow.

13.3.1.3 *Expanded Metal Cartridge*

These comprise a sheet of expanded metal which is wrapped in a fashion similar to a cartridge filter element. Diamond-shaped openings in the expanded metal sheet are nonaligned during wrapping such that there is no direct path from one layer to the next (Figure 13-4c). This design tends to reduce the incidence of plugging by suspended solids since these will not be

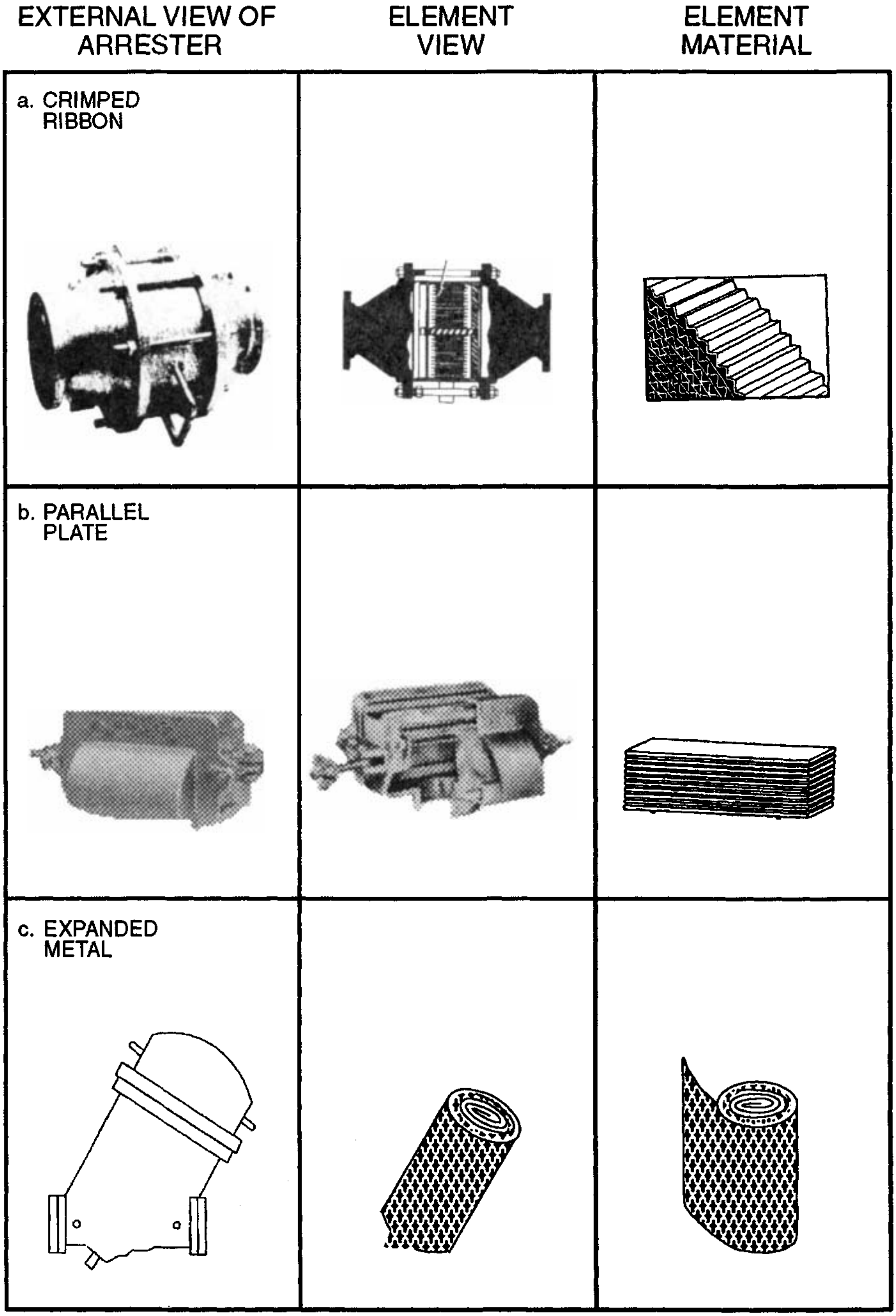

Figure 13-4 Types of arresters: (a) crimped ribbon; (b)parallel plate; (c) expanded metal cartridge (Sources: Protectoseal 1991; Knittel 1992)

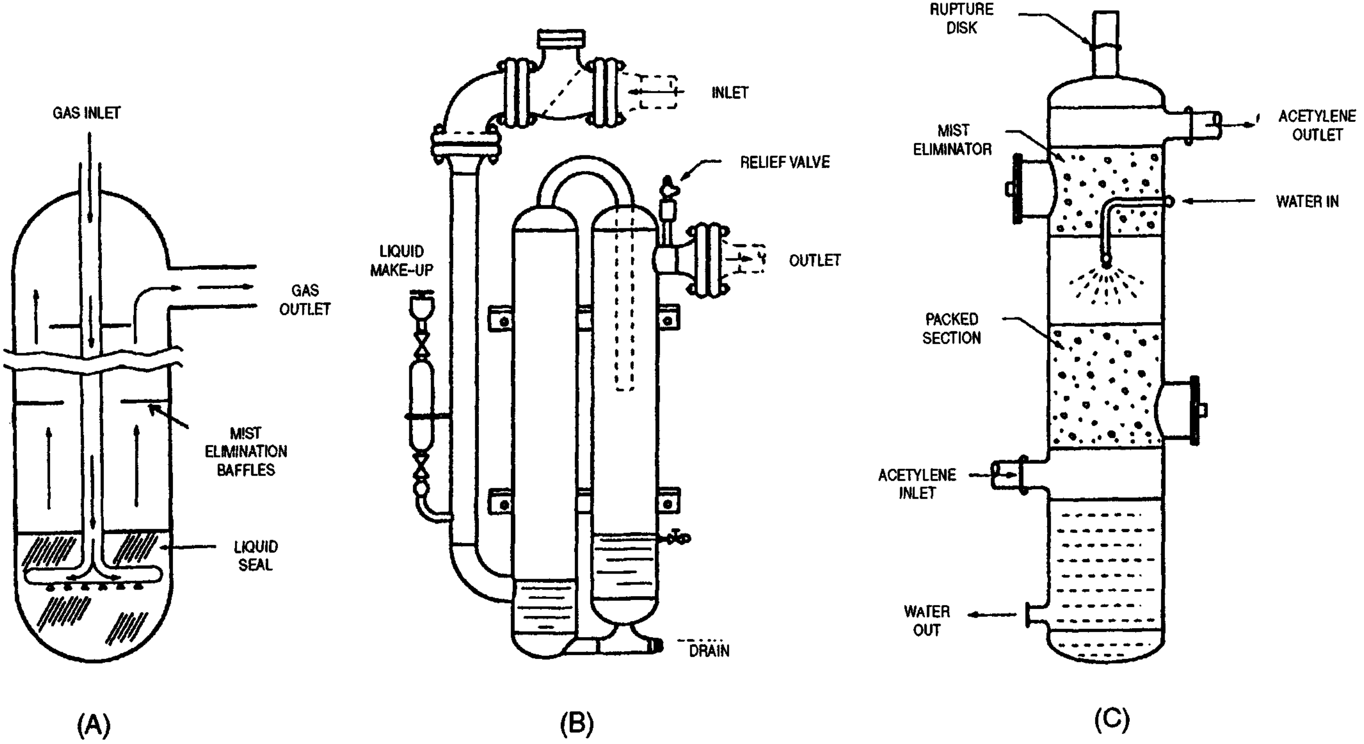

Figure 13-5 (A) Liquid seal arrester; (B) Linde hydraulic valve arrester; (C) packed bed arrester (Howard 1972).

heavily deposited on the inlet face. The elements are normally offset rather than in-line with respect to the gas flow so that the flow passes radially towards the cartridge axis. This creates a relatively large inlet surface area which further reduces plugging problems. Other advantages include liquid and solids drop-out into the external container surrounding the inlet, hence the design may be suitable for reactive monomer service. Disadvantages of units for larger pipe diameters include size and weight except where mounted at or near grade.

13.3.1.4 Hydraulic (Liquid Seal)

Hydraulic arresters are filled with a liquid, usually water, to provide a flame barrier (Figure 13-5a,b). Gas permeability requires that the gas flow be broken into discrete bubbles in which any flame reaction will quench prior to breakthrough. A mechanical nonreturn valve is often incorporated to prevent the displacement of liquid during or after a flame event.

These devices are usually designed to be effective in one direction only. Proper design should ensure mechanical integrity of the vessel during the flame event, and provisions to prevent back-flow plus loss of the liquid seal prior to arrival of the flame event. Suitable testing should also be performed.

These arresters are bulky and require the liquid level to be maintained either automatically or by regular inspection. At low liquid levels these arresters might fail, and if water seal is lost there is no effective barrier to flame propagation. Although hydraulic arresters are not normally prone to plugging it is essential that the liquid used does not react with the gas components and that appropriate measures be taken to prevent freezing.

Fundamental test work (Overhoff et al. 1989) demonstrated mechanisms whereby waterseal arresters may fail to prevent flashback even if gas streams are broken up into discrete, small bubbles. The mechanisms are particularly valid for gas mixtures of high burning velocity, such as hydrogen–air or hydrocarbon–oxygen. Ignition transfer can occur between adjacent bubbles without contact, due to hydrodynamic jet effects. The jets occur upon rapid collapse of bubbles of burned gas in the vicinity of discontinuities, which may be adjacent bubbles (the jet effect is analogous to cavitation, known to produce "jet" erosion at discontinuities such as ship propellers). The high velocity, hydrodynamic jet may produce compression-ignition of an adjacent bubble, and this process may be transmitted. Alternatively, more closely spaced bubbles might transfer ignition via jets of hot gas, or, in the limiting case of a very high void fraction, via direct flame transfer. Several novel designs of water-seal arrester were suggested to mitigate ignition transfer through sparged bubble streams.

13.3.1.5 *Packed Bed*

These consist of a tower of other container packed with pebbles, Raschig rings or other medium to a prescribed height and packing density (Figure 13-5c). The dimensions of the discrete fill medium (for example ring dimensions) are usually also prescribed. To increase effectiveness, oil or water wetting is sometimes used depending on compatibility.

Their advantages include robustness and ease of dismantling for maintenance. However, there are few design data except for 100% acetylene and 100% ethylene oxide service as described in Section 13.6.1.

13.3.1.6 *Wire Gauze*

These consist of layers of wire gauze (60 mesh or larger) and have the advantages of low cost, wide availability and ease of installation. Their disadvantages include limited effectiveness for high velocity flames and the flow resistance of fine gauzes.

13.3.1.7 *Perforated Plate*

These comprise metal plate perforated with circular holes. They have greater mechanical strength and are less likely to overheat than gauze arresters, but the flow resistance is high.

13.3.1.8 *Sintered Metal*

Sintered metal is effective as an arresting element but offers a high resistance to gas flow, so that it is most frequently used where the gas flow rate is small. The main uses are for protecting the sensing heads of gas detectors for flammable atmospheres and in flashback arresters for welding equipment. It is however possible to use many such units in parallel to offset flow resistance, as has been done for 100% acetylene in process units.

An advantage of sintered metal is that it can be produced in a variety of shapes to suit the application. In common with some other arresters, there is a risk that a stabilized flame on one arrester face might slowly penetrate the sintered matrix. Hence, these arresters often incorporate a pressure or thermally activated flow shut-off device.

13.3.2 *Detonation Flame Arresters*

Detonation flame arresters must be able to withstand the mechanical effects of a detonation shock wave in addition to quenching the flame. Two particular mechanical challenges presented by detonation waves are (1) high pressure, short duration loading during DDT and (2) lower pressure, long duration loading from long-run stable detonations. Quenching the flame is difficult since flame speeds can exceed 2500 m/s, giving the arrester little time to quench the flame.

Detonation flame arresters must also be able to stop flame propagation during deflagrations. While this may seem trivial in comparison to stopping the higher pressure supersonic detonation, testing has shown that this may not necessarily be the case. Arrester designs have been tested successfully even for overdriven detonations only to fail under restricted end deflagration test conditions (see Section 13.4.4).

As of early 1993 crimped ribbon and expanded metal cartridge detonation flame arresters have proven successful in arresting all types of deflagrations and detonations under the UL and USCG test protocols (see Section 13.4.4). An active detonation (and deflagration) arresting system has been tested and passed a USCG-approved test protocol on 6-inch and 24-inch pipe scale at 19.7 psia with propane–air as the combustible. The USCG is currently reviewing the test results (Senecal 1993). Active deflagration and detonation systems, though relatively less known and understood, have been important where the disadvantages of passive devices preclude their use.

13.3.2.1 Crimped Ribbon

Crimped ribbon detonation flame arresters work analogously to crimped ribbon deflagration flame arresters. As the flame enters the arrester element it is channeled into a number of flamelets. The flamelets are extinguished by quenching before they can penetrate the matrix. Since detonations propagate much faster than deflagrations, the detonation flame arrester must use smaller channels of longer length to provide the required quenching time.

Owing to the larger impulse of detonations, the detonation arrester must be structurally reinforced. This requires extensive support structures which typically take the form of cross bracing on the element facing. With the requirement of smaller flame cells within the arrester and extensive support structures there is a greater obstructed area, typically about 45%. This may lead to increased pressure drop and fouling of the element.

13.3.2.2 Expanded Metal Cartridge

Expanded metal cartridge type arresters designed for use as detonation flame arresters are described in Section 13.3.1.3.

13.4 REGULATORY USE, TESTING AND CERTIFICATION

For an arrester to be certified or listed it must either pass tests conducted by a recognized agency such as Factory Mutual (FM) or Underwriters Laboratory (UL), or by a test center with demonstrated ability to test to recognized standards.

In the United States, UL 525 standard, *Flame Arresters for Use on Vents of Storage Tanks for Petroleum Oil and Gasoline,* and Factory Mutual Research

Corporation (FMRC) Class No. 6061, *Flame Arresters for Vent Pipes of Storage Tanks,* are the most widely used standards for deflagration flame arresters. The proposed 6th edition of UL 525 now also includes standards for detonation flame arrester testing.

The British Standards Institution (BSI) has issued a draft document titled *Specification for Flame Arresters for General Use.* This draft (as in the case of UL 525) addresses detonation flame arrester testing and was under consideration at the time of writing this Chapter. The International Maritime Organization (IMO) has published a standard for testing detonation flame arresters, titled *Revised Standards for the Design, Testing and Locating of Devices to Prevent the Passage of Flame into Cargo Tanks in Tankers.* The United States Coast Guard (USCG) has published a standard titled *Standard Specification for Detonation Flame Arresters,* which applies at this time exclusively to marine vapor recovery operations (see Chapter 7). Factory Mutual Researcy Corporation (FMRC) has adopted the USCG Standard (33CFR Part 154, Appendix A) as part of their test protocol, modified with respect to the endurance burn test (Febo 1993).

In this Section the regulations are briefly described and the various test procedures are contrasted.

13.4.1 Deflagration Flame Arrester Regulation

OSHA and NFPA 30 designate where conservation vents and flame arresters are required on storage tanks or process vessels containing flammable or combustible liquids at atmospheric pressure. The OSHA requirements (Piotrowski 1991) are:

> OSHA 1910.106(b)(2)(iv)(f). Tanks or process vessels storing Class IA liquids shall be equipped with venting devices which shall be normally closed except when venting to pressure or vacuum conditions, or with approved flame arresters. Exemption—Tanks of 3000 bbls. capacity or less containing crude petroleum in crude producing areas; and, outside aboveground atmospheric tanks under 1000 gals. capacity containing other than Class 1A flammable liquids may have open vents. (g) Flame arresters or venting devices required in subdivision (f) of this subdivision may be omitted for Class 1B and 1C liquids where the conditions are such that their use may, in case of obstruction, result in tank damage.

The requirements here and in NFPA 30 must be properly applied after evaluation to ensure that the recommendations are correct for the tank system concerned. See Section 13.6.2 for a discussion of conservation (breather) vents.

The USCG accepts deflagration flame arresters in two categories:

> Type I: Flame arresters acceptable for end-of-line applications. Where a Type I arrester is provided with cowls, weather hoods or deflectors (etc.), it shall be tested in each configuration.

> Type II: Flame arresters acceptable for in-line applications. Type II arresters shall be specifically tested with the inclusion of all pipes, tees, bends, cowls, weather hoods (etc), which may be fitted between the arrester and the atmosphere. Owing to the prohibitive cost of testing deflagration flame arresters for each particular installation the Type II (in-line) category is generally not encountered.

13.4.2 Detonation Flame Arrester Regulation

Appendix A to Part 154 of 33 CFR *Marine Vapor Control Systems; Final Rule,* by the Department of Transportation, Coast Guard, dated Thursday June 21st 1990, contains *Guidelines for Detonation Flame Arresters.* This Appendix contains the draft ASTM Standard and devices meeting this standard will be accepted by the USCG Commandant (G-MTH). The standard is intended for detonation flame arresters protecting systems containing vapors of flammable or combustible liquids where temperatures do not exceed 60C.

An important part of the USCG standard is the testing protocol. Provided the MESG (see Section 13.4.5) of the gas or vapor to be protected is equal or greater than 0.9 mm, detonation flame arresters may be tested with industrial grade gasoline or hexane vapor. For that part of the test protocol dealing exclusively with deflagration and detonation tests, the use of propane is acceptable. However, if the gas or vapor to be protected has a MESG less than 0.9 mm, the arrester can only be tested with the specific vapor concerned or, alternatively, one having an even lower MESG value.

Thus, if a gas or vapor has a MESG equal to or greater than 0.9 mm there should be no problem finding a certified detonation flame arrester, since extensive testing has been done with such test mixtures (propane, gasoline etc) up to very large pipe diameters. However, if a gas or vapor has a lower MESG than 0.9 mm, there are potential problems finding a certified arrester, particularly if a certain type of arrester is desired. These problems increase with increased pipe diameter, increased operating pressure, and decreased MESG of the mixture concerned.

For any mixture of unknown MESG, it is required to first establish the MESG value at the worst-case composition. Even this step is relatively expensive. If the MESG is less than 0.9 mm, an arrester must be found that has been certified for MESGs less than 0.9 mm according to the USCG test protocol. At the present time this means with ethylene–air, whose behavior has been selected by arrester designers to envelope most gases with MESGs less than 0.9 mm. Since ethylene has proved challenging in terms of maximum pipe diameter and operating pressure, considerable development work will probably be necessary for any gas mixture with a lower MESG than ethylene (see Table 13-4 for MESG values).

Table 13-1 Deflagration Flame Arrester Test Standards[a, b]

TEST	USCG	UL525	BSI
Deflagration : Restricted	No	No	No
Deflagration : Unrestricted	3 tests	3 tests	9 tests
Endurance Burn	2 hours	1 hour	30 min
Flow Capacity	Yes	Not finalized	Yes
Corrosion Resistance	Yes	Not finalized	Yes
Hydrostatic Test	Yes	Not finalized	Yes
Pneumatic Test	Yes	Not finalized	Yes

[a] As of this writing, Factory Mutual Research Corporation has adopted the USCG Standard (33 CFR, Part 154, Appendix A) and is in the process of modifying their test protocol, in particular with respect to the endurance burn test (Febo 1993).

[b] Sources: USCG, Appendix B of 33 CFR Part 154, 1990; UL525 1991; BSI 1990.

13.4.3 Deflagration Flame Arrester Testing

Certification of arresters comes from many organizations throughout the world. Different organizations have set forth minimum standards for deflagration (end-of-line) flame arresters.

Table 13-1 summarizes the principal requirements of three organizations. None requires deflagration tests with line restrictions (as is necessary by most current standards for detonation flame arresters) but each requires a minimum number of unrestricted tests. The "endurance burn" test is designed to simulate a flame which has stabilized on the arrester face without penetration, under conditions where the flame is sustained by gas flow. The minimum requirements in each category may vary from one standard-setting organization to the next, such as the duration of the endurance burn or the specified hydrostatic and pneumatic test pressures.

13.4.4 Detonation Flame Arrester Testing

Table 13-2 summarizes the minimum requirements set by several standards-setting organizations, either as published or at the draft stage. Section 13.8 discusses possible future developments of standards for flame arresters.

A detonation flame arrester must stop both detonations and deflagrations, and, as noted earlier, deflagrations may in some cases penetrate arresters that have successfully stopped even overdriven detonations. To properly address deflagration flame arrestment, it is usually specified that both restricted and unrestricted conditions be tested (see "Definitions"). In addition the arrester must meet minimum standards for mechanical strength, leakage pressure, and withstanding penetration by a flame which has stabilized on one face ("endurance burn test"). Other tests might be required such as a corrosion test for marine applications.

It has been found that the maximum allowable operating pressure for an in-line arrester may be determined by the worst-case condition at which a deflagration flame arriving at the arrester meets a weak deflagration shock reflected back from a line restriction downstream of the arrester (relative to the flame approach direction). For a test the restriction comprises a circular orifice of specified dimensions simulating the real case of a downstream elbow, tee or valve. Present standard test conditions do not assure that the worst-case is encountered since the upstream distance at which the deflagration flame is initiated is not varied. However, experimental work has shown that if this distance is varied under restricted end conditions, the maximum operating pressure falls through a minimum corresponding to the simultaneous arrival of the flame and its reflected weak shock at the arrester (Figure 13-6).

Three of the five standards summarized in Table 13-2 require 5 tests using overdriven detonations and 5 using stable detonations.

Table 13-2 Detonation Flame Arrester Test Standards[a,b]

TEST	USCG	CSA	UL525	IMO	BSI
Deflagration (Restricted)	10	15	10	None	None
Deflagration (Unrestricted)	10	15	10	None	1
Overdriven Detonation	5	5	5	3	11
Stable Detonation	5	5	5	None	1
Long-run Stable Detonation	No	No	No	No	No
Endurance Burn	2 hr Type I 15 min Type II	3 hr	See text	2 hr	30 min
Flow Capacity	Yes	Yes	Not finalized	Yes	Yes
Corrosion Resistance	Yes	Yes	Not finalized	Yes	Yes
Hydrostatic Test	Yes	Yes	Not finalized	Yes	Yes
Pneumatic Test	Yes	No	Not finalized	Yes	Yes

[a] As of this writing, Factory Mutual Research Corporation has adopted the USCG Standard (33 CFR, Part 154, Appendix A) and is in the process of modifying their test protocol, in particular with respect to the endurance burn test (Feb. 1993).

[b] Sources: USCG 1990 (Appendix B of 33CFR); UL 1991; BSI 1990; CSA 1991; IMO, MSC/Circ.373/Rev.1; Feb. 1993.

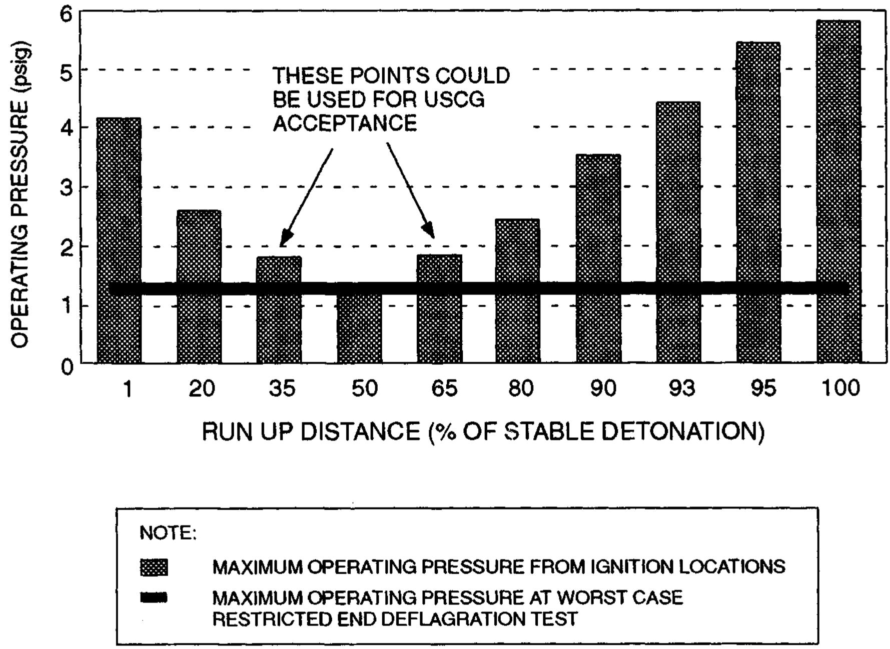

Figure 13-6 Flame of run-up distance on maximum allowable pressure—restricted end deflagrations (Knittel 1992)

In order to test for overdriven detonations it is essential that DDT occurs in the vicinity of the arrester, since the overdriven condition resulting from DDT persists only for a few pipe diameters. This limitation has been given as a reason to exclude overdriven detonations as a standard test requirement. With experience however, it has been found possible to produce overdriven detonations at the arrester with 70% or greater repeatability (Seebold 1992).

At present there is no requirement to test using "long run" stable detonations established with large upstream pipe runs. Long run stable detonations impart a larger integrated momentum flow and duration of thermal loading to the arrester. Stable propane–air detonations in 18 inch diameter pipe displayed increasing shock wave durations up to 350 pipe diameters (Lapp and Thibault 1992). At greater distances an asymptote was reached with a shock wave duration about ten times that produced by short stable detonation runs (note that the required distance to obtain "long run" stable detonations varies with the conditions involved).

There is also no present requirement to systematically vary the test mixture composition used in the flame arrestment tests. As discussed in Section 13.8, near-limit mixtures may give rise to special detonations of the "spin" or "galloping" types. Further, it is presently not known to what degree the maximum operating pressure found under restricted end deflagration test conditions might be further depressed were the test mixture systematically optimized. It has already emerged that for ethylene–air mixtures the maximum allowable operating pressure (after optimizing the flame initiation distance as described above) is only a few psig at stoichiometric composition. It is clearly of considerable importance that the maximum allowable operating pressure does not fall to impractically low levels under any conditions. However, certain testing that might uncover such limitations is presently voluntary.

There is considerable variation in standard requirements regarding "endurance burn" capability, which is a measure of the length of time an arrester can withstand a stabilized flame on one face without penetration. Stabilization can occur under various conditions of flow rate, pipe diameter and gas composition. See Section 13.8 for a discussion of the effect of arrester configuration on its endurance burn performance.

Under various "endurance burn" testing protocols, a flame is allowed to stabilize on the arrester element and the fuel mixture and flow rate are then adjusted to achieve the maximum temperature on the unprotected side. The time to failure is measured from the point the maximum temperature condition has been achieved. The proposed Canadian Standards Association (CSA) burn test is based on four fixed flow velocities independent of pipe diameter and the arrester performance is based on the lowest recorded failure time. By using fixed velocities, the number of test variables in achieving maximum temperature is reduced and hence the subjectivity in the time taken to begin the test is in principle also reduced. The CSA method is discussed by Dainty and Lobay (1991). Possible improvements in reproducibility might alternatively be gained by specifying the test mixture to be used for standard gases. The IMO and USCG requirements are summarized in Table 13-3. See "Definitions" for USCG acceptance types.

13.4.5 MESG Values and NEC Groups

The Maximum Experimental Safe Gap (MESG) is used in the USCG standard (with respect to detonation arresters) to compare different gases and vapors under the assumption that smaller MESGs indicate flames that are more

Table 13-3 IMO and USCG Endurance Burn Requirements

Organization	Endurance Burn Time for Acceptance
IMO	2 hours minimum
USCG Type I Acceptance	2 hours
USCG Type II Acceptance	15 minutes

difficult to stop. This assumption has not yet been verified by comprehensive flame arrester tests, although related work by Frobese and Forster (1992) found that "the MESG is indeed a suitable ordering and evaluating parameter, independent of the specific fuel," for evaluating detonation processes at branches. Phillips (1972) discusses MESG theory.

The MESG as described in IEC 79-1A (see below) is intrinsically a better single parameter than quenching distance in evaluating flame penetration of small gaps, since it not only involves quenching but also the forcing of a hot gas jet through an orifice at a velocity determined by the mixture deflagration rate. Reignition might occur on the other side of the gap without true flame penetration, thus MESG can involve several combustion properties (burning velocity, flame temperature, expansion ratio, autoignition temperature) of the test mixture.

Table 13-4 shows MESG values published by USCG in the Federal Register, compared with a more extensive listing published in IEC Standard 79-1A. Table 13-4 suggests that many of the USCG values were found using the Underwriters Laboratory test apparatus while others are identical with those in the IEC listing, which were measured either in the IEC standard apparatus (IEC) or in the British 8 liter apparatus (UK). The most notable difference is in the case of acetylene, whose USCG value is more than an order of magnitude smaller than that published by IEC. Note that the third place of decimals cited by the USCG has no significance in MESG value since the IEC Standard allows a reproducibility of up to 0.04 mm. IEC Standard 79-1 is the applicable document for MESG cited by USCG Regulations for Marine Vapor Control Systems (33 CFR Part 154 et al).

As discussed by Piotrowski (1991) the NEC (National Electrical Code) Group (see NFPA 70) gives some indication of gas behavior with respect to flame arresters, and for deflagration arresters in vent lines a device tested with a Group D gas or vapor may be considered suitable for other Group D atmospheres under similar conditions. However, this procedure is not acceptable for detonation arresters under the USCG standard. Table 13-4 shows that some Group D vapors such as acrylates have MESGs less than 0.9 mm. Also, the extension of the procedure to compare gases and vapors of higher Groups (such as propylene oxide with hydrogen in Group B or carbon monoxide with dioxane in Group C) would be an extremely dubious procedure even for deflagration arresters.

Table 13-4 Comparison of Published MESG Values

Gas or Vapor (NEC Group)	Optimum Mixture (vol% in air)	MESG (mm)	Source	USCG Value (mm)
acetone (D)		1.02	UK	1.016
acetonitrile (D)	7.2	1.50	IEC	
acetylene (A)	8.5	0.37	IEC	<0.025
acrylonitrile (D)	7.1	0.87	IEC	
ammonia (D)		3.17	UK	
amyl acetate		0.99	UK	0.99
amyl alcohol (D)				0.99
benzene (D)				0.99
1,3-butadiene (B)	3.9	0.79	IEC	
butane (D)	3.2	0.98	IEC	1.068
iso-butanol (D)		0.96	UK	0.965
n-butanol (D)		0.94	UK	0.94
n-butyl acetate (D)		1.02	UK	1.016
n-butyl chloride	3.9	1.06	IEC	
butyl glycolate	4.2	0.88	IEC	
carbon disulfide (A+)	8.5	0.34	IEC	0.203
carbon monoxide (C)	40.8	0.94	IEC	0.915
cyclohexane		0.94	UK	0.94
cyclohexanone	3.0	0.95	IEC	
decane		1.02	UK	1.016
1,2-dichloroethane	9.5	1.80	IEC	
di-*n*-butyl ether	2.6	0.86	IEC	
diethyl ether (C)	3.47	0.87	IEC	0.864
diisopropyl ether (D)	2.6	0.94	IEC	
dimethyl ether (C)	7.0	0.84	IEC	
1,4-dioxane (C)	4.75	0.70	IEC	
ethane (D)	5.9	0.91	IEC	
ethanol (D)	6.5	0.89	IEC	1.016
ethylene (C)	6.5	0.65	IEC	0.71
ethylene oxide (B)	8	0.59	IEC	0.65
ethyl acetate (D)	4.7	0.99	IEC	1.04
ethyl acrylate (D)	4.3	0.86	IEC	
ethyl nitrite		0.96	UK	0.922

Table 13-4 Comparison of Published MESG Values—*Continued*

Gas or Vapor (NEC Group)	Optimum Mixture (vol% in air)	MESG (mm)	Source	USCG Value (mm)
ethyl nitrate				<0.025
heptane (D)	2.3	0.91	IEC	0.965
hexane (D)	2.5	0.93	IEC	0.965
hexanol	3.0	0.94	IEC	
hydrogen (B)	27	0.29	IEC	0.102
hydrogen cyanide (C)	18.4	0.80	IEC	
methane (D)	8.2	1.14	IEC	1.170
methanol (D)	11.0	0.92	IEC	0.915
methyl acetate		0.99	UK	0.990
methyl acrylate (D)	5.6	0.85	IEC	
methyl ethyl ketone (D)	4.8	0.92	IEC	1.016
methyl isobutyl ketone (D)	3.0	0.98	IEC	
iso-octane (D)	1.94	0.94	IEC	1.040
n-octane (D)	1.94	0.94	IEC	
iso-pentane (D)	2.45	0.98	IEC	
n-pentane (D)	2.55	0.93	IEC	1.016
2,4-pentanedione	3.3	0.95	IEC	
pentanol		0.99	UK	
phenyltrifluoromethane	19.3	1.40	IEC	
propane (D)	4.2	0.92	IEC	0.965
iso-propanol (D)	5.1	0.99	IEC	
n-propyl acetate		1.04	UK	1.04
propylene (D)	4.8	0.91	IEC	
propylene oxide (B)	4.55	0.70	IEC	
vinyl acetate (D)	4.75	0.94	IEC	
vinyl chloride (D)	7.3	0.99	IEC	
vinylidene chloride (D)	10.5	3.91	IEC	
xylene (D)				1.066

Notes:

IEC = International Electrotechnical Commission, IEC 79-1A, First Supplement to Publication 79-1 (1971) *Electrical Equipment for Explosive Gas Atmospheres*, Part 1, Appendix D, Table 1, 2nd Impression (1982).

UK = United Kingdom 8 liter sphere method, value cited in IEC 79-1A.

13.5 APPLICATION CONSIDERATIONS

13.5.1 Materials of Construction

When the materials stored in storage tanks and process vessels are noncorrosive, the arrester vendor's standard materials of construction for the housing and arrester element are commonly used. Housings are often available in aluminum, carbon steel, ductile iron, and 316 stainless steel while the elements are often available in aluminum or 316 stainless steel.

In some cases it may be desirable to specify an all stainless steel arrester to avoid system contamination by rust or other particles from the housing. Note that solids deposited on arrester elements might hasten blockage by slowly catalyzing polymerization in gas streams containing monomers.

Consideration should be given to the corrosion allowance for the element material as well as the arrester housing. Element corrosion will reduce the effectiveness of the arrester in quenching a flame and withstanding the destructive pressure effect of detonations. Also, increased element thickness will allow for greater periods between element replacement.

For corrosive service such as involving high HCl concentrations, it may be more economical to use a proprietary hydraulic arrester than a more conventional type with Hastelloy or other corrosion-resistant matrix material.

13.5.2 System Constraints

The length and configuration of the piping system on the run-up (unprotected) side of the arrester can determine whether a detonation will occur. This includes the positioning of any turbulence-promoting flow obstructions such as tees, elbows and valves. Thus it is of great importance to establish where ignition might occur in the system and how this will affect the flame path to the arrester. Pipe diameter also affects the distance required for DDT; larger pipe diameters typically require larger run-up distances for detonation. Testing has also shown that reductions in pipe diameter along the pipe run dramatically increase the local flame speed and pressure. The opposite effect occurs with increased pipe diameter. Although detonations may fail on encountering branches into smaller diameter pipes, run-up to detonation may later be reestablished (Frobese and Forster 1992).

Also important are the ranges of mixture composition plus operating temperature and pressure. As discussed earlier, unless a detonation arrester is used, it is essential to ensure that DDT will not occur after a flame enters the system. Even if a detonation arrester is used, it is important to use the correct type of arrester for the service. For example, if it is possible for a flame to approach from either direction, a bidirectional detonation flame arrester must be selected.

13.5.2.1 *Mixture Composition*

Detonations can only take place within the "detonable limits" which fall inside the flammable limits. Mixture composition may vary widely in some systems, and this can further depend on the number of connections feeding a manifolded header. There are few cases where it can be assured that a nondetonating flammable mixture will be produced, hence most in-line arrester applications involve detonation flame arresters.

Testing protocols presently do not address systematic variation of the mixture composition for all types of flame propagation. However, it is possible that worst cases may exist away from the near-stoichiometric mixtures used, particularly for restricted end deflagration flames (see Section 13.8).

13.5.2.2 *Operating Temperature and Pressure*

Testing should address the maximum operating temperature and pressure normally seen at the arrester location. This does not include certain upset conditions (such as emergency shutdown) that produce unusually high system pressures. In many cases it may not be possible to design an arrester for such service unless ignition can be discounted during the upset.

It may be necessary to position arresters away from heat sources that could cause the allowable operating temperature of the arrester to be exceeded. Positioning must be with due consideration of DDT run-up constraints. Testing should allow the presence of the heat source (including connection to boilers or incinerators) to be simulated.

Operating pressure is extremely critical as explained in Section 13.4. The maximum allowable operating pressure may be as small as a few psig depending on the gas involved. This constraint must be ascertained when selecting both the type of arrester that may be used and where it may be positioned in the system. This is true for both detonations and deflagrations. Note that the operating pressure relevant to arrester function is the initial pressure on the unprotected (flame) side. Thus, it is important to consider the pressure drop across the arrester including the effects of partial blockage due to fouling.

13.5.2.3 *Ignition Location*

Where a single tank vent system employs an end-of-line deflagration flame arrester, only flames entering from outside the system need to be considered. Obviously, if a flame is propagating from the protected tank side, arrester performance is already academic. In selecting a deflagration arrester, it is necessary to (1) ensure that DDT cannot occur between the atmospheric ignition source (for example an external flame) and the arrester, and (2) test the arrester under the configuration and conditions to be encountered in practice. Available test protocols are discussed in Section 13.4.

In systems where tanks have a common collection system there should be one arrester protecting each tank (see Figure 13-3). When evaluating ignition sources in manifolded tank systems, the individual tanks must be considered potential ignition sources within the system. In order to provide protection from tank-to-tank, detonation flame arresters should be installed not only on the main header but on the collection line to each tank. Wherever sufficient run-up distance exists in both directions for DDT to occur, the detonation flame arrester must be bidirectional.

Chapter 17 provides information on possible sources of ignition both internal and external to the system. These potential sources must be carefully considered before determining where arresters should be placed and the kind of arrester that is needed.

13.5.2.4 Pressure Drop, Fouling and Liquid Accumulation

In addition to manufacturers' published pressure drops for clean arrester elements, two additional factors must in practice be considered. These are due to element fouling and liquid accumulation, which will depend on the system involved. Designing the arrester for a 20% fouling factor will in many instances allow for less frequent element removal and cleaning without operational problems. A larger element area allows for a greater dispersal of particulates with a correspondingly lower pressure drop. Fouling problems may be mitigated by selecting the least sensitive type of arrester design (see Section 13.5.5). A simple method for sizing an arrester involves:

1. Determine vapor flow rate (air equivalent).
2. Determine allowable pressure drop for arrester.
3. Reduce allowable pressure drop by 20% or greater depending on the system.
4. Reduce allowable pressure drop by liquid entrainment factor (depends on arrester design).
5. Determine arrester size from manufacturers published flow curves.

Arrester designs have considerably different flow characteristics and solid / liquid blockage factors. Due to the need to allow for the hidden costs of fouling and liquid blockage, often the most economical arrester will be that with the lowest pressure drop. Note that the pressure drop can be critical in some applications such as most vapor recovery systems. Thus it is important to refer to certified test curves for arrester flow rather than calculated curves. Calculated flow rates may in some cases be several times actual.

Arrester design should allow mitigation of condensate build-up that restricts gas flow. In some cases liquid could obstruct a significant fraction of the free-flow area creating a large pressure drop plus additional problems should freezing or corrosion occur. Allowance for condensate accumulation may be made for periods where manual drainage is not possible. Any drains provided should neither provide a flame path around the element nor provide leakage in either direction when closed.

As noted earlier, if an arrester is mounted in a breather vent on an atmospheric tank, blockage might cause damage or even collapse of the tank.

13.5.2.5 Changes in Pipe Diameter

Arrester performance can be impaired if the pipe diameter increases within a minimum distance of it. A study by Lapp and Vickers (1992) showed a marked decrease in maximum allowable operating pressure when the pipe size was increased within 120 pipe diameters of the arrester. The configuration considered was in-line using a transition piece between the two pipe sizes.

Superficially the result does not agree with the findings of Frobese and Forster (1992). However, the latter study considered branch lines involving a tee piece, with the larger line open to the atmosphere. Hence, detonation propagation into the smaller pipe was side-on and much of the available energy from the detonation flowed to the atmosphere rather than through the arrester in the branch line.

An additional finding by Lapp and Vickers (1992) was that changes in pipe diameter (as above) had the largest detrimental effect during restricted-end deflagration testing. From the overall study it was concluded that a minimum separation of 120 pipe diameters must be observed for change to a larger pipe diameter.

13.5.3 Installation

13.5.3.1 Piping System and Supports

Consideration must be given to the design, selection and installation of the piping system for in-line detonation flame arresters. Of particular concern are:

- Pipe and arrester pressure ratings
- Piping structure and support
- Heat tracing and insulation

Although the peak pressure seen during DDT is very high, this pressure has a very short duration (typically 1–2 ms). During this time the structural loading seen by the piping system is minimal since the natural period of the piping components is not reached. However it is important to ensure that the detonation flame arrester be designed and tested (hydrostatic and pneumatic pressure tests) to withstand the maximum line pressure that can be seen. One typical example is arrester installation in a low pressure vapor line that may see high pressures during an emergency shut down condition. The arrester must be designed so that the housing is able to withstand this ESD situation. Even though the arrester will not be capable of arresting a flame propagating at this high an initial pressure it must be capable of withstanding the line pressure without damage.

The piping system should be designed to allow for routine access to the arrester for both inspection and maintenance. Too often this is not considered and the arrester is not assigned as part of preventative maintenance programs. Regular and routine monitoring and maintenance of the arrester is critical to ensure performance.

13.5.3.2 Heat Tracing and Insulation

For installations in cold climates, as well as applications where product freezing or crystallization is a concern, the arrester should be insulated and possibly heat traced. Where polymerization is a concern, the temperature of the heat tracing should be kept as low as possible. It is important to ensure that the temperature of the heat tracing be kept below the accepted operating range of the arrester.

13.5.4 Operation

13.5.4.1 Monitoring

The pressure drop across the arrester element can be monitored to determine the need to clean the element. It is important that the monitoring device does not provide a flame path around the arrester. Monitoring of temperature can be important to detect the presence of a stabilized flame on an arrester face. Depending on the endurance burn capability of the arrester, the temperature monitor may need to actuate a quick closing valve and stop the gas flow feeding the stabilized flame. Temperature monitors can also be used to detect if a flame ever reaches an arrester, to identify the need for inspection and maintenance.

13.5.4.2 Venting of Combustion Products

For in-line applications it is necessary to allow for the volume expansion produced in the system as gas deflagrates or detonates. The excess pressure produced by combustion will relieve through the flame arrester(s) either to the atmosphere or to protected vessels such as storage tanks.

For slow deflagrations in a relatively small volume of affected pipe there may be negligible excess pressure produced in large vessels. The most conservative case to consider is that of a detonation, for which case the storage vessel should be designed with a capacity to handle 9 times the pipe volume affected by the flame event. In practice, the factor of 9 (static pressure ratio) should be conservative owing to heat losses and other vent paths that might be present.

The arrester itself attenuates the detonation pressure peak by as much as 96% depending on the arrester design (Lapp 1992) and therefore protects from both flame penetration and much of the associated pressure pulse. To further reduce the pressure pulse, emergency relief rupture disks or pins might be incorporated at the arrester.

13.5.5 Maintenance

Lack of maintainability has long been a major weakness of matrix-type arresters. In many cases arresters have been removed from systems owing to the impracticality of cleaning at the required frequency. Some deflagration and detonation flame arrester designs allow for removal, inspection and cleaning of the element without having to expand the line as is necessary with wafer style elements. This facilitates removal and replacement while generally reducing downtime and maintenance costs. On some larger arresters the use of multiple elements facilitates removal, cleaning, and replacement of the resulting smaller elements.

For crimped ribbon styles, cleaning must be done carefully owing to the small and delicate flow channels involved. It is important not to clean the element with sharp objects that might open the flow channels and disable the arrester. At the same time, the same small flow channels may tenaciously hold solids filtered from the line. It is recommended that spare elements are available for maintenance and that special procedures be adopted for storing, transporting and cleaning the elements. If fouling problems are severe, alternative arrester designs should be considered such as the parallel plate, expanded metal cartridge, or hydraulic type, depending on the application.

For vapor lines which cannot be shut down to remove and clean arrester elements, parallel arresters with a 3 way valve may be used to allow uninterrupted operation.

It is recommended that arrester element(s) be inspected and possibly replaced after they have functioned to stop a flame. To do this there must be some method of detecting a flame. Unless a flame stabilizes on the arrester, thermocouples may not detect the heat from a successfully arrested flashback event. If used in this application, thermocouples of adequately fast response time should be selected.

13.6 SPECIAL APPLICATIONS AND ALTERNATIVES

13.6.1 Decomposition Flames

A number of gases may propagate decomposition flames in the absence of any oxidant provided they are above minimum conditions of pressure, temperature, and pipe diameter. Common examples include acetylene, ethylene oxide, and ethylene.

The best known example, acetylene, will propagate decomposition flames under atmospheric conditions in large pipe although under typical conditions an elevated pressure is required. Acetylene, unlike the other gases mentioned, can also decompose in a detonative manner.

Neither ethylene oxide nor ethylene are known to detonate in the absence of oxidant whatever the run-up distance. This is based on practical experience in addition to experimental test work. Thus, deflagration flame arresters have been developed for in-line application. Ethylene oxide arresters consisting of tube bundles of specified length and diameter have been used for many years in process units (Britton 1990). Recklinghausen of Chemische Werke Huls AG (1978) describes an alternative ethylene oxide arrester of the packed bed type. Ethylene can also propagate decomposition flames at elevated pressure. At room temperature this requires pressures in excess of 700 psig, but typical storage and transmission pressures exceed this value. Britton et al. (1986) review decomposition incidents with ethylene and mitigation methods including a U-tube bundle arrester developed and patented by ARCO. The latter arrester, mounted in a bath of water–antifreeze mixture, requires a flame detection device to indicate any flame stabilization at the arrester. Ethylene decomposition flames are exceedingly slow moving (about 1 m/s or less) and readily stabilize against gas flow. For this reason "detect, valve-in and vent down" systems featuring fast-acting valves may be preferable.

Three types of arrester used for acetylene are sintered metal, packed bed and hydraulic types. Types of dry and wetted packed bed designs using Raschig rings are discussed by Schmidt (1971). Howard (1992) discusses acetylene arresters associated with flares and recommends the use of dilution to prevent the phenomenon of "burn down" from the flare tip. Per unit mass of acetylene flared, dilution with about 1/3 this mass of natural gas or steam, or about 1/2 this mass of nitrogen, can be effective. Suitable control and monitoring instrumentation are required.

13.6.2 Conservation Vents

These devices are also known as pressure/vacuum (PV) valves or breather valves, comprising a pressure valve to allow vapor to escape plus a vacuum valve to allow air in.

Flame arresters are not considered necessary below a conservation vent on a storage tank provided the valve is set to close when the upstream pressure falls below ¾ inch water gauge and discharge is not through a piping system in which a detonation can occur. Under this condition the gas velocity through the valve will be considerably greater than the speed at which the flame can propagate past it to the tank. To address the possibility of airborne "sparks" (such as hot cinders) being drawn through the vent without being quenched, the USCG requires a tested flame screen be installed on the vacuum port.

If flame arresters are installed they must be maintained to prevent possible blockage that could disable the vent, possibly damaging or destroying the tank. This is difficult to assure at all times, while such vents will normally be required to be in operating condition constantly. While conservation vents do not act as flame arresters, it has been shown that their mode of operation effectively prevents flame penetration through the vent line as recognized in API 2000, *Venting Atmospheric and Low Pressure Storage Tanks.*

13.6.3 Velocity Flame Stopper

Howard (1975, 1992) discusses the use of these devices in certain end-of-line applications. The principle of operation is that if the flow velocity through an orifice is larger than the flashback velocity for that size of hole, the flame will be arrested on the downstream side. The hole will however allow flame passage if flow velocity falls below the required value. Grumer et al. (1985) of the U.S. Bureau of Mines discuss the principles of flashback and provide a large body of experimental data.

13.6.4 Flame Arresters in Series

As discussed in API 2028 (1991), placing two flame arresters in series offers only slight additional protection when compared to a single arrester. There has been little test work to investigate possible benefits of arresters in series, such as any reduction in reflected shock effects (restricted-end deflagrations). However, if a unidirectional arrester is required to have bidirectional capability, the use of series arresters back-to-back might be considered (this would normally not be cost effective compared with a single bidirectional arrester).

13.7 CONCLUSIONS

Deflagration and detonation flame arresters can be the last line of defense in facility protection. For this reason a number of guidelines for arrester selection, installation and operation must be followed:

1. Use only an arresting device accepted by standards setting organizations within the range of the testing parameters used for acceptance, including:
   —Operating pressure
   —Vapor composition
   —Pipe length
2. If a device is not already certified as meeting the above condition it should either be so tested or subjected to testing under simulated operating conditions, including
   —Vapor composition
   —Operating pressure and temperature
   —Pipe configuration
   —Flow rate

3. If an arrester is provided with cowls, weather hoods, deflectors, etc., it must be tested for the configuration involved.
4. Maintenance of the arrester should not adversely impact its performance.
5. The arrester should be inspected internally once per year, or sooner, if operational experience has demonstrated frequent fouling or deterioration of the arrester element.
6. The arrester must not be installed in pipes larger than the arrester has been tested for.
7. When a flame may arrive from a larger diameter pipe the arrester should be installed no closer than 120 pipe diameters from the larger line. This allows transient large overpressures and velocities produced by the reduction in pipe diameter to dissipate.
8. Continuous monitoring should be carried out. After an arrester has successfully stopped a flame, internal inspection should be made with possible element replacement.

13.8 FUTURE DEVELOPMENTS

Owing to the cost and difficulty in carrying out full scale flame arrester tests there is considerable benefit in obtaining an international consensus on performance standards, including the testing used to prove standard compliance. At present there are obvious flaws in a process that regulates an arrester in marine service according to the highest published standards, yet is flexible regarding selection and use of a nonmarine arrester which can be in analogous service. The existence of several contemporary but disparate standards and test methods reflects, at the very least, a large duplication of effort. One likely future development is in the area of consensus.

As noted in Section 13.4 of the text there are several areas in which arrester test methods might be improved or extended:

1. Endurance burn tests are presently subjective owing to the need to optimize variables as the test is underway. Reproducibility might be improved by specifying flow velocities or mixture compositions for typical standard gases such as propane and ethylene. It is essential that burn tests use appropriate configuration. For example, if the flame is stabilized on the upper face of a vertically mounted arrester, the arrester will receive minimal heat flux. This could lead to a significant overestimate of the arrester's endurance in practical service should the arrester encounter a flame on its lower face or be horizontally mounted.
2. Closed end deflagration testing with optimized run-up distance is presently voluntary, despite evidence that an optimized run-up distance can

provide the limiting condition for maximum acceptable operating pressure.

3. It is not easy to subject an arrester to overdriven detonations during a limited series of tests. Different test centers may succeed to different degrees. A reliable technique is needed for producing overdriven detonations at the arrester being tested, so that the requisite number of tests can be standardized.
4. Long run detonation tests are not mandated although this condition may easily be achieved in practical situations.
5. The stoichiometry of the test mixture is not systematically varied under present test protocols. The use of near-limit mixtures may produce overdriven spin or galloping detonations whose effect on detonation arrester performance has not been investigated. Significantly rich mixtures usually produce the fastest burning deflagrations, the lowest minimum ignition energies and lowest autoignition temperatures. Using such rich mixtures the acceptable operating pressure found for optimized closed end deflagration testing might be further reduced. To mitigate this effect, minimum lengths of straight pipe run downstream of the arrester might be specified to avoid the coincident arrival of the flame and its reflected weak deflagration shock at the arrester.
6. Fundamental work has yet to be done to prove the relevance of MESG in arrester performance.
7. Novel arrester designs are needed to meet the challenges likely to arise from optimized tests. It will be necessary to increase the acceptable operating pressure for arrester function, in particular for faster burning gases such as ethylene.

13.9 REFERENCES

13.9.1 Regulations, Codes of Practice and Industry Standards

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4

EQUIPMENT DESIGN

4.1 INTRODUCTION

The discussion in this chapter follows the usual sequence of plant operations, of first unloading and storing raw materials and then processing raw materials in various major pieces of equipment. Design codes represent only minimum requirements and must be supplemented by good engineering judgment based upon a thorough knowledge of the equipment service and its potential hazards.

4.2 LOADING AND UNLOADING FACILITIES

"At least 27 people were taken to area hospitals after a late night chemical spill sent toxic fumes over two . . . industrial plants. The leak . . . occurred about 10:45 p.m. when a freshly loaded tank truck left a loading dock with hoses still attached, officials said" (*Houston Post,* June 1992).

Loading and unloading facilities have long been recognized as plant operations with a high potential for hazardous material accidents. This is due to a combination of the high traffic required in the area compared to other plant operations, the problems of providing secondary containment and safety shutoffs, the high probability of personnel exposure, and the constant connection/disconnection between the transport containers and the fixed piping. While the actual design of the loading/unloading facilities will differ greatly between plants, facilities may be grouped into four general types:

- *Containers*—for gas, liquid, or solid materials. Containers range from a gallon or less, to the standard 55 gallon drums, to the relatively recent Flexible Intermediate Bulk Containers (FIBC) that may contain 1 to 6 m^3, with mass capacity ranging from 300–1000 kg.
- *Tank trucks/tank cars*—for gas and liquid materials, tanks for overland transport ranging from approximately 4,500 gallons to 35,000 gallons.
- *Ships/barges*—for gas, liquid or solid materials.
- *Bulk solid hopper cars and trucks*— for powders, granular and lumpy solids, and pellets.

Common elements addressed in the design phase for these facilities include:

- *Traffic patterns and vehicle movements*—The facilities should include adequate room to maneuver vehicles. Proper design of the unit will reduce the chances of two vehicles colliding in the unit or of a vehicle hitting plant equipment while maneuvering. This is particularly important when dealing with containers, where dozens of vehicle trips may be made in a day. Protection can come from placing and designing the loading facility to eliminate through traffic and minimize cross traffic and by the installation of fences and crash barriers to protect fixed equipment and hoses.
- *Control of ignition sources*—For facilities dealing with flammable/explosive materials, open flames, hot surfaces, electric and static electric discharges, and other potential ignition sources, should be eliminated or minimized. The elimination of these sources should include the use of plant pumps and power to transfer the materials rather than using the internal combustion (IC) powered pumps on the transport vehicle. The transport IC motors should be turned off and locked out to prevent restarting the engine prior to the completion of the material transfer and the disconnection of the grounding equipment.

  Electrostatic buildup is possible in many systems where organic and other materials are being transferred, but proper grounding techniques can eliminate this problem. See Chapter 11 for a discussion on static buildup and the proper grounding techniques. In some cases, such as during marine terminal transfers, grounding may introduce hazards due to stray current arcs. Refer to Chapters 12 and 17 for a description of this problem and the use of insulating flanges.
- *Flammable/explosive materials*—Flammable and explosive vapors and dusts need to be retained within a closed system. For vapors, it is sometimes possible to create a closed-loop system where the vapors displaced during the transfer are sent back to replace the liquid removed from the delivery tank or tank truck. In many cases, however, this is not possible due to the plant having the incorrect type of tank to receive the vapors, the plant not wanting to mix air with the inert atmosphere in a tank, or the plant not wanting to take the chance of cross-contaminating their material with vapors from a common carrier. In these cases it is frequently necessary to install a treatment/recovery system to minimize vapor releases to the atmosphere. These units may be material recovery units, such as condensers or adsorbers, scrubbers, or thermal destruction units, such as flares separate from the main plant flare systems. The vapor control units need to be spaced and controlled in the same manner as any other operating unit. Dusts are normally controlled through the use of scrubbers, baghouses or electrostatic precipitators that use physical means to collect and store the dusts.

The loading areas will also require fire detection systems, hydrants, monitors, and fixed water/foam delivery systems to protect the area in case of a fire. See Chapter 16, Fire Protection, for greater details on these requirements.

- *Toxic materials*—Many of the systems used to control flammable or explosive materials also apply to controlling toxic material releases. Additional measures may be required, however, for certain highly toxic materials. These measures may include:
  —The use of dry-connect, spring loaded couplings to prevent the spillage of material from hoses
  —The purging of piping and hoses to remove the toxic materials between loadings
  —The rinsing and cleaning of empty containers, tank cars, and tank trucks to prevent the possibility of offsite material exposure. These rinses must also be properly collected and handled.
  —Toxic gas detection sensors and alarms
  —Special clothing and safety equipment for personnel in the area
- *Connections and material routing*—Where it is necessary for a loading/unloading area to handle multiple products, several actions can be taken to ensure that potentially incompatible materials are not mixed. Whenever possible, separate feed lines should be constructed to allow each material its own piping system. Well marked pipes and hoses, hoses of different size and hoses with different types of connectors can reduce the chances for an operator to make a mistake.

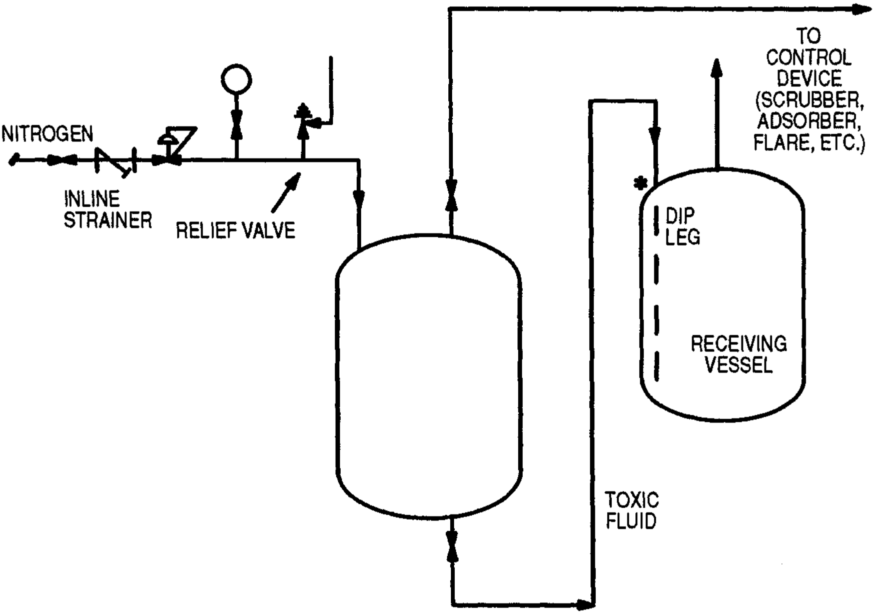
  It is sometimes necessary, however, to transfer multiple products through a common line or pump. Engineering controls, such as use of a programmable logic controller with interlocked systems or built-in system redundancies for reliability can reduce the possibility for mixing incompatible materials. Special procedures and operator training must be provided to ensure all controls are safely performed.

  Care should be taken in the choice of piping connectors between the transport tank and the plant piping. Swing arms offer the added safety of hard piping but the swivel joints tend to develop small leaks and the swing radius of the arm may limit the placement of the transport vehicle. Flexible hoses can be run anywhere and connected in any position but their greater vulnerability to material failure (due to abrasion or kinking) means that inspection, maintenance, and replacement requirements will be higher than those for the swing arm.
- *Secondary containment*—Secondary containment should be installed at all liquid loading/unloading stations. The containment should be sized to hold the contents of the largest container that will be used at the facility plus the rainfall from a specific design storm, usually a 25- to 100-year maximum storm. The curbed area should be sloped to drain the liquids away from the area immediately under the transport vehicle. If the material is flammable, reactive or otherwise immediately dangerous, the

material should be directed to a collection area or sump placed away from the loading area. If flammable materials are being transported, additional freeboard may also be required to handle the water/foam used in fighting a loading area fire. Secondary containment is not normally provided for solids or for materials that are gases at ambient temperatures.

- *Procedures*—Internal procedures, including physical interlocks, checklists, and training should be developed to ensure that all required safety measures are taken prior to material loading/unloading. These measures may include:
  —Chocking the transport vehicle's wheels
  —Turning off all vehicle motors and preventing a motor restart
  —Grounding
  —Checking the level of the receiving vehicle or plant tank to make sure that adequate storage capacity is available
  —Inspection of the hoses and connectors, safety devices and alarms
  —Identification of cargo contents

Hazardous liquids and some hazardous powders can be transferred by using a pressurized gas or a vacuum to avoid pumping the materials (Figure 4-1). Some chemical manufacturers recommend these methods for unloading



*Note: Provide an anti–siphon device.

Figure 4-1. Pressurized inert gas forces liquid from tank at left into one at right (Grossel 1990) products to reduce degradation to the product that may be caused by mechanical shear in the pump. Pressurized systems use nitrogen, air, or other gas under moderate to high pressure to force the material from one container or tank to another through the connecting piping. To protect the vessels against overpressure, should a pressure reducing valve fail, and also to prevent venting of the hazardous material, the gas supply line should be provided with a pressure safety valve set below the maximum working pressure of the tanks. Standard precautions should be taken to prevent the asphyxiation of personnel in a confined area if a gas other than air is used; these precautions may include a low level oxygen alarm and shutdown along with providing short term self-contained breathing apparatus (SCBA) equipment, whenever hazardous liquids are transferred by pressurized gas, it should be possible to quickly depressurize the system by a rapid bleed-off of pressure to a safe location.

Materials that are normally stored and transferred as liquified gases, such as dimethylether or ammonia, may require a pressurized closed loop pumping system where vapor from the receiving tank is recompressed and returned to the sending tank. This type of system may include the use of coolers or chillers to remove the heat added to the material in the recompression. If a sudden leak occurs in the system, a quick depressuring relief may be required to rapidly bleed off pressure to a safe location.

Some materials such as acetylene, ethylene, and other compounds may decompose if suddenly pressurized or depressurized. Operating procedures and supplementary equipment should be provided to reduce the possibility of such occurrence.

Vacuum suction transfer, common in batch process operations, can also be used to move materials. The vacuum system can be designed to handle multiple transfers simultaneously while using only one set of vacuum pumps or ejectors in a central location. The vacuum system usually consists of a branch line and header network, a decant drum or condenser with knockout, and the vacuum pump or ejector.

Safety design problems deal primarily with those cases in which an explosive or flammable mixture can be created in the vacuum system. Design solutions include sealing the system to prevent the infiltration of outside air, the use of inert gas in the tanks, explosion-proof pump motors, and the removal of ignition sources.

Other design problems can include the reuse/disposal of the liquid recovered from the decant/condenser unit, which may contain several materials and the treatment of the vacuum exhaust, which may contain significant quantities of regulated or toxic materials. It may be necessary to treat the exhaust effluent with a scrubber, adsorber or incinerator prior to the exhaust's final release to the atmosphere.

4.3 MATERIAL STORAGE

Storage areas in the plant usually contain the largest volumes of hazardous materials. Frequently storage areas contain flammable liquids or liquefied gases. The main concern in the design of storage installations for such liquids is to reduce the hazard of fire by reducing the amount of spillage, controlling the spill, and controlling fire.

It cannot be emphasized enough that reducing the quantities of hazardous materials is the single greatest method for reducing the hazards of fire or explosion. Minimizing storage quantities also reduces the potential for large spills and further damage. Pipeline feeds from a reliable source can eliminate the requirement for large storage areas.

Solid chemicals may be stored in bulk in bins, hoppers, piles or containers. Liquid chemicals may be stored in tanks, reservoirs or specified shipping containers. Gases may be stored in low pressure gas holders, in high pressure tanks or cylinders; or in liquid form in tanks or containers under pressure, refrigeration or both. Pressure and temperature of storage greatly affects dispersion/emission of liquid or vapor in case containment is lost (see Chapter 2). Important considerations are separation distances and diking arrangements (see Chapter 3).

4.3.1 Design of Storage Tanks and Vessels

Detailed information on mechanical design, fabrication and nondestructive examination of storage vessels is found in many standard references. A recent survey of design guidelines is provided in *Guidelines for Storage and Handling of High Toxic Hazard Materials* (CCPS 1988). Those *Guidelines* also provide a listing of relevant design standards.

Design of storage vessels and related piping is addressed in:

- API Std 650 Welded Steel Tanks for Oil Storage
- API Std 620 Recommended Rules for Design and Construction of Large, Welded, Low Pressure Storage Tanks
- API Std 2000 Venting Atmospheric and Low Pressure Storage Tanks
- ASME Boiler and Pressure Vessel Code, Section VIII
- API Std 2510 Design and Construction of Liquified Petroleum Gas (LPG) Installations
- ASME Code for Pressure Piping B31.3, Chemical Plant and Petroleum Refinery Piping.
- UL 58—Steel Underground Tanks for Flammable and Combustible Liquids
- UL 142—Steel Above-ground Tanks for Flammable and Combustible Liquids

- Miscellaneous NFPA guidelines
- Design guidelines and recommended practices provided by industrial insurers (FM, IRI). This information is often intended for storage of specific materials, but may have wider application.

Whether intended for use at atmospheric, low pressure, or high pressure conditions, the primary considerations of tank design are stresses, both pressure and thermal, including fire exposure. The objective is to maintain working pressure within permissible limits by providing pressure relief (outbreathing) and vacuum relief (inbreathing).

The two main types of large tanks (50,000 gallons) used for storing liquids at near atmospheric conditions are the welded vertical flat bottom tank with a fixed cone, flat, or domed roof, and the welded vertical tank with a floating roof in place of the cone roof (see Figure 4-2). Both types can be used to store

ORDINARY CONE ROOF TANK

FLOATING ROOF TANK

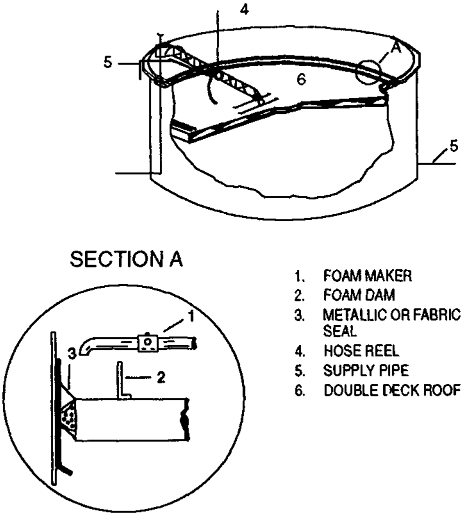


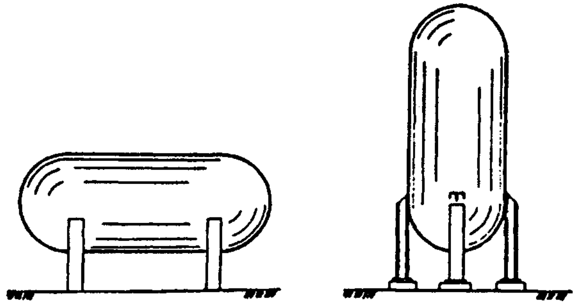
Figure 4-2. Schematic representation of various types of storage tanks.

hazardous materials. The fixed tank is normally preferred in applications where it is desirable to collect and treat all emissions from the tank or where an inert gas is used to reduce the possibility of fire, explosion, or chemical reaction. Floating roof tanks are typically used where the vapor pressure of the stored fluid would be excessive for a cone roof tank or where collection of emissions from the tank is not required but it is still desirable to minimize them. It should be recognized that a drain can be provided, but drains can plug up and the roof could then flood and sink. For environmental emissions controls, domed or cone roof tanks with internal floaters are also now common. For many types of materials, particularly for organics, the type of tank that may be used will be governed by the EPA or by state environmental authorities. The material's vapor pressure (VP) is the main determining factor. Most organics with a VP below 1.5 psia can be stored in fixed roof tanks; materials with a VP between 1.5 and 11 psia must be stored in at least a floating roof tank; and for organics with a VP over 11 psia tank emissions must be recovered for reuse or destruction. For some specific compounds, these regulations may be stricter.

For smaller near-atmospheric tanks, horizontal tanks, at ground level on saddles or on legs or vertical tanks on legs or skirts are used. These are normally cylindrical tanks with various combinations of heads (see Figure 4-3). For materials such as butane or ammonia that are normally stored as pressurized liquids, pressure spheres are normally used. These spheres may be insulated; pressure is normally maintained by recompressing the tank vapor and returning the liquid to the tank after cooling it. For liquids or gases requiring high pressure storage horizontal tanks on saddles are used. These tanks are cylindrical with elliptical or domed pressure heads.

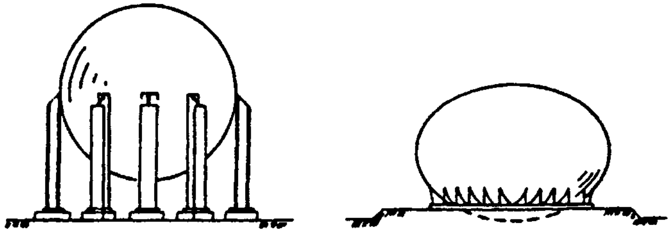
Safety design considerations are:

- Pressure/vacuum relief valves (including conservation vents for atmospheric tanks) and relief discharge venting
- Fire relief and protection, including fire loops and monitors, protective sprays, foam application, and flame arresters
- Foundations, fabrication techniques and anchorages
- Materials of construction and corrosion
- Design considerations for related pipework and fittings including stresses due to movement, expansion/contraction, vibration, connections, valves, and layout (see Chapter 6, Piping Systems)
- Selection of ancillary equipment including pumps, compressors, vaporizers, etc.
- Consideration of the range of operations as well as nonoperational periods such as commissioning, decommissioning, unit shutdowns, and tank cleaning.



HORIZONTAL CYLINDRICAL TANK

VERTICAL CYLINDRICAL TANK



SPHERE

SPHEROID

Figure 4-3. Representative types of pressure tanks for the storage of voltile liquids.

Instrumentation for monitoring and control, as discussed in Chapter 9 and elsewhere (CCPS 1988), is critical in regulating normal storage and handling operations and anticipating conditions that could result in loss of containment. Monitoring of pressure, temperature, level, and flow are commonly used. Some generic concerns about instrumentation include provisions for uninterruptible power supply for critical instrumentation and control systems, reliability, redundancy, and calibration.

4.3.1.1 Safety Considerations for Atmospheric Storage Tanks

Hazards associated with atmospheric tanks (ambient pressure to 15 psig) include overpressure and underpressure, vapor generation, spills, tank rupture, fire and product contamination. In addition, differential settlements, seismic and wind loadings are important concerns. (See API RP 620 and RP 650.)

Overpressure and Underpressure. Internal deflagration is a concern because of the presence of a flammable organic/air mixture in the presence of an ignition source. This mixture can occur during filling, emptying, or mixing in tanks that contain vapors of organics near their flash point. The mixture may also occur in stored products containing impurities or light gases such as hydrogen in petroleum fractions as a result of an upset in an upstream process unit.

Fixed-roof tanks can be constructed as "weak-seam roof tanks" which are designed so that the roof-to-shell connection will fail preferentially to any other joint and the excess pressure will be safely relieved if the normal venting capacity should prove inadequate (API Std 2000). The pressure-venting capabilities can be defeated by erroneous construction. A peripheral railing and walkway, if attached to the top of the wall and to the outer portion of the roof, make the wall-to-roof joint too strong relative to the strength of the wall-to-floor joint. The result is that overpressure may cause the bottom to cup up and tear loose from the wall, instead of tearing off the roof (Howard 1988). This is a critical concern for tanks with a diameter less than 10 m (30 feet). Weak seam tanks for storing toxic materials are generally discouraged since a tank rupture would release the material to the atmosphere. Additional pressure relief devices, directing the hazardous material to a safe area, are used to protect the tank.

Roof sections that could be propelled during an explosion must be restrained with a roof hinge, or cable and springs.

Underpressure (vacuum) in fixed roof tanks can be caused when material is rapidly withdrawn or when a sudden drop in temperature or pressure, usually caused by weather conditions, reduces the volume of the vapor in the tank. The underpressure protection should be sized to handle the maximum withdrawal rate plus the maximum temperature/ volume reduction occurring simultaneously (see API Std 2000 and NFPA 30). The vacuum relief device should be located at, or near, the highest point in the tank. In addition, differential pressure measurement relative to local ambient conditions must be provided.

Excessive Vapor Generation. Excessive vapor generation is the result of a deviation of temperature or routing of products more volatile than the design fluid. For tanks provided with internal heaters, adequate level should be maintained above the surface of the heater so as not to overheat the tank contents and cause vapor generation or reach the autoignition temperature. Adequate venting capacity should be provided for excess vapor generation or coil rupture.

The polymerization of materials in a tank can yield sudden high overpressure combined with elevated temperatures in the tank. In this situation standard pressure relief valves may not be enough, both because very large two-phase flows may be involved, and because solid, polymerized materials may plug the relief valve. In these cases rupture discs with ducting leading to the atmosphere may be used, with the relief effluent being directed to a safe area of the plant. If the polymerization of the tank can yield potentially hazardous materials, the safe area may include an isolation or containment tank or sump for the hazardous material. Additionally, the discharge piping should be anchored, and the pipe elbows braced to counteract the thrust placed on them by a discharge of this type.

Another example of excessive vapor generation occurs in pressure sphere storage tanks where rollover has occurred. This phenomenon is due to stratification of the tank contents causing a dense upper layer which ultimately rolls to the bottom releasing a massive vapor load from the lower (warmer) tank contents. This phenomenon is avoided by carefully keeping the contents mixed and by not loading warm material into the bottom of the sphere using a dip leg. A recent accident attributed to a process similar to rollover is described by Kletz (1991a). Warm (+10°C) ammonia was loaded into the bottom of a tank of refrigerated (–33°C) ammonia. Kletz suggests that the warm ammonia rose to the surface, evaporated, and the overpressure overwhelmed the relief valves, resulting in the tank failing. The tank split from top to bottom, releasing 7000 tonnes of liquid ammonia, forming a pool about 2 feet (0.7 m) deep which caught fire; the fire subsequently spread and resulted in loss of life and many injuries.

Tank Spills . Common causes of spills are:

- overfilling due to operator error or high level alarm failure (vehicular as well as stationary tanks)
- withdrawal of water from the tank bottom without operator attention
- mechanical failure of tank support causing collapse of roof
- accumulation of a large volume of water, snow or ice on the tank roof causing collapse and subsequent exposure of liquid surface

An additional cause of spills is specific to floating roof tanks. It is possible for the roof platform to tilt slightly and become wedged into one position. Withdrawal of material from the tank, leaving the roof unsupported, or the addition of material to the tank, forcing fluid up over the roof, may cause the collapse of the floating roof. This is most common when the interior of the tank must be serviced and the roof must be supported on its legs rather than by the tank fluid.

Strategies to avoid spills and minimize damage to other units are:

- Instrumentation for tank high level and flow total alarms and shutoffs should be completely separate from the normal level and flow measurement with separate sensors and control units. Inherently safer design incorporates overflow lines routed to a safe location and secondary

containment. Level sensors that depend upon pressure differential to detect level changes should be avoided where changes in the specific gravity of the tank contents are expected.
- Provide safe method of water withdrawal from tanks storing organics and water drainage from the roof the tank.
- Provide secondary containment around tanks to prevent spills from spreading to other areas. This can take the form of dikes, double walled tanks, or tanks in a concrete vault. The containment should be capable of holding the total volume of the largest tank within the containment area plus the rainfall from a specified storm, usually a 25- to 100-year rainfall event. Consideration should also be given to the need to contain firefighting water within the secondary containment. The appropriate EPA and state environmental codes should be checked to determine the exact amount of secondary storage as regulatory requirements may vary depending on the chemical and the location. The diked area should be sloped to a low point or sump to allow for the easy removal of liquids. Care should be taken to make sure that the materials stored within a containment area are compatible and that an adverse reaction will not take place if the materials are mixed during an accident.
- Overflow lines should be sized to allow full flow in case of a tank overflow. A general rule of thumb for estimating the size of overflow piping is that it should be sized at least one standard pipe size larger than the inlet pipe, but the exact size will be dependent upon the pressure drop in the pipe. The minimum overflow line size for a self-venting line is $D(\text{inches}) = 0.92(Q[\text{gpm}])^{0.4}$ (Simpson and Weirick 1978). For extremely cold locations, overflow lines should be heated to avoid freezing of condensed atmospheric moisture which can restrict the pipe.

It should be noted that atmospheric tank overflow lines are also a source of vapor releases when volatile fluids are introduced.

Tank Rupture. A tank rupture is the sudden loss of tank integrity over a relatively large area of the tank structure, causing a large loss of contents. It can be caused by any of several conditions: overfilling, overpressure due to an internal chemical reaction or material boiling due to a constant exposure to heat, continued impingement of flame over an area of the tank, loss of wall integrity due to corrosion, or loss of wall weld integrity. In a major rupture, such as a tank failure near Pittsburgh, Pennsylvania in January, 1988, the force of the falling material can be so great that large amounts of the material can be pushed up and over the diking and into the environment (Loss Prevention Bulletin 1992).

The chances of tank rupture can be reduced by attention to several design features:

- the proper use and sizing of overflow piping and pressure relief safety valves and rupture disks.
- the installation of the appropriate high level alarms and flow shutoffs to prevent overfilling
- the installation of water sprays to protect exposed tank walls during a fire
- the diked area should be sloped to a sump within the diked area
- the proper specification of tank materials and thickness, including corrosion allowances
- the inspection of tank welding during and after construction and the pressure testing of the tank prior to use.

Frothover/Boilover. A frothover occurs when the tank temperature increases to the point where water in the tank starts to boil, forming a froth of organics and steam. If froth formation is violent, it may result in frothover of ignitable organics or other fluids, causing a major fire. Frothovers may be caused by:

- mistakenly routing water into a storage tank containing hot oil, creating a steam explosion
- an equipment failure upstream causing water to leak into products being routed to storage
- routing cold light hydrocarbons to hot tanks or hot heavy hydrocarbons to cold tanks
- water in the bottom of mixed or crude oil storage tanks vaporizing during a fire.

Storage temperatures should be at least 7°C (12°F) below the boiling point of water to avoid water boilover.

Fire. When flammable materials are being stored, fire is the greatest hazard normally addressed in the design of the storage system. Design items that should be addressed in this area are given below.

- Protection against electrostatic charges which can cause ignition. This may include the bonding and grounding of the tank, piping, and other ancillary equipment and the use of bottom or dip-pipe loading to minimize material splashing in the tank.
- Fire fighting facilities applicable to the type of tank protected. This can include fire loops with hydrants and monitors in the storage area, foam systems for the individual tanks, and deluge spray systems to keep the exposed surfaces of tanks cool in case of fire in an adjacent tank.

  Foam systems usually consist of a foam storage tank, an incoming firewater line, a mixing fixture, foam / water piping up the side of the tank, and foam / water applicator nozzles. The systems for fixed roof tanks are designed to create a foam layer over the flammable material in the tank.

The systems for floating roof tanks are designed to cover the space immediately over the seal area, but if an internal floating roof is constructed of lightweight materials, the foam system should be designed as if the tank were a cone roof type.

- Adequate spacing between tanks.
- Install flame arresters on atmospheric vents to prevent impinging fire on the outside of the tank from reaching the vapor space inside the tank (see Chapter 13, Deflagration and Detonation Flame Arresters).
- Do not use air to mix flammable materials.
- Provide fire resistant insulation for critical vessels, piping, outlet valves on tanks, valve actuators, instruments lines, and key electrical facilities.
- Provide remote controlled, automatic, and fire-actuated valves to stop loss of tank contents during an emergency; provide fire protection to these valves. Valves should be close-coupled to the tank, and must be resistant to corrosion or other deleterious effects of spilled fluids.

Contamination of Product. The contamination of material in tanks by the introduction of incompatible materials or material of the wrong temperature can cause runaway reactions, polymerization, high temperature excursions, or underpressurization of the tank. To avoid potential contamination of products or routing wrong materials to tanks, piping valves and manifolds to the tank should be clearly marked, operating procedures should be simple and well-defined, and periodic operator training should be provided.

Plant upsets or emergency shutdowns can affect the quality of product routed to tankage. The designer must evaluate the potential effects of these events and mitigate them. Protection features can be incorporated into the design of *process* units that can reduce or eliminate hazards in tank storage areas. Two such features are:

- Monitor streams routed to tankage for deviations from product specifications.
- Emergency rundown coolers for hot streams routed from a process unit to tankage in the event of downstream unit shutdown, if the fluid temperature exceeds the acceptable tank temperature.

4.3.1.2 Inerting

Inerting can be used to reduce the possibility of tank fires in fixed roof tanks by preventing the formation of a flammable vapor mixture in a tank. An inert gas, usually nitrogen or carbon dioxide, is used to replace the air in the tank's vapor space, removing the oxygen needed to support combustion. The inert gas is usually fed into the tank by one of two control methods—a pressure demand system or constant flow regulation. Care must be taken to ensure that the inerting system is sized to deliver the maximum flow of gas needed during operations in order to prevent underpressurizing the tank. It is also necessary to make a decision on what should happen if the inerting system fails in the off position. A vacuum safety valve can be installed so that air is used as the backup for the inerting gas to prevent tank failure so long as no additional hazards are introduced; some companies, however, prefer to allow the tank to collapse rather than introduce air into a tank containing flammable materials. The inerting system should be designed so that there are no low-point pockets in the inert gas supply line downstream of the pressure regulator. It must also be noted that inerting a tank does not prevent the release of material vapors into the tank's vapor space. Material vapors will diffuse into the inerting gas until an equilibrium is reached, just as it would with air. This is important to remember when designing tank purging systems and when estimating the toxic and volatile organic compounds (VOC) material releases for the plant.

Tanks containing hazardous materials can be placed above ground or under ground. Underground tanks offer increased safety for flammable and explosive materials and they require a smaller buffer zone between the tanks and other plant processes. The underground placement, however, adds to the probability of soil and groundwater contamination due to the difficulty of inspecting the underground tanks. To reduce the chances of leakage, the tanks should be double-walled or contained in concrete vaults. The space between the primary tank and the secondary containment should be equipped with some form of leak detection system. Double-walled piping with a leak detection system is also strongly recommended for underground installations. Above ground tanks are more vulnerable to fire or collision, but the tank and its ancillary piping are generally capable of being visually inspected for leakage. The only portion of the tank that cannot be regularly inspected is the floor, which should be checked by nondestructive testing on an regular basis. When specifying new tanks or revamping an existing tank, a second, false floor with supports can be put into the tank 8 to 10 cm above the main floor. The space created can be used as a secondary containment tank floor, and leak detection systems can be installed to warn of leaking product.

The new API Standard 653 "makes allowance for constantly improving leak- and corrosion-detection technologies, or for advanced inspection practices. . . . Because the interval between internal inspections is governed by such factors as the use of a liner, amount of corrosion allowed, cathodic protection and leak detection, these items should be taken into account when a new tank is considered" (Myers 1992).

4.3.1.3 *Pressurized Storage Tanks*

Pressurized storage tanks for gases, generally sphere or bullet, must meet all requirements under the ASME boiler and pressure vessel codes as well as the applicable NFPA codes such as 58 for LPG storage. Many of the safety considerations that apply to atmospheric tanks also apply to these tanks. Design differences in the two types of tanks are detailed below.

Overpressure is handled by means of pressure relief valves and rupture disks (see Chapter 14, Pressure Relief Systems). When the tank contents are organic the tank often relieves to the plant's flare system for burning prior to atmospheric release. Underpressure is not normally a problem as many pressurized storage tanks are also designed for full or partial vacuum, but some types, such as large butane storage spheres, can collapse under certain conditions.

Pressurized tanks are designed to relieve overpressure due to flame impingement or heat radiation from nearby fires. Protective water sprays for the tank are sized to cool and protect the exposed tank faces, but not to extinguish any flame coming from the tank. A depressurization valve may be provided to prevent a boiling liquid expanding vapor explosion (BLEVE) from occurring.

Pressure vessel tanks may also be designed in accordance with UL 58 and UL 142 for atmospheric storage.

4.3.2 Safety Considerations for Container Storage

The primary additional safety concern when hazardous materials are stored in containers is the large amount of vehicle and employee traffic associated with containers combined with the hazard caused by constant handling. Storage areas should be designed to allow the smooth flow of traffic without the need to constantly maneuver a forklift or truck. The storage area should be arranged to allow personnel access to inspect all containers for leakage or other damage on a regular basis. The storage of compressed gases should meet all the requirements specified in the applicable OSHA standards, while flammable materials storage should meet those specified in NFPA 30. It is recommended that the warehouse storage areas of hazardous liquids include secondary containment similar to that required for liquid hazardous wastes in 40 CFR 264—an area with an impermeable liner that can contain at least 10% of the total volume of the containers or the largest container, whichever is larger. Incompatible materials should be kept separated so that any spills cannot mix. The storage of containers in rack areas may require specialized fire control systems such as individual sprinkler lines to deliver water or foam directly to each rack level. The placement of drums in processing area for the dispensing of the contents may not need to meet the same stringent storage specifications, but it will still be necessary to meet all pertinent safety requirements. The process drums area may include safety barriers to prevent traffic from hitting the drums, portable drum sumps to contain any spills, a ventilation system to control fumes, and double valving or a valve and plug to minimize drum leakage.

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4.3.3 Safety Considerations for Bin Storage

The safety considerations for the bin storage of powdered or pelleted materials is similar to that for fixed roof tanks. The primary danger in the bins comes from dust in the vapor space above the material creating an explosive or ignitable condition. Ignition sources should be minimized and dust conditions reduced by the use of filters or baghouses. A safety vent or rupture disk should be included to prevent overpressurization in case the filter bags clog during operations. Care should be taken during the design of the bin to reduce horizontal surfaces inside the bin where material can remain and create a hazard when the bin is opened for maintenance; the air above such areas has been known to explode while work inside the bins was being performed during normal repairs. Additionally, the bin can be inerted in a manner similar to that used for atmospheric storage tanks (NFPA 68 and 69). The pneumatic transfer of solids can also be preformed using an inert or a low-oxygen gas with a closed loop return to the sending tank.

4.4 PROCESS EQUIPMENT

Unit operations may include physical operations and further processing or preparation for further reactions or for shipment. These operations include mixing or separating, size reduction or enlargement, and heat transfer. General hazards in physical operations are:

- vaporization and diffusion of flammable liquids and gases
- spraying or misting of flammable liquids
- dispersion of combustible dusts
- mixing highly reactive chemicals
- increase in the temperature of unstable chemicals
- friction or shock of unstable chemicals
- pressure increase in vessels
- loss of inertants or diluents

Both design and operations are important in maintaining the integrity of the process and equipment. The high pressures and temperatures frequently used in the process accelerate the dispersion (release) of hazardous materials after loss of containment; therefore, maintaining the integrity of the system is critically important.

Failure of a column, associated piping or equipment may release substantial quantities of vapors or liquids above their boiling points, resulting in a flammable vapor cloud explosion or flash fire (FMEC 1974a,b). Failures of liquid/solids and solids handling equipment may release hazardous liquids and dust, creating a fire, explosion, or health hazard.

10

DOCUMENTATION

Documentation is important to long term management as well as the day to day safe operation of a chemical facility. As the regulatory mandate for documentation evolves, failure to maintain accurate and complete records can become a legal liability. Documentation is frequently the means to implement a corporate process safety management program and to verify plant compliance to its provision.

Many industry guidelines (e.g., API RP 750 and the CMA Process Safety Code) and regulations (e.g., 29 CFR 1910.119, California Risk Management & Prevention Program legislation, New Jersey Toxic Catastrophe Prevention Act) dictate document requirements and retention periods. This chapter does not discuss the specifics for each of these statutes, but in general they are similar and form the basis for the guidelines described here. Essential components of a chemical process safety management program are listed in Table 10-1. Several of the components (such as emergency planning and response, incident investigation, contractor issues) are not within the scope of these Guidelines. Other components are not directly related to the efforts of the process engineer but are discussed briefly here to emphasize that process safety issues touch on all aspects of plant design and operation. All components require documentation.

Table 10-1 Elements of Chemical Process Safety Management[a]

Accountability: Objectives and Goals
Process Knowledge and Documentation
Capital Project Review and Design Procedures (for new or existing plants, expansions and acquisitions)
Process Risk Management
Management of Change
Process and Equipment Integrity
Incident Investigation
Training and Performance
Human Factors
Standards, Codes and Laws
Audits and Corrective Actions
Enhancement of Process Safety Knowledge

[a] CCPS 1992b

Process safety depends on how a unit is designed, constructed, operated and maintained. The input of the process engineer is essential in establishing a permanent record of the design basis and operational requirements. Thorough documentation is necessary so that the design basis is not defeated incorrect by fabrication, operation, or maintenance techniques. In this chapter, safety aspects of management systems used to record and control design, operation and maintenance of a chemical facility are discussed. The primary elements of a document management program are procedures, retention and control.

10.1 DESIGN

The original design package (and subsequent revisions), a set of design specifications, standards and drawings used to construct a chemical facility, is usually the most accurate and complete set of information assembled for that particular processing unit. The design documents are used as the basis for all future improvement projects and the need for maximum completeness and accuracy cannot be overemphasized. Therefore it is best to immediately institute a procedure for storage, control, and revision of this information. Design documents typically include those described below.

10.1.1 Design Basis Documents

Process definition and design criteria are usually the initial information assembled. The basic process knowledge includes process chemistry, energy and mass balances, general control philosophy, process hazard analysis, etc. Applicable codes and design standards are identified. Supporting documents including design calculations and research and development reports, which explain the original design bases with their underlying philosophy and define safe operating ranges for process variables. The latter are often a useful place to begin troubleshooting or planning alternative operating conditions.

10.1.2 Equipment Specifications

These documents describe all of a plant's equipment in a concise yet complete way. The original design basis is clearly stated. Sufficient process and mechanical data is provided to allow procurement of the items listed in Table 10-2. Changes sometimes occur after the purchase order is awarded. The specifications should be updated to show "as delivered" and installed.

Table 10-2 Typical Design Documents

Process Definition and Design Criteria

- Process flow diagrams
- Energy and mass balances
- Safe operating ranges for process variables
- Protective systems
- Preliminary hazard analysis

Equipment Specifications

- Pumps
- Heat exchangers
- Furnaces
- Instruments
- Packaged units
- Tanks
- Reactors
- Separators
- Dryers
- Compressors
- Cooling towers
- Vessels
- Relief valves and rupture disks
- Boilers
- Filters and centrifuges
- Flares
- Specialty Items
- Agitators and solids blenders

Design Standards

- Site preparation
- Foundations
- Painting
- Insulation
- Piping
- Electrical
- Fireproofing
- Structural
- Welding
- Equipment (general)
- Instruments (general)

Drawings

- Process flow diagrams (PFDs) or flowsheets
- Piping (isometrics, elevations, fabrications, and flexibility drawings; hanger lists and specifications)
- Electrical area classifications
- Equipment design drawings
- Line schedules
- Civil (Structural, foundations)
- Plot plans
- Electrical schematics and one-line diagrams
- Piping and instrumentation diagrams (P&IDs)
- Hydrostatic testing diagrams
- Stream trap schedules

10.1.3 Design Standards

Design standards explain in detail the proper components, fabrication, assembly or construction techniques, or references used for items other than specific equipment. Design standards may be developed for components listed in Table 10-2.

10.1.4 *Drawings*

While design standards may go through minor adjustments, engineering drawings are revised frequently to reflect the addition of equipment and instruments or rerouting of lines. Drawings most commonly used are listed in Table 10-2. Regulatory agencies most often require retention of P&IDs and plot plans; these documents encompass the essence of the facility in a condensed form.

10.1.5 *Process Safety Reviews*

One of the most common elements of industry guidelines and regulations is the performance and documentation of a process safety review. This review does not ensure that all hazards have been identified, but it is currently the most effective method to systematically review a process and its components for hazards. Winter et al. (1992) discuss computer based software to simulate the process, incorporate hazards of specific chemicals, technology, and equipment.

The original process safety review (for example, Hazard and Operability Study, What-If, or Failure Modes and Effects Analysis) provides the basis for assessing future revisions and the hazardous consequences they might produce. The safety review should be thoroughly documented with detailed minutes of meetings and records of decisions and actions taken. Besides serving as a reference against which potential changes may be assessed, the safety review can serve as a case study for similar process units. For more information on safety reviews, consult *Guidelines for Hazard Evaluation Procedures* (CCPS 1992a).

Prior to making any revisions to an operating unit, process safety reviews should be performed as part of a management of change program. For instance, selection of a laboratory instrument may seem insignificant, but if not intrinsically safe, its use in an explosive atmosphere can be catastrophic. Another example is the use a new type of block valve for hazardous service: if its internals or packing materials are incompatible with the process, leaks could develop that could be disastrous.

It must be remembered that a safety review triggered by management of change may occur 2, 5, or 10 years after original design, yet the documentation must be complete enough to reconstruct the original design basis.

10.1.6 *Vendor Information*

Prior to, or with, the delivery of each piece of equipment, the vendor provides drawings and operating manuals. These drawings and manuals are useful because they reflect exact detail or "as built" descriptions and include proper operating instructions intended to ensure safe and trouble-free operation.

These documents are particularly useful in establishing the historical background of specific pieces of equipment. Vendor training manuals are useful for ensuring proper and consistent maintenance of equipment.

Vendors may deliver documents almost anywhere in the plant unless specific instructions are given. Manuals, drawings and Material Safety Data Sheets (MSDSs) and all test reports should be retained in the plant maintenance department, the engineering office or operating department.

10.1.7 Quality Control: New Equipment

Procedures should be developed to ensure that equipment is purchased, fabricated, inspected, tested and installed to meet equipment design specifications and assure process safety. The process engineer may be involved, along with the materials engineer, quality surveillance reps and equipment specialists, in developing these specifications.

Original materials, thickness, and construction details must be known for an accurate determination of corrosion rates and equipment life. Chemical composition of alloy piping and pressure components require verification as detailed in the fabrication specification. Records of weld integrity, post weld heat treatment, and testing of material and/or equipment are often required. Original shell and nozzle wall thickness should be verified on pressure vessels and exchangers. Material verification may be required for process piping.

Pressure testing requirements are described as minimum requirements in ASME/ANSI Codes, API RP 510, and the National Board Inspection Code (NBIC). Pressure testing of piping repairs should, as a minimum, be in accordance with the ASME B31 Piping Code. Pressure testing of large vessels should be covered by a written procedure defining test pressure; location of pressure and temperature indicators, test fluid temperature, venting, and pressurization/inspection sequencing and any safety requirements.

10.2 OPERATIONS

There are numerous variables to control, observe, and record for even the simplest of chemical processes. Documentation refers both to the procedures that operators use to set the variables and to the data recorded during actual operation. The best way to manage the data is to segregate the reasonably permanent items (e.g., procedures, setpoint parameters, etc.) from the data collected on the process variables. The permanent documents are usually placed under the control of the operating superintendent for strict control as described for the design documents. To ensure consistency of operating procedures, operating manuals should be prepared by the technical staff but with the involvement of plant operators. These manuals can then be the basis for operator training and for auditing for operator compliance to procedures.

10.2.1 Preoperational Testing

Pressure or vacuum testing of vessels and piping should be addressed by a written procedure defining test pressure, location of temperature and pressure indicators, test fluid temperature, venting and pressurization/inspection sequencing and any safety requirements. ASME/ANSI, API RP 510, and the NBIC describe requirements for pressure testing new equipment and may be useful in determining testing requirements for vessels followings repairs or alterations. Vacuum testing is as important as pressure testing. A written procedure must also be prepared for all equipment and piping that are to operate at pressure below atmospheric.

A pressure testing procedure for assuring the tightness of systems that were opened during routine and emergency maintenance must be in place and followed.

10.2.2 Operating Procedures

Procedures are developed to provide standardized instructions intended to prevent mistakes, improve product quality and reduce waste. Procedures are prepared for every aspect of operating a chemical plant, including:

- Start-up
- Shutdown
- Preparation for maintenance (for example, clean-out, steam-out, purge)
- Operating deviations
- Loading/unloading
- Emergencies
- Operating specific equipment

The process engineer should be provided with a way to incorporate his detailed knowledge of the process, control philosophy, and protective equipment. The transfer of information from designer to operator is a complex issue that shouldn't be neglected.

10.2.3 Changes in Operating Parameters

Changes in operating parameters should be controlled and monitored; many plants use a "management of change" program to track changes (CCPS 1992b). Changes in some operating parameters may not require a full process safety review but should still undergo review by management. If changes are deemed significant, then comprehensive process safety reviews may be required. All changes in the way a processing unit or even an individual piece of equipment is operated should be scrutinized for the potential to create hazards or increase existing hazards.

10.2.4 Operating Data

Operating logs are kept on everything from tank levels, temperatures, pressures, and flows to a multitude of other process variables. Large amounts of data are generated daily; determining what to keep and for how long is not easy. Operating data sheets are usually routed through the various departments for information purposes, retained for a short period, and then discarded. Traditionally only typical or periodic (first of the month) sets of data were preserved. Now, regulatory agencies may require operating data retention for specific periods of time particularly those related to outfalls and stack discharges. Historical operating data are primarily important for accounting control of raw materials and products, or for investigative studies into how to improve the process and equipment performance.

Operating data may be useful in safety analysis as well. When analyzing hazards, the frequency of certain events (e.g., high or low temperatures or pressures) can be useful when determining the likelihood of a specific event. The acceptable range of operating variables can be determined and the effect of excursions evaluated. With computerized data acquisition systems available to the process engineer, process optimization from both a quality and safety standpoint becomes easy and documentation needs are readily achieved as well.

10.3 MAINTENANCE

Documentation of maintenance is important for:

- Performing the correct maintenance procedure
- Scheduling the proper frequency of maintenance
- Preserving historical data and trends on equipment
- Determining necessary spare parts

The objective of maintenance is to assure the integrity of the process equipment.

The maintenance department of a process facility should be responsible for archiving maintenance records and preserving other documents such as service manuals. Maintenance procedures should be reviewed periodically and updated as required. Maintenance schedules can be computerized with only the work order forms actually used in the field, documented by hard copy. Routinely required spare parts lists are compiled by the warehouse department with details on suppliers, number required in stock, when to order, delivery time and costs.

10.3.1 Maintenance Procedures

The plant maintenance group establishes procedures for maintenance of major process equipment in accordance with manufacturers' recommendations and OSHA requirements for personnel safety.

Preventive maintenance records provide the historical base for judging the effectiveness of a plant's maintenance program and for establishing predictive maintenance programs. Frequency of maintenance can be adjusted according to equipment failure rates. A good inspection and equipment history file system greatly facilitates keeping good preventive maintenance records.

10.3.2 Inservice Inspection and Testing

Maintaining a comprehensive inspection and testing program is important in insuring integrity of process equipment. Virtually every item of equipment or piping can be included in an inspection schedule. Boiler and relief device inspection programs are usually required by state regulatory agencies. Resource commitments must be prioritized so that areas with greatest susceptibility for failure or highest consequence are given greatest priority. Inspection programs, e.g., lube oil analysis or measurement of rotating equipment vibration, may uncover potential failures prior to serious damage. Inspection and test data are usually retained for the life of the equipment.

Inspection of safety equipment (alarm systems, fire protection systems, personal protective equipment and other items) is covered by the OSHA Process Safety Management Regulation (29 CFR 1910.119).

Administration of the inservice inspection and testing program requires: training of inspectors, development of written procedures, application of quality control and a mechanism to take corrective action.

Determining the inspection interval requires a knowledge of applicable codes, equipment service, deterioration modes, nondestructive examination (NDE) techniques and limitations, past history, and proposed turnarounds. Special conditions may call for more frequent inspections: start-up, shutdown, idle standby. Special consideration should be given to inspection of localized hot-spots, corrosion and erosion, stress corrosion cracking (in moist hydrogen sulfide environments or chloride environments); high pressure service; mechanical forces due to thermal shock, vibration, etc.; and faulty fabrication (poor welding, improper heat treatment, defective lamination). See Appendix A, Typical Inspection Points and Procedures.

Determining the scope of inspections is a function of regulatory requirements, service, metallurgy, repair history, and test methods (ASME Code, Section V and API RP 510).

10.3.2.1 Nondestructive Examination

Nondestructive tests are used to detect defects in process equipment, primarily pressure vessels and piping. Examples of nondestructive examination (NDE) techniques are given in Table 10-3. Contractors performing NDE must comply with the training and certification requirements of ASNT-TC-1A. For a thorough discussion of less conventional methods consult the latest edition of the ASM Metals Handbook.

10.3.2.2 Retention of Inspection Records

NDE findings, details of construction, repairs, alterations, or other conditions may affect the future evaluation of the equipment's integrity. From the point of view of tracking the service history of equipment, the following records in addition to the equipment specifications listed earlier, are useful:

Table 10-3 Typical Nondestructive Examination Techniques

Technique	Useful to Detect	Applicable Standards
Visual inspection	Corrosion, contamination, surface finish, cracks, leaks	API guidelines ASME Code
Liquid penetrant testing (PT)	Discontinuities that are open to the surface	ASME Code, Section V, and ASTM Standard
Magnetic particle testing (MT), e.g., wet fluorescent magnetic testing	Surface and subsurface discontinuities (small and shallow cracks) in ferromagnetic materials, e.g., for carbon steel in wet H_2S service	ASME Codes, ASTM and ASNT Standards
Radiographic (x-ray or gamma ray) testing (RT)	Subsurface flaws, extensively used on castings and weldment	ASME Codes, ASTM and ASNT Standards
Ultrasonic testing (UT) —longitudinal wave or —shear wave	Surface and subsurface flaws; wall thickness	ASME Codes, ASTM and ASNT Standards
Eddy current testing (ET)	Defects in ferromagnetic materials	ASTM E-268-68, ASME Code, Section V
Acoustic emission	Flaws in pressure vessels, piping	ASME Code, Section V

- ASME Code Data Reports for pressure vessels.
- Field-verified inspection drawings for major equipment with reference inspection points. Wall thickness measurements (including original measurements), and other nondestructive examination findings, both past and present should be on the drawings or a separate sheet.
- A copy of jurisdictional reports and permits that are required to operate boilers or pressure vessels (for the duration of the permit).
- Repair and alteration documentation for major equipment and process piping.

10.3.3 Equipment History

Maintaining accurate and complete equipment history files is critical when investigating failures, anticipating possible repairs, or making modifications. Materials of construction, welding procedures, and descriptions of internals and design allowances are examples of the data frequently required from these files. This information is often readily accessible in the maintenance department.

The equipment history data base can be used to estimate the likelihood of equipment failure. Methods of quantitative reliability and risk analysis are applied to the equipment data base in an attempt to determine the frequency and consequences of various types of mechanical failures. Comprehensive procedures are required for data collection, and the ability to audit and trace the origins of finished data must be assured. The data must be accurate, complete, and coded so that it can be located within a well designed failure rate taxonomy. For more information on data bases, review *Guidelines for Process Equipment Reliability Data with Data Tables* (CCPS 1989b) and *Guidelines for Quantitative Risk Analysis* (CCPS 1989a).

10.3.4 Taking Corrective Action

A critical part of the process safety management plan, although usually not the responsibility of the process engineer, is prompt notification to supervision when corrective action is required. Specific procedures may be required to assign responsibility and authority for these actions. If inservice inspection reveals deterioration, detailed engineering analysis may be required to evaluate the options of allowing continued operation, removing damage without repair, or repairing the damage.

If a repair is necessary, procedures need to spell out the method of repair. If repair is by welding, for example, the procedure should specify post weld heat treatment or other alternatives. The procedure should identify applicable Codes that cover the materials used and the qualifications of the repair organization that performs the repair.

10.4 RECORDS MANAGEMENT

Administration of a document control program has been discussed under the separate types of records, but common elements must be addressed for all types of documents: location, accessibility, managing revisions to procedures and process.

10.4.1 Location

Documents need to be accessible, yet secure and controllable. Often documents are kept only at the facility with the risk of being removed and never returned or being destroyed during a disaster (e.g., hurricane, flood, fire). If documents are to be removed from their normal location, a procedure should be developed to "check-out" the material as from a library. Avoid the tendency to make the check-out complicated: a single page check-out procedure is normally effective.

Backup copies of documentation should be preserved off-site for reference. The most useful location is the company headquarters. Design documents and operating data should either be microfilmed, computerized, or hard copy, file maintained with destruction dates and names of responsible individuals.

10.4.2 Document Control and Access

Typically, design documents should be identified, microfilmed, and placed under the responsibility of the engineering department. If a facility is large enough, a central library is the ideal location; however, these facilities often are unable to exercise proper control (that is, access is unlimited). Design documents should be accessible, but since only a single copy of each may exist, strict control is required. A checkout card system is highly recommended. Files should be locked after hours. A higher degree of security can be provided by establishing a nonloanable file of design documents; only copies can be removed from the library unless revisions are required to the original document. Periodic audits should be made to ensure that important documents are available and current.

Recent developments in computer database records allow documentation to be shared by several users (Holley 1992; Kovar et al. 1992: Winter et al. 1992). Administrative controls are required to limit changes in the database to authorized personnel. Electronic records facilitate the management of change documentation.

10.4.3 Management of Change: Revisions

Within a short time after construction, it is common to have changes to the physical equipment; revisions to the design are made to correct minor deficiencies or to improve operability of a unit once the actual layout comes together.

Proposed modifications to the process or the plant should be subjected to critical analysis and safety assessment; construction, inspection and testing specifications and codes must be determined. These changes should be reflected in revisions to the original design package. The documents strictly required for fabrication are always modified, but the complementary documentation used for other purposes (process flow diagram, piping and instrumentation diagrams, plot plan, etc.) should not be neglected. Unless these design documents are assigned to someone for ownership and control, maintaining them becomes more difficult with each passing day.

Revisions are made in all types of documents related to design, operations, maintenance, and safety. Revisions should be clearly stated and contain the following facts:

- What was changed?
- When was it changed?
- Who made the change?
- What was the purpose of the change?
- Identify the authority for the change.

The individual overseeing the change (or project) should determine whether other documents are affected, and should be responsible for making sure that all complementary documentation is also revised.

10.4.4 Retention/Purge Schedule

A plant-wide guideline or procedure to assign the responsibility and ownership of the many documents is required in order to have a manageable document system. This topic is covered in *Plant Guidelines for Technical Management of Process Safety* (CCPS 1992b). Required documents and their fate (retention or destruction) should be described. The responsibility to carry through is made part of each individual's job requirements.

10.4.5 Auditing

Procedures need to be established to monitor compliance with all aspects of records management. Quality assurance audits may be required to comply with internal guidelines and government regulations.

APPENDIX 10-A: TYPICAL INSPECTION POINTS AND PROCEDURES

- Tube skin thermocouples are typically located at the point of highest anticipated tube temperatures. Visually inspect support systems such as guy wires, spring hangers and counter balance systems for condition, alignment, and clearance problems.
- Nozzles and adjacent shell areas for distortion and cracking if any settling of the vessel has occurred. Flange faces may be checked with a flange square for distortion.
- Exposed gasket surfaces for scoring and corrosion.
- External metal surfaces of a vessel. The degree of surface preparation required for external inspection will depend on the type and extent of deterioration expected. Examine the external surface for cracks, buckles, bulges, in addition to corrosion. A thorough method of examination shall be employed.
- Identify and statistically-sample every nipple and nozzle on process equipment where they are vulnerable to deterioration.
- Monitor corrosion rate of pipe nipples and small piping using periodic radiography and observe special problems such as with couplings.
- Piping up and downstream of previous replacements.
- Turbulent areas such as downstream of control valves for erosion.
- Piping downstream of water/acid injection points for corrosion.
- Points at which acid carry-over from process operations is likely to occur.
- Points at which naphthenic or other organic acids may be present in the process, or where 600–800°F sulfur corrosion may occur.
- Points at which condensation of acid gases and/or water is likely to occur.
- Stagnant areas where water and/or acid, or the build-up of corrosive matter may concentrate and accelerate corrosion.
- Dead ends subject to turbulence or where liquid-to-vapor interface or concentration may occur. Dead legs subject to stagnation and/or water.
- Equipment subject to stress corrosion cracking, especially austenitic stainless steel where chlorides may concentrate.
- Alkali lines subject to caustic embrittlement, especially where steam or electric tracing may make contact and raise temperatures without awareness.
- Locations where conditions may result in high-temperature or low-temperature hydrogen attack.
- Areas near flange or welded attachments which act as cooling fins and cause changes in protective scale formation and local corrosion.
- Welded areas subject to preferential attack or deterioration.
- High velocity and turbulence locations in concentrated H_2SO_4 equipment.

- Piping direction-change and turbulence points when carrying catalyst, flue gases, or entrained particles such as slurries.
- Hydrocarbon equipment operating above 400°F should receive more-concentrated inspection attention because of a greater likelihood of corrosion in addition to autoignition of C_6 through C_{18}.
- Increase inspection frequency on equipment containing environments having corrosion rates of 0.020 inches per year or higher.
- Consider expanding the inspection sample for piping systems having maximum/average corrosion rate ratios greater than 4/1 because the potential for extremes is great. These result from multiple corrosion mechanisms.
- Watch for dewpoints in furnace and boiler convection sections, stacks and supports.
- Watch for coke drum and large vessel skirt cracking when subjected to temperature gradients. Watch for radial cracking in flame-cut keyholes.
- Skirts and supports hidden by fire protection. Periodically spot check at the worst expected locations especially when significant spalling occurs.
- Waterproofing of insulation.
- Mount stop valves under relief valves horizontally so gravity cannot automatically close a gate separated from a stem.
- Cathodically protect tank bottoms and buried pipe subject to corrosion.
- Grade and drain water from around equipment and storage tanks.
- Closely monitor water in vacuum towers to avoid tray upsets.
- Consider special inspection measures where temperature gradients and fatigue are likely.
- Consider special inspection measures where creep is likely in equipment.
- Inspect steam systems subject to "wire cutting" or graphitization or where condensation and CO_2 corrosion may occur.
- Inspect aluminum lines at points of accidental contact or insulator breakdown that cause contact with other metals.
- Brace small piping and lines subject to significant vibration.
- Watch for and strengthen inadequately supported piping.
- Consider the possibility of unacceptable stress levels in equipment where changed operating conditions have evolved over a period of time due to revamps.
- Include worst-case inspection samples of *all* expected problem locations in addition to <u>all</u> typical configurations when inspecting environments subject to corrosion, wastage, or other deterioration.
- Protective equipment liners and clads. Mechanical damage can eventually allow corrosion to penetrate the shell.
- Check for catalyst erosion at nozzles and cavities and protrusions where turbulence is created. Check on outside sweeps of short radius bends in catalyst lines.

- Watch low flow conditions in heaters where only the outlet temperature is monitored. (Low flow can reduce outlet temperature and this may call for additional heat which can overheat the tubes.)
- Thoroughly inspect for water hammering of equipment and piping that is not stress relieved.

10.5 REFERENCES

10.5.1 Regulations, Codes of Practice and Industry Standards

The editions that were in effect when these *Guidelines* were written are indicated below. Because standards and codes are subject to revision, users are encouraged to apply only the most recent edition.

API RP 510. 1989. *Pressure Vessel Inspection Code*. American Petroleum Institute, Washington, D. C.

API RP 530. 1988. *Calculation of Heater-Tube Thickness in Petroleum Refineries*. American Petroleum Institute, Washington, D. C.

API RP 750. 1990. *Management of Process Hazards*, 1st ed. American Petroleum Institute, Washington, D. C.

API Publ. 941. 1990. *Steels for Hydrogen Services at Elevated Temperatures and Pressures in Petroleum Refineries and Petrochemical Plants*. American Petroleum Institute, Washington, D. C.

ASME. *Boiler and Pressure Vessel Code*. American Society of Mechanical Engineers, New York.

ASME/ANSI B31. *Code for Pressure Piping*. American Society of Mechanical Engineers and American National Standards Institute, New York.

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State of California, Governor's Office of Emergency Services. 1989. *Guidance for the Preparation of a Risk Management and Prevention Program.*

State of New Jersey, Division of Environmental Quality. 1988. *Toxic Catastrophe Prevention Act.*

UBC. *Unified Building Code.* 1991. International Conference of Building Officials.

10.5.2 Specific References

ASM (American Society for Metals). 1987. *Metals Handbook.* Vol. 11, 8th ed. American Society for Metals, Metals Park, Ohio.

CCPS (Center for Chemical Process Safety). 1989a. *Guidelines for Chemical Process Quantitative Risk Analysis.* American Institute of Chemical Engineers, New York. ISBN 0-8169-0402-2.

CCPS (Center for Chemical Process Safety). 1989b. *Guidelines for Process Equipment Reliability Data, with Data Tables.* American Institute of Chemical Engineers, New York. ISBN 0-8169-0422-7.

CCPS (Center for Chemical Process Safety). 1992a. *Guidelines for Hazard Evaluation Procedures, Second Edition with Worked Examples.* American Institute of Chemical Engineers, New York. ISBN 0-8169-0491-X.

CCPS (Center for Chemical Process Safety). 1992b. *Plant Guidelines for Technical Management of Chemical Process Safety.* American Institute of Chemical Engineers, New York. ISBN 0-8169-0499-5.

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10.5.3 Suggested Reading

CMA (Chemical Manufacturers Association). 1990. *A Resource Guide for Implementing the Process Safety Code of Management Practices*. Chemical Manufacturers Association, Washington, D.C.

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