Section 26

Process Safety

Stanley M. Englund, M.S., Ch.E., *Fellow American Institute of Chemical Engineers; Process Consultant, The Dow Chemical Company (retired). (Section Editor, Section 26; Introduction; Hazard Analysis; Storage and Handling of Hazardous Materials; Reactive Chemicals; Combustion and Flammability Hazards; Hazards of Vacuum; Hazards of Inert Gases)*

Frank T. Bodurtha, Sc.D., *E. I. du Pont de Nemours and Co., Inc., (retired); Consultant, Frank T. Bodurtha, Inc. (Gas Explosions; Unconfined Vapor Cloud Explosions [UVCEs] and Boiling Liquid Expanding Vapor Explosions [BLEVEs])*

Laurence G. Britton, Ph.D., *Research Scientist, Union Carbide Corporation. (Flame Arresters)*

Daniel A. Crowl, Ph.D., *Professor of Chemical Engineering, Chemical Engineering Department, Michigan Technological University; Member, American Institute of Chemical Engineers, American Chemical Society. (Gas Dispersion)*

Stanley Grossel, *President, Process Safety & Design, Inc.; Fellow, American Institute of Chemical Engineers; Member, American Chemical Society; Member, The Combustion Institute; Member, Explosion Protection Systems Committee of NFPA. (Emergency Relief Device Effluent Collection and Handling)*

W. G. High, C.Eng., B.Sc., F.I.Mech.E., *Burgoyne Consultants Ltd., W. Yorks, England. (Guidelines for Estimating Damage)*

Trevor A. Kletz, D.Sc., *Senior Visiting Research Fellow, Department of Chemical Engineering, Loughborough, University U.K.; Fellow, American Institute of Chemical Engineers, Royal Academy of Engineers (U.K.), Institution of Chemical Engineers (U.K.), and Royal Society of Chemistry (U.K.). (Inherently Safer Design)*

Robert W. Ormsby, M.S., ChE., *Manager of Safety, Chemicals Group, Air Products and Chemicals, Inc.; Air Products Corp.; Fellow, American Institute of Chemical Engineers. (Risk Analysis)*

John E. Owens, B.E.E., *Electrostatics Consultant, Condux, Inc.; Member, Institute of Electrical and Electronics Engineers, Electrostatics Society of America. (Static Electricity)*

Carl A. Schiappa, B.S. Ch.E., *Process Engineering Associate, Michigan Division Engineering, The Dow Chemical Company; Member, AIChE and CCPS. (Project Reviews and Procedures)*

Richard Siwek, M.S., *Explosion Protection Manager, Corporate Unit Safety and Environment, Ciba-Geigy Ltd., Basel, Switzerland. (Dust Explosions)*

Robert E. White, Ph.D., *Principal Engineer, Chemistry and Chemical Engineering Division, Southwest Research Institute. (Flame Arresters)*

David Winegardner, Ph.D., *Engineering Associate, Michigan Division Engineering, The Dow Chemical Company; Member, AIChE and CCPS. (Pressure Relief Systems)*

John L. Woodward, Ph.D., *Principal, DNV Technica, Inc. (Discharge Rates from Punctured Lines and Vessels)*

PROCESS SAFETY INTRODUCTION

INHERENTLY SAFER DESIGN AND OTHER PRINCIPLES

PROCESS SAFETY ANALYSIS

SAFETY DEVICES

HAZARDOUS MATERIALS AND CONDITIONS

PROCESS SAFETY INTRODUCTION

In recent years there has been an increased emphasis on process safety as a result of a number of serious accidents. This is due in part to the worldwide attention to issues in the chemical industry brought on by several dramatic accidents involving gas releases, major explosions, and environmental incidents. Public awareness of these and other accidents has provided a driving force for industry to improve its safety record. Local and national governments are taking a hard look at safety in industry as a whole and the chemical industry in particular. There has been an increasing amount of government regulation.

The Chemical Process Industries constitutes one of the safest of the manufacturing sectors, but a single major accident or disaster can do irreparable damage to a company's reputation and possibly affect the entire industry (Sheridan, "OSHA, EPA and Process Sampling," *Chem. Proc.,* September 1994, pp. 24–28). One reason the chemical industry gets bad press is that its activities are very noticeable. Large chemical works are striking features on the landscape. Chemical plants are often noisy and garishly lit, and many of the effluents cause nuisances which are well below the health and safety limits. Hazardous chemicals are transported in bulk in highly visible container vehicles, adding to the public's image of the industry as hazardous and dangerous (Benson and Ponton, "Process Miniaturisation—A Route to Total Environmental Acceptability," *Institution of Chemical Engineers* 0263-8762/93). For many reasons, the public often associates the chemical industry with environmental and safety problems and, unfortunately, sometimes the negative image that goes with the problems is deserved. It is vital to the future of the chemical industry that process safety have a high priority in the design and operation of chemical process facilities.

Environmental pressures on the process industries will prove to be the most significant change for the next 50 years. Not only will new processes change, but mature industries will have to develop new process technology to survive (Benson et al., op. cit.).

Hazards from combustion and runaway reactions play a leading role in many chemical process accidents. Knowledge of these reactions is essential for control of process hazards. It is important that loss of containment be avoided. For example:

- Much of the damage and loss of life in chemical accidents results from the sudden release of material at high pressures which may or may not result from fire. Chemical releases caused by fires and the failure of process equipment and pipelines can form toxic clouds that can be dangerous to people over large areas.
- Vapor cloud explosions can result if clouds of flammable vapor in air are formed. It is important to understand how liquids and gases flow through holes in equipment and how resulting vapor or gas clouds are dispersed in air.
- Understanding how sudden pressure releases can occur is important. They can happen, for example, from ruptured high-pressure tanks, runaway reactions, flammable vapor clouds, or pressure developed from external fire. The proper design of pressure relief systems can reduce the possibility of losses from unintended overpressure.
- Static electricity is often a hidden cause in accidents.
- It is important to understand the reactive nature of the chemicals involved in a chemical facility.
- Loss of containment due to mechanical failure or misoperation is a major cause of chemical process accidents. The publication, *One Hundred Largest Losses: A Thirty Year Review of Property Damage Losses in the Hydrocarbon Chemical Industry,* 9th ed. (M&M Protection Consultants, Chicago), cites loss of containment as the leading cause of property loss in the chemical process industries.

Government regulations require hazard and risk analysis as part of *process safety management* (PSM) programs. These are part of the process safety programs of many chemical process facilities.

Process safety includes many subjects that could not be included in this section because of lack of space. The following describes the organization of Section 26:

Inherently Safer Design Rather than add on equipment to control hazards or to protect people from their consequences, it is better to design user-friendly plants which can withstand human error and equipment failure without serious effects on safety, the environment, output, and efficiency. This part is concerned with this matter.

Process Safety Analysis This part treats the analysis of a process or project from the standpoint of hazards, risks, procedures for making potential damage estimates, and project reviews and audits. It can be helpful to management in assessing risks in a project. It consists of the following:

Hazard Analysis
Risk Analysis
Guidelines for Estimating Damage
Project Reviews and Procedures

Safety Devices Pressure relief devices, flame arresters, and methods for handling effluent from controlled releases provide control of accidental undesirable events. Special equipment should be considered for highly toxic chemical service. The following matters are considered:

Pressure Relief Systems
Emergency Relief Device Effluent Collection and Handling
Flame Arresters
Storage and Handling of Hazardous Materials

Hazardous Materials and Conditions The chemical and physical situations that can result when operating with hazardous materials should be understood so these materials may be handled safely. This part covers the following:

Reactive Chemicals
Combustion and Flammability Hazards
Gas Explosions
Unconfined Vapor Cloud Explosions (UVCEs) and Boiling Liquid Evaporating Vapor Explosions (BLEVEs)
Dust Explosions
Static Electricity
Hazards of Vacuum
Hazards of Inert Gases
Gas Dispersion
Discharge Rates from Punctured Lines and Vessels

INHERENTLY SAFER DESIGN AND OTHER PRINCIPLES

INTRODUCTION: WHAT IS PROCESS SAFETY?

Process safety differs from the traditional approach to accident prevention in a number of ways (Lees, *Loss Prevention in the Process Industries,* 2d ed., Butterworth-Heinemann, 1996, p. 1.8):

- There is more concern with accidents that arise out of the technology.
- There is more emphasis on foreseeing hazards and taking action before accidents occur.

- There is more emphasis on a systematic rather than a trial-and-error approach, particularly on systematic methods of identifying hazards and of estimating the probability that they will occur, and their consequences.
- There is concern with accidents that cause damage to plants and loss of profit but do not injure anyone, as well as those that do cause injury.
- Traditional practices and standards are looked at more critically.

Process safety can be applied in any industry, but the term and the approach have been particularly widely used in the process industries, where it usually means the same as loss prevention.

Although process safety is as old as process engineering, it did not become recognized as a distinct branch of the subject until the 1960s, when a new generation of plants, larger than earlier ones and operating at higher temperatures and pressures, was involved in a number of serious fires and explosions. They made the industry realize that accident prevention needed the same sort of systematic and technical study as every other aspect of plant design and operation. Since then the number of publications and specialist journals, and the number and caliber of engineers specializing in the field, have grown rapidly.

INHERENTLY SAFER AND MORE USER-FRIENDLY DESIGN

For many years the usual procedure in plant design was to identify the hazards, by one of the systematic techniques described later or by waiting until an accident occurred, and then add on protective equipment to control future accidents or protect people from their consequences. This protective equipment is often complex and expensive and requires regular testing and maintenance. It often interferes with the smooth operation of the plant and is sometimes bypassed. Gradually the industry came to realize that, whenever possible, one should design user-friendly plants which can withstand human error and equipment failure without serious effects on safety (and output and efficiency). When we handle flammable, explosive, toxic, or corrosive materials we can tolerate only very low failure rates, of people and equipment—rates which it may be impossible or impracticable to achieve consistently for long periods of time.

The most effective way of designing user-friendly plants is to avoid, when possible, large inventories of hazardous materials in process or storage. "What you don't have, can't leak." This sounds obvious, but until the explosion at Flixborough, England, in 1974, little systematic thought was given to ways of reducing inventories. The industry simply designed a plant and accepted whatever inventory the design required, confident they could keep it under control. Flixborough weakened that confidence and the disaster ten years later at Bhopal, India, almost destroyed it. Plants in which we avoid a hazard, by reducing inventories or avoiding hazardous reactions, are usually called *inherently safer.*

The principle ways of designing inherently safer plants and other ways of making plants user-friendly are summarized as follows, with examples (Kletz, *Plant Design for Safety—A User-Friendly Approach,* Hemisphere, 1991).

Intensification This involves using so little hazardous material that it does not matter if it all leaks out. For example, at Bhopal, methyl isocyanate (MIC), the material that leaked and killed over 2000 people, was an intermediate for which it was convenient but not essential to store. Within a few years many companies had reduced their stocks of MIC and other hazardous intermediates.

As another example, at one time nitroglycerin (NG) was manufactured in batch reactors containing about a ton of raw materials and product. If the reactor got too hot, there was a devastating explosion. In modern plants, NG is made in a small continuous reactor containing about a kilogram. The severity of an explosion has been reduced a thousandfold, not by adding on protective devices, which might fail or be neglected, but by redesigning the process. The key change was better mixing, achieved not by a better stirrer, which might fail, but by passing one reactant (acid) through a device like a laboratory water pump so that it sucks in the other reactant (glycerin) through a sidearm. If the acid flow stops, the glycerin flow also stops, not through the intervention of a flow controller, which might fail, but as an inevitable result of the laws of physics (Bell, *Loss Prevention in the Process Industries,* Institution of Chemical Engineers Symposium Series No. 34, 1971, p. 50).

Intensification is the preferred route to inherently safer design, as the plants, being smaller, are also cheaper.

Substitution If intensification is not possible, then an alternative is to consider using a safer material in place of a hazardous one. Thus it may be possible to replace flammable solvents, refrigerants, and heat-transfer media by nonflammable or less flammable (high-boiling) ones, hazardous products by safer ones, and processes which use hazardous raw materials or intermediates by processes which do not. As an example of the latter, the product manufactured at Bhopal (carbaryl) was made from three raw materials. Methyl isocyanate is formed as an intermediate. It is possible to react the same raw materials in a different order so that a different and less hazardous intermediate is formed.

Attenuation Another alternative to intensification is attenuation, using a hazardous material under the least hazardous conditions. Thus large quantities of liquefied chlorine, ammonia, and petroleum gas can be stored as refrigerated liquids at atmospheric pressure instead of storing them under pressure at ambient temperature. (Leaks from the refrigeration equipment should also be considered, so there is probably no net gain in refrigerating quantities less than a few hundred tons.) Dyestuffs which form explosive dusts can be handled as slurries.

Limitation of Effects of Failures Limitation can be done by equipment design or change in reaction conditions, rather than by adding on protective equipment. For example:

- Spiral-wound gaskets are safer than fiber gaskets because, if the bolts work loose or are not tightened correctly, the leak rate is much lower.
- Tubular reactors are safer than pot reactors, as the inventory is usually lower and a leak can be stopped by closing a valve.
- Vapor phase reactors are safer than liquid phase ones, as the mass flow rate through a hole of a given size is much less. (This is also an example of attenuation.)
- A small, deep diked area around a storage tank is safer than a large, shallow one, as the evaporation rate is lower and the area of any fire is smaller.
- Heating media such as steam or hot oil should not be hotter than the temperature at which the materials being heated are liable to ignite spontaneously or react uncontrollably.
- Many runaway reactions can be prevented by changing the order of operations, reducing the temperature, or changing another parameter.
- Reduce the frequency of hazardous operations such as sampling or maintenance. What is the optimum balance between reliability and maintenance?

Simplification Simpler plants are friendlier than complex ones, as they provide fewer opportunities for error and less equipment which can fail. Some of the reasons for complication in plant design are:

- The need to control hazards. If one of the other actions already discussed, such as intensification, can be carried out, less add-on protective equipment is needed and plants will therefore be simpler.
- A desire for flexibility. Multistream plants with numerous crossovers and valves, so that any item can be used on any stream, have numerous leakage points, and errors in valve settings are easy to make.
- Lavish provision of installed spares with the accompanying isolation and changeover valves.
- Continuing to follow rules or practices which are no longer necessary.
- Design procedures which result in a failure to identify hazards until late in design. By this time it is impossible to avoid the hazard and all that can be done is to add on complex equipment to control it.

Knock-on Effects Plants should be designed so that those incidents that do occur do not produce knock-on or domino effects. This can be done, for example, by:

- Providing firebreaks, about 15 m wide, between sections, like firebreaks in a forest, to restrict the spread of fire.
- Siting equipment which is liable to leak outdoors so that leaks of flammable gases and vapors are dispersed by natural ventilation.

Indoors, a few tens of kilograms are sufficient for an explosion that can destroy the building. Outdoors, a few tons are necessary for serious damage. A roof over equipment such as compressors is acceptable, but walls should be avoided. (If leaks of toxic gases are liable to occur, it may be safer to locate the plant indoors, unless leaks will disperse before they reach the public or employees on other units.)

- Constructing storage tanks so that the roof-wall weld will fail before the base-wall weld, thus preventing spillage of the contents. In general, equipment designers should consider the way in which it is most likely to fail and, when possible, locate or design the equipment so as to minimize the consequences.

Avoiding Incorrect Assembly Plants should be designed so that incorrect assembly is difficult or impossible. For example, compressor valves should be designed so that inlet and exit valves cannot be interchanged.

Status Clear It should be possible to see at a glance if equipment has been assembled or installed incorrectly or whether a valve is in the open or shut position. For example:

- Check valves should be marked so that installation the wrong way round is obvious. It should not be necessary to look for a faint arrow hardly visible beneath the dirt.
- Gate valves with rising spindles are friendlier than valves with nonrising spindles, as it is easy to see whether they are open or shut. Ball valves are friendly if the handles cannot be replaced in the wrong position.
- Figure-eight plates (spectacle plates) are friendlier than slip plates (spades), as their positions are apparent at a glance. If slip plates are used, their projecting tags should be readily visible, even when the line is insulated. In addition, spectacle plates are easier to fit than slip plates, if the piping is rigid, and they are always available on the job. It is not necessary to search for them, as with slip plates.

Tolerance Whenever possible, equipment should tolerate poor installation or operation without failure. Expansion loops in pipework are more tolerant of poor installation than bellows are. Fixed pipes, or articulated arms, if flexibility is necessary, are friendlier than hoses. For most applications, metal is friendlier than glass or plastic.

Bolted joints are friendlier than quick-release couplings. The former are usually dismantled by a fitter after issue of a permit to work. One person prepares the equipment and another person opens it up; the issue of the permit provides an opportunity to check that the correct precautions have been taken. In addition, if the joints are unbolted correctly, any trapped pressure is immediately apparent and the joint can be remade or the pressure allowed to blow off. In contrast, many accidents have occurred because operators opened up equipment which was under pressure, without independent consideration of the hazards, using quick-release couplings. There are, however, designs of quick-release couplings which give the operator a second chance.

Low Leak Rate If friendly equipment does leak, it does so at a low rate, which is easy to stop or control. Examples already mentioned are spiral-wound gaskets, tubular reactors, and vapor phase reactors.

Ease of Control Processes with a flat response to change are obviously friendlier than those with a steep response. Processes in which a rise of temperature decreases the rate of reaction are friendlier than those with a positive temperature coefficient, but this is a difficult ideal to achieve in the chemical industry. However, there are a few examples of processes in which a rise in temperature reduces the rate of reaction. For example, in the manufacture of peroxides, water is removed by a dehydrating agent. If magnesium sulfate is used as the agent, a rise in temperature causes release of water by the agent, diluting the reactants and stopping the reaction (Gerrison and van't Land, *I&EC Process Design* **24,** 1985, p. 893).

Software In some programmable electronic systems (PES), errors are much easier to detect and correct than in others. Using the term *software,* in the wider sense, to cover all procedures, as distinct from hardware or equipment, some software is much friendlier than others. Training and instructions are obvious examples. As another example, if many types of gaskets or nuts and bolts are stocked, sooner or later the wrong type will be installed. It is better, and cheaper in the long run, to keep the number of types stocked to a minimum, even though more expensive types than are strictly necessary are used for some applications.

Designing Inherently Safer and More User-Friendly Plants The following actions are needed for the design of inherently safer and more user-friendly plants:

1. Designers need to be made aware that there is scope for improving the friendliness of the plants they design.
2. To achieve many of the changes previously suggested, it is necessary to carry out much more critical examination and systematic consideration of alternatives during the early stages of design than has been customary in most companies. Two studies are suggested: one at the conceptual or business analysis stage when the process is being chosen, and another at the flowsheet stage. For the latter, the usual hazard and operability (HAZOP) study questions may be suitable but with one difference. In a normal HAZOP on a line diagram, if, for example, "more of temperature" is being discussed, it is assumed that this is undesirable and ways of preventing it are sought. In a HAZOP of a flowsheet, it should be asked if "more of temperature" would be better. For the conceptual study, different questions are needed.
3. Many companies will say that they do consider alternatives during the early stages of plant design. However, what is lacking in many companies is a formal, systematic, structured procedure of the HAZOP type.

To achieve the more detailed improvements suggested here, it may be necessary to add a few questions to those asked during a normal HAZOP. For example, what types of valves, gaskets, and so forth, will be used?

INCIDENT INVESTIGATION AND HUMAN ERROR

Although most companies investigate accidents (and many investigate dangerous incidents in which no one was injured), these investigations are often superficial, and we fail to learn all the lessons for which we have paid the high price of an accident. The facts are usually recorded correctly, but often only superficial conclusions are drawn from them. Identifying the causes of an accident is like peeling an onion. The outer layers deal with the immediate technical causes and triggering events while the inner layers deal with ways of avoiding the hazard and with the underlying weaknesses in the management system (Kletz, *Learning from Accidents,* 2d ed., Butterworth-Heinemann, 1994).

Dealing with the immediate technical causes of a leak, for example, will prevent another leak for the same reason. If so little of the hazardous material can be used that leaks do not matter or a safer material can be used instead, as previously discussed, all significant leaks of this hazardous material can be prevented. If the management system can be improved, we may be able to prevent many more accidents of other sorts.

Other points to watch when drawing conclusions from the facts are:

1. Avoid the temptation to list causes we can do little or nothing about. For example, a source of ignition should not be listed as the primary cause of a fire or explosion, as leaks of flammable gases are liable to ignite even though we remove known sources of ignition. The cause is whatever led to the formation of a flammable mixture of gas or vapor and air. (Removal of known sources of ignition should, however, be included in the recommendations.) Similarly, human error should not be listed as a cause. See item 6 below.
2. Do not produce a long list of recommendations without any indication of the relative contributions they will make to the reduction of risk or without any comparison of costs and benefits. Resources are not unlimited and the more we spend on reducing one hazard, the less there is left to spend on reducing others.
3. Avoid the temptation to overreact after an accident and install an excessive amount of protective equipment or complex procedures which are unlikely to be followed after a few years have elapsed. Sometimes an accident occurs because the protective equipment available was not used; nevertheless, the report recommends installation of more protective equipment; or an accident occurs because complex procedures were not followed and the report recommends extra procedures. It would be better to find out why the original equipment was not used or the original procedures were not followed.
4. Remember that few, if any, accidents have simple causes.
5. When reading an accident report, look for the things that are not said. For example, a gland leak on a liquefied flammable gas pump caught fire and caused considerable damage. The report drew atten-

tion to the congested layout, the amount of redundant equipment in the area, the fact that a gearbox casing had been made of aluminum, which melted, and several other unsatisfactory features. It did not stress that there had been a number of gland leaks on this pump over the years, that reliable glands are available for liquefied gases at ambient temperatures, and, therefore, there was no need to have tolerated a leaky pump on this duty.

As another example, a fire was said to have been caused by lightning. The report admitted that the grounding was faulty but did not say when it was last checked, if it was scheduled for regular inspection, if there was a specification for the resistance to earth (ground), if employees understood the need for good grounding, and so on.

6. At one time most accidents were said to be due to human error, and in a sense they all are. If someone—designer, manager, operator, or maintenance worker—had done something differently, the accident would not have occurred. However, to see how managers and supervisors can prevent them, we have to look more closely at what is meant by human error:

a. Some errors are due to poor training or instructions: someone did not know what to do. It is a management responsibility to provide good training and instructions and avoid instructions that are designed to protect the writer rather than help the reader. However many instructions are written, problems will arise that are not covered, so people—particularly operators—should be trained in flexibility—that is, the ability to diagnose and handle unforeseen situations. If the instructions are hard to follow, can the job be simplified?

b. Some accidents occur because someone knows what to do but makes a deliberate decision not to do it. If possible the job should be simplified (if the correct method is difficult, an incorrect method will be used); the reasons for the instructions should be explained; checks should be carried out from time to time to see that instructions are being followed; and if they are not, this fact should not be ignored.

c. Some accidents occur because the job is beyond the physical or mental ability of the person asked to do it—sometimes it is beyond anyone's ability. The plant design or the method of working should be improved.

d. The fourth category is the commonest: a momentary slip or lapse of attention. They happen to everyone from time to time and cannot be prevented by telling people to be more careful or telling them to keep their minds on the job. All that can be done is to change the plant design or method of working to remove opportunities for error (or minimize the consequences or provide opportunities for recovery). Whenever possible, user-friendly plants (see above) should be designed which can withstand errors (and equipment failures) without serious effects on safety (and output and efficiency).

INSTITUTIONAL MEMORY

Most accidents do not occur because we do not know how to prevent them but because we do not use the information that is available. The recommendations made after an accident are forgotten when the people involved have left the plant; the procedures they introduced are allowed to lapse, the equipment they installed is no longer used, and the accident happens again. The following actions can prevent or reduce this loss of information.

- Include a note on "the reason why" in every instruction, code, and standard, and accounts of accidents which would not have occurred if the instruction, code, or standard had been followed.
- Describe old accidents, as well as recent ones, in safety bulletins and newsletters and discuss them at safety meetings.
- Follow up at regular intervals (for example, during audits) to see that the recommendations made after accidents are being followed, in design as well as operations.
- Make sure that recommendations for changes in design are acceptable to the design organization.
- On each unit keep a memory book, a folder of reports on past accidents, which is compulsory reading for new recruits and which others dip into from time to time. It should include relevant reports from other companies but should not include cuts and bruises.
- Never remove equipment before you know why it was installed. Never abandon a procedure before you know why it was adopted.
- Devise better information retrieval systems so that details of past accidents, in our own and other companies, and the recommendations made afterward are more easily accessible than at present.
- Include important accidents of the past in the training of young graduates and company employees. Suitable training material is available from the American Institute of Chemical Engineers and the U.K. Institution of Chemical Engineers (Crowl and Louvar, *Chemical Process Safety: Fundamentals and Applications,* Prentice Hall, 1990).

KEY PROCEDURES

Safety by design should always be the aim, but it is often impossible or too expensive and we then have to rely on procedures. Key features of all procedures are as follows:

- They should be as simple as possible and written in simple language, to help the reader, rather than protect the writer.
- They should be explained to and discussed with those who will have to carry them out, not just sent to them through the post.
- Regular checks and audits should be made to confirm that they are being carried out correctly. They will corrode more rapidly than the steelwork, once those in charge lose interest or turn a blind eye.

Many accidents have occurred because the two procedures discussed in the following sections were unsatisfactory or were not followed.

Preparation of Equipment for Maintenance The essential feature of this procedure is a permit-to-work system: the operating team prepares the equipment and writes down on the permit the work to be done, the preparation carried out, the remaining hazards, and the necessary precautions. The permit is then accepted by the person or group that will carry out the work and is returned when the work is complete. The permit system will not make maintenance 100 percent safe, but it does reduce the chance that hazards will be overlooked, list ways of controlling them, and inform those doing the job of the precautions they should take. The system should cover such matters as who is authorized to issue and accept permits to work, the training they should receive (not forgetting deputies), and the period of time for which permits are valid. It should also cover the following:

- *Isolation of the equipment under maintenance.* Poor or missing isolation has been the cause of many serious accidents. Do not rely on valves except for quick jobs; use blinds or disconnection and blanking unless the job is so quick that blinding (or disconnection) would take as long and be as hazardous as the main job. Valves used for isolation (including isolation while fitting blinds or disconnecting) should be locked shut (for example, by a padlock and chain). Blinds should be made to the same standard (pressure rating and material of construction) as the plant. Plants should be designed so that blinds can be inserted without difficulty; that is, there should be sufficient flexibility in the pipework or a slip ring or figure-eight plate should be used. Electricity should be isolated by locking off or removal of fuses. Do not leave them lying around for anyone to replace. Always try out electrical equipment after defusing to check that the correct fuses have been withdrawn.
- *Identification of the equipment.* Many accidents have occurred because maintenance workers opened up the wrong equipment. Equipment which is under repair should be numbered or labeled unambiguously. Temporary labels should be used if there are no permanent ones. Pointing out the correct equipment is not sufficient. "The pump you repaired last week is leaking again" is a recipe for an accident.
- *Freeing from hazardous materials.* Equipment which is to be repaired should be freed as far as possible from hazardous materials. Gases can be removed by sweeping out with nitrogen (if the gases are flammable) or air, water-soluble liquids by washing with water, and oils by steaming. Some materials, such as heavy oils and materials that polymerize, are very difficult or impossible to remove completely. Tests should be carried out to make sure that the concentration of any hazardous material remaining is below an agreed level. Machinery should be in the lowest energy state. Thus the forks of forklift trucks should be lowered and springs should not be compressed or extended. For some machinery, the lowest energy state is less obvious. Do not work under heavy suspended loads.

- *Jobs which raise special problems.* Such jobs might include entry to vessels and other confined spaces, hot work, and responsibilities of contractors.
- *Handover.* Permits should be handed over (and returned when the job is complete) person to person. They should not be left on the table for people to sign when they come in.
- *Change of intent.* If there is a change in the work to be done, the permit should be returned and a new one issued [Crowl and Grossel (eds.), *Handbook of Toxic Materials Handling and Management,* Chap. 12, Marcel Dekker, 1995].

Control of Plant and Process Modifications Many accidents have occurred because plant or process modifications had unforeseen and unsafe side effects (Sanders, *Management of Change in Chemical Plants: Learning from Case Histories,* Butterworth-Heinemann, 1993). No such modifications should therefore be made until they have been authorized by a professionally qualified person who has made a systematic attempt to identify and assess the consequences of the proposal, by hazard and operability study or a similar technique. When the modification is complete, the person who authorized it should inspect it to make sure that the design intention has been followed and that it "looks right." What does not look right is usually wrong and should at least be checked.

Unauthorized modifications are particularly liable to occur:

- During start-ups, as changes may be necessary to get the plant on line.
- During maintenance, as the maintenance workers may be tempted to improve the plant as well as repair it. They may suggest modifications but should put the plant back as it was unless a change has been authorized.
- When the modification is cheap and no financial authorization is necessary. Many seemingly trivial modifications have had tragic results.
- When the modification is temporary. Twenty-eight people were killed by the temporary modification at Flixborough, one of the most famous of all time (Lees, *Loss Prevention in the Process Industries,* 2d ed., Butterworth-Heinemann, 1996; p. 2).
- When one modification leads to another, and then another (Kletz, *Plant/Operations Progress* **5,** 1986, p. 136).

PROCESS SAFETY ANALYSIS

HAZARD ANALYSIS

GENERAL REFERENCES: *ALOHA—Area locations of hazardous atmospheres* (computer program), Version 5.05 User's Manual, Hazardous Material Response Branch, National Oceanic and Atmospheric Administration (NOAA), Seattle, 1992. Applied Technology Corp. Chemical Manufacturers Association, *A Manager's Guide to Quantitative Risk Assessment,* December 1989. Arendt, JBF Associates, Inc., "Management of Quantitative Risk Assessment in the Chemical Industry," *Plant/Operations Progress,* vol. 9, no. 4, October 1990. Arthur D. Little, Inc., *FaultrEASE®*, 1991. *Chemical Exposure Index, Second Edition,* AIChE, New York, 1994. *CPQRA, Guidelines for Chemical Process Quantitative Risk Analysis,* CCPS-AIChE, New York, 1989. Crowl and Louvar, *Chemical Process Safety Fundamentals with Applications,* Prentice Hall, Englewood Cliffs, N.J., 1990. Delboy, Dubnansky, and Lapp, "Sensitivity of Process Risk to Human Error in an Ammonia Plant," *Plant/Operations Progress,* vol. 10, no. 4, October 1991. *Development of an Improved LNG Plant Failure Rate Data Base,* prepared for Gas Research Inst., Chicago, September 1981. DNV Technica, PHAST and SAFETI, *Process Hazard Analysis Software Tools, Version 4.0,* Technica Inc., London, 1991. *Dow Fire and Explosion Index,* AIChE, New York, January 1994. Dowell, Rohm and Haas Texas, Inc., "Managing the PHA Team," *Process Safety Progress* **13,** no. 1, January 1994. *Fault Tree Handbook,* National Technical Information Service, January 1981. Golay and Todras, "Advanced Light-Water Reactors," *Scientific American,* April 1990. *Guidelines for Safe Storage and Handling of Highly Toxic Hazard Materials,* CCPS-AIChE, New York, 1989. HAZOP-PC, Risk and Hazard Analysis Software Version 3 (computer program), PrimaTech Inc., Columbus, Ohio, 1994. Knowlton, *Hazard and Operability Studies,* Chemetics International Co., Ltd., Vancouver, B.C., February 1989. Latino, *Strive for Excellence . . . the Reliability Approach,* Reliability Center Inc., 1980. Lees, *Loss Prevention in the Process Industries,* Butterworths, London, 1980. Moore, "The Design of Barricades for Hazardous Pressure Systems," *Nuc. Eng. Des.* **5,** 1550–1566, 1967. Munich Re (Münchener Rück) Report, "Losses in the Oil, Petrochemical and Chemical Industry: A Report," Munich, Germany, 1991. NFPA 69, *Explosion Prevention Systems,* National Fire Protection Association, Quincy, Mass., 1992. NFPA 704, *Standard System for the Identification of the Fire Hazards of Materials,* National Fire Protection Association, Quincy, Mass., 1990. Pape and Nussey, "A Basic Approach for the Analysis of Risks from Toxic Hazards," *The Institution of Chemical Engineering Symposium Series No. 93,* University of Manchester Institute for Science and Technology (England), 22–24 April 1985. PHAST, "Process Hazard Analysis Software Tool," DNV Technica Limited, London, October 1990. *Process Safety Progress,* AIChE, New York, January and April 1994 (issues devoted largely to chemical process safety management). *Reliability Guidelines for Process Equipment,* CCPS-AIChE, New York, 1989. Stern and Keller, "Human Error and Equipment Design in the Chemical Industry," *Professional Safety,* May 1991. Swain and Gutterman, *Handbook of Human Reliability Analysis with Emphasis on Nuclear Power Plant Applications* (NUREG/CR-1278), Nuclear Regulatory Commission, Washington, 1983.

Introduction The meaning of *hazard* is often confused with *risk.* Hazard is defined as the inherent potential of a material or activity to harm people, property, or the environment. Hazard does not have a probability component.

There are differences in terminology on the meaning of *risk* in the published literature that can lead to confusion. *Risk* has been defined in various ways (*CPQRA*, 1989, pp. 3, 4). In this edition of the handbook, *risk* is defined as: "A measure of economic loss or injury in terms of both the incident likelihood and magnitude of loss or injury." *Risk* implies a probability of something occurring.

Definition of Terms Following are some definitions that are useful in understanding the components of hazards and risk (*CPQRA,* 1989, pp. 3, 4).

acceptable risk The average rate of risk considered tolerable for a given activity.

accident A specific combination of events or circumstances that leads to an undesirable consequence.

acute hazard The potential for injury or damage to occur as a result of an instantaneous or short-duration exposure to the effects of an accident.

chronic hazard The potential for injury or damage to occur as a result of prolonged exposure to an undesirable condition.

Cause-Consequence A procedure using diagrams to illustrate the causes and consequences of a particular scenario. They are not widely used because, even for simple systems, displaying all causes and outcomes leads to very complex diagrams.

Chemical Exposure Index (CEI) The CEI provides a method of rating the relative potential of acute health hazard to people from possible chemical release incidents.

consequence The direct, undesirable result of an accident, usually measured in health and safety effects, loss of property, or business costs, or a measure of the expected effects of an incident outcome case. For example, an ammonia cloud from a 10-lb/s leak under stability class D weather conditions and a 1.4-mi/h wind traveling in a northerly direction may injure 50 people.

consequence analysis Once hazards have been established, methods exist for analyzing their consequences (size of vapor cloud, blast damage radius, overpressure expected, etc.). This is independent of frequency or probability.

domino effect An incident which starts in one piece of equipment and affects other nearby items, such as vessels containing hazardous materials, by thermal blast or fragment impact. This can lead to escalation of consequences or frequency of occurrence. This is also known as a *knock-on effect.*

event An occurrence involving equipment performance or human action or an occurrence external to the system that causes system upset. An event is associated with an incident, either as a cause or a contributing cause of the incident, or as a response to an initiating event.

event sequence A specific, unplanned sequence of events composed of initiating events and intermediate events that may lead to an incident.

event tree Seeks to identify the ultimate consequence of an event, while fault tree analysis aims to identify the basic causes of a specific event. Event trees can grow quite large very quickly.

failure mode and effect analysis (FMEA) A hazard identification technique in which all known failure modes of components or features of a system are considered in turn and undesired outcomes are noted. It is usually used in combination with fault tree analysis. It is a complicated procedure, usually carried out by experienced risk analysts.

fault tree A method for representing the logical combinations of various system states which lead to a particular outcome, known as the *top event.*

Fire and Explosion Index (F&EI) The F&EI is used to rate the potential of hazard from fires and explosions.

frequency The rate at which observed or predicted events occur.

HAZOP HAZOP stands for "hazard and operability studies." This is a set of formal hazard identification and elimination procedures designed to identify hazards to people, process plants, and the environment. See subsequent sections for a more complete description.

incident The loss of containment of material or energy; for example, a leak of a flammable and toxic gas.

incident outcome The physical outcome of an incident; for example, a leak of a flammable and toxic gas could result in a jet fire, a vapor cloud explosion, a vapor cloud fire, a toxic cloud, etc.

probability The likelihood of the occurrence of events or a measure of the degree of belief, the values of which range from 0 to 1.

probability analysis Evaluates the likelihood of an event occurring. Using failure rate data for equipment, piping, instruments, and fault tree techniques, the frequency (events/year) can be quantified.

process hazard analysis (PHA) See subsequent section for description.

quantitative risk assessment (QRA) The systematic development of numerical estimates of the expected frequency and/or consequence of potential accidents associated with a facility or operation. Using consequence and probability analyses and other factors such as population density and expected weather conditions, QRA predicts the fatality rate for a given event. This methodology is useful for evaluation of alternates, but its value as an absolute measure of risk should be considered carefully.

risk analysis The development of a quantitative estimate of risk based on engineering evaluation and mathematical techniques for combining estimates of incident consequences and frequencies.

risk assessment The process by which results of a risk analysis are used to make decisions, either through a relative ranking of risk reduction strategies or through comparison with risk targets. The terms *risk analysis* and *risk assessment* are often used interchangeably in the literature.

worst credible incident The most severe incident, considering only incident outcomes and their consequences, of all identified incidents and their outcomes.

Process Hazard Analysis (PHA) (Dowell, 1994, pp. 30–34.) The OSHA rule for Process Safety Management (PSM) of Highly Toxic Hazardous Chemicals, 29 CFR 1910.119, part (e), requires an initial PHA and an update every five years for processes that handle listed chemicals or contain over 10,000 lb (4356 kg) of flammable material. The PHA must be done by a team, must include employees such as operators and mechanics, and must have at least one person skilled in the methodology employed. Suggested methodologies from Process Safety Management are listed in Table 26-1.

The PHA must consider hazards listed in the PSM Rule, part (e), including information from previous incidents with potential for catastrophic consequences, engineering and administrative controls and consequences of their failure, facility siting, and human factors. Consequences of failure of controls must be considered.

TABLE 26-1 Process Hazard Analysis Methods Listed in the OSHA Process Safety Management Rule

- What-if
- Checklist
- What-if/checklist
- Hazard and operability study (HAZOP)
- Failure mode and effect analysis (FMEA)
- Fault tree analysis (FTA)
- An appropriate equivalent methodology

SOURCE: Dowell, 1994, pp. 30–34.

Documentation is important. Everything considered should be documented. "If it is not documented, then you didn't do it." (Dowell, 1994, pp. 30–34.) The key to PHA documentation is to do it right away before it gets cold. Periodic follow-up is needed by management and safety professionals to confirm that all recommendations have been addressed.

Hazard and Risk Assessment Tools The hazard and risk assessment tools used vary with the stage of the project from the early design stage to plant operations. Many techniques are available, both qualitative and quantitative, some of which are listed in the following section. Reviews done early in projects often result in easier, more effective changes.

Qualitative Tools for Hazard Analysis

SHEL (Safety, Health, Environmental, and Loss Prevention Reviews) These reviews are performed during design. The purpose of the reviews is to have an outsider's evaluation of the process and layout from safety, industrial hygiene, environmental, and loss prevention points of view. It is often desirable to combine these reviews to improve the efficiency of the use of time for the reviewers.

Checklists Checklists are simple means of applying experience to designs or situations to ensure that the features appearing in the list are not overlooked. Checklists tend to be general and may not be appropriate to a specific situation. They may not handle adequately the novel design or unusual process.

What-if At each process step, what-if questions are formulated and answered to evaluate the effects of component failures or procedural errors. This technique relies on the experience level of the questioner.

Failure Mode and Effect Analysis (FMEA) This is a systematic study of the causes of failures and their effects. All causes or modes of failure are considered for each element of a system, and then all possible outcomes or effects are recorded. This method is usually used in combination with fault tree analysis, a quantitative technique. FMEA is a complicated procedure, usually carried out by experienced risk analysts.

Cause-Consequence Diagram These diagrams illustrate the causes and consequences of a particular scenario. They are not widely used because, even for simple systems, displaying all causes and outcomes leads to very complex diagrams. Again, this technique is employed by experienced risk analysts.

Reactive Chemicals Reviews The process chemistry is reviewed for evidence of exotherms, shock sensitivity, and other instability, with emphasis on possible exothermic reactions. It is especially important to consider pressure effects—"Pressure blows up people, not temperature!" The purpose of this review is to prevent unexpected and uncontrolled chemical reactions. Reviewers should be knowledgeable people in the field of reactive chemicals and include people from loss prevention, manufacturing, and research.

Industrial Hygiene Reviews These reviews evaluate the potential of a process to cause harm to the health of people. It is the science of the anticipation, recognition, evaluation, and control of health hazards in the environment. It usually deals with chronic, not acute, releases and is involved with toxicity.

Toxicity is the ability to cause biological injury. Toxicity is a property of all materials, even salt, sugar, and water. It is related to dose and the degree of hazard associated with a material. The amount of a dose is both time and duration dependent. Dose is a function of exposure (concentration) and duration and is sometimes expressed as dose = $(\text{concentration})^n \times \text{duration}$, where n can vary from 1 to 4.

Industrial hygiene deals with hazards caused by chemicals, radiation, and noise. Routes of exposure are through the eyes, by inhalation, by ingestion, and through the skin. An industrial hygiene guide is based on exposures for an 8-hour day, 40-hour week and is to be used as a guide in the control of health hazards. It is not to be used as a fine line between safe and dangerous conditions. Types of controls used include:

- Engineering, such as containment, ventilation, and automation
- Administrative, such as use of remote areas and job rotation
- Protective equipment

Facilities Reviews There are many kinds of facilities reviews that are useful in detecting and preventing process safety problems. They include pre-start-up reviews (before the plant operates), new-plant reviews (the plant has started, but is still new), reviews of existing plants (safety, technology, and operations audits and reviews), management reviews, critical instrument reviews, and hazardous materials transportation reviews.

HAZOP (Knowlton, 1989; Lees, 1980; *CPQRA*, 1989, pp. 419–422). HAZOP stands for "hazard and operability studies." This is a set of formal hazard identification and elimination procedures designed to identify hazards to people, process plants, and the environment. The techniques aim to stimulate in a systematic way the imagination of designers and people who operate plants or equipment so they can identify potential hazards. In effect, HAZOP studies make the assumption that a hazard or operating problem can arise when there is a deviation from the design or operating intention. Corrective actions can then be made before a real accident occurs.

Some studies have shown that a HAZOP study will result in recommendations that are 40 percent safety-related and 60 percent operability-related. HAZOP is far more than a safety tool; a good HAZOP study also results in improved operability of the process or plant, which can mean greater profitability.

The primary goal in performing a HAZOP study is to identify, not analyze or quantify, the hazards in a process. The end product of a study is a list of concerns and recommendations for prevention of the problem, not an analysis of the occurrence, frequency, overall effects, and the definite solution. If HAZOP is started too late in a project, it can lose effectiveness because:

1. There may be a tendency not to challenge an already existing design.
2. Changes may come too late, possibly requiring redesign of the process.
3. There may be loss of operability and design decision data used to generate the design.

HAZOP is a formal procedure that offers a great potential to improve the safety, reliability, and operability of process plants by recognizing and eliminating potential problems at the design stage. It is not limited to the design stage, however. It can be applied anywhere that a design intention (how the part or process is expected to operate) can be defined, such as:

- Continuous or batch processes being designed or operated
- Operating procedures
- Maintenance procedures
- Mechanical equipment design
- Critical instrument systems
- Development of process control computer code

These studies make use of the combined experience and training of a group of knowledgeable people in a structured setting. Some key concepts are:

- *Intention*—defines how the part or process is expected to operate.
- *Guide words*—simple words used to qualify the intention in order to guide and stimulate creative thinking and so discover deviations. Table 26-2 describes commonly used guide words.
- *Deviations*—departures from the intention discovered by systematic application of guide words.
- *Causes*—reasons that deviations might occur.
- *Consequences*—results of deviations if they occur.
- *Actions*—prevention, mitigation, and control
  - —Prevent causes.
  - —Mitigate the consequence.
  - —Control actions, e.g., provide alarms to indicate things getting out of control; define control actions to get back into control.

The HAZOP study is not complete until response to actions has been documented. Initial HAZOP planning should establish the management follow-up procedure that will be used.

The guide words can be used on broadly based intentions (see Table 26-2), but when intentions are expressed in fine detail, some restrictions or modifications are necessary for chemical processes, such as:

No flow
Reverse flow
Less flow
More temperature
Less temperature
Composition change
Sampling
Corrosion/erosion

This gives a process plant a specific HAZOP guide-word list with a process variable, plant condition, or an issue.

HAZOP studies may be made on batch as well as continuous processes. For a continuous process, the working document is usually a set of flow sheets or piping and instrument diagrams (P&IDs). Batch processes have another dimension: time. Time is usually not significant with a continuous process that is operating smoothly except during start-up and shutdown, when time will be important and it will resemble a batch process. For batch processes, the working documents consist not only of the flow sheets or P&IDs but also the operating procedures. One method to incorporate this fourth dimension is to use guide words associated with time, such as those described in Table 26-3.

HAZOP studies involve a team, at least some of whom have had experience in the plant design to be studied. These team members apply their expertise to achieve the aims of HAZOP. There are four overall aims to which any HAZOP study should be addressed:

1. Identify as many deviations as possible from the way the design is expected to work, their causes, and problems associated with these deviations.
2. Decide whether action is required, and identify ways the problem can be solved.
3. Identify cases in which a decision cannot be made immediately and decide what information or action is required.
4. Ensure that required actions are followed through.

The team leader is a key to the success of a HAZOP study and should have adequate training for the job. Proper planning is important to success. The leader is actually a facilitator (a discussion leader and one who keeps the meetings on track) whose facilitating skills are just as important as technical knowledge. The leader outlines the boundaries of the study and ensures that the design intention is clearly understood. The leader applies guide words and encourages the team to discuss causes, consequences, and possible remedial actions for each deviation. Prolonged discussions of how a problem may be solved should be avoided.

Some people believe that it may be an advantage for the team leader not to have an intimate knowledge of the plant or process being studied in order to maintain neutrality. Ideally, the team leader should

TABLE 26-2 Some Guide Words Used in Conjunction with Process Parameters

Guide Word	Meanings	Comments
No, Not, None	Complete negation of design intentions	No part of intention is achieved and nothing else occurs
More of	Quantitative increases of any relevant physical parameters	Quantities and relevant physical properties such as flow rates, heat
Less of	Quantitative decreases	Same as above
As well as	Qualitative increase	All design and operating intentions are achieved as well as some additional activity
Part of	A qualitative decrease	Some intentions are achieved, some are not
Reverse	Logical opposite of intention	Activities such as reverse flow or chemical reaction, or poison instead of antidote
Other than	Complete substitution	No part of intention is achieved; something quite different happens

SOURCE: Knowlton, 1989.

TABLE 26-3 Guide Words Associated with Time

Guide word	Meaning
No time	Step(s) missed
More time	Step does not occur when it should
Less time	Step occurs before previous step is finished
Wrong time	Flow or other activity occurs when it should not

SOURCE: Knowlton, 1989.

be accompanied by a scribe or recorder, freeing the leader for full-time facilitating. The scribe should take notes in detail for full recording of as much of the meeting as is necessary to capture the intent of actions and recommendations.

Computer tools are available to aid information capture. In some cases, the facilitator may use the computer tool for recording, replacing the secretary. For example, PrimaTech offers a very useful computer program to aid in HAZOP studies (HAZOP-PC, 1994). Other excellent computer aids for HAZOP are also commercially available.

Team size is important. Less than three contributing members, excluding the secretary and leader, will probably reduce team effectiveness. A team size of five to eight, including the leader and scribe, is probably optimum.

The time required for HAZOP studies is significant. It has been estimated that each line or *node* (a node is usually a line or an item of equipment) may require in the range of about 30 minutes for an experienced team, although the time may vary widely. It should be recognized that the time required for HAZOP studies may not really be additional time for the project as a whole, particularly if started early enough in the design, and may actually save time on the project. It may make design of parts of the process more efficient, reduce the changes required later, and reduce the time required for safety and other reviews. It should make the safety reviews that should accompany any project much faster, as there will be fewer safety problems to discuss. It also should make possible smoother start-ups and make the process or plant safer and easier to operate, which will more than pay back the cost of the HAZOP study during the life of the plant. The results of a HAZOP study should be the basis for the operating discipline of a process, which in itself is a very valuable contribution.

Quantitative Tools for Hazard Analysis

Quantitative Fire and Explosion Index (F&EI) (*Dow Fire and Explosion Index Hazard Classification Guide,* 1994; Lees, 1980, pp. 149–160). The F&EI is used to rate the potential of hazard from fires and explosions. Its purpose is to quantify damage from an incident. It identifies equipment that could contribute to an incident and ways to mitigate possible incidents. It is a way to communicate to management the quantitative hazard potential.

The F&EI measures realistic maximum loss potential under adverse operating conditions. It is based on quantifiable data. It is designed for flammable, combustible, and reactive materials that are stored, handled, or processed. It does not address frequency (risk) except indirectly, nor does it address specific hazards to people except indirectly.

The goals of the F&EI are to raise awareness of loss potential and identify ways to reduce potential severity and potential dollar loss in a cost-effective manner. The index number has significance as a comparison and in calculations to estimate the *maximum probable property damage* (MPPD). It also provides a method for measuring the effect of outage (plant being shut down) on the business. It is easy for users to get credible results with a small amount of training.

Chemical Exposure Index (CEI) (*Chemical Exposure Index,* 1994). The CEI provides a method of rating the relative potential of acute health hazard to people from possible chemical release incidents. It may be used for conducting the initial process hazard analysis and it establishes the degree of further analysis needed. The CEI also may be used as part of the site review process.

The system provides a method of ranking one risk relative to another. It is not intended to define a particular containment system as safe or unsafe but provides a way of comparing toxic hazards. It deals with acute, not chronic, releases. The procedure focuses on the necessary degree of concern and will provide the opportunity for recommendations, improvements, and concurrence from the appropriate knowledgeable people. Flammability and explosion hazards are not included in this index.

The CEI and hazard distance determine the level of review that is necessary. To develop a CEI, the following information is needed:

- An accurate plot plan of the plant and surrounding area
- A simplified process flow sheet showing containment vessels, major piping, and quantity of chemicals
- Physical and chemical properties of the chemical, including boiling point, molecular weight, and flash point
- Pressure and temperature of materials contained
- Toxicity (acute health hazard rating)
- Quantity (volatilized portion)
- Distance (to area of concern)
- Process variables (temperature, pressure, reactivity)
- Sights, odors, or sounds that could cause public concern or inquiries, such as smoke and odors below hazardous levels—for example, mercaptans or amines
- ERPG/EEPG—usually ERPG-2 is used
- Definition of ERPG

The Emergency Response Planning Guidelines (ERPG) are values established by the American Industrial Hygiene Association and intended to provide estimates of chemical concentration ranges where one might reasonably anticipate observing adverse effects as follows:

ERPG-1 The maximum airborne concentration below which it is believed that nearly all individuals could be exposed for up to one hour without experiencing other than mild transient adverse health effects or perceiving a clearly defined objectionable odor.

ERPG-2 The maximum airborne concentration below which it is believed that nearly all individuals could be exposed for up to one hour without experiencing irreversible or other serious health effects or symptoms that could impair their ability to take protective action.

ERPG-3 The maximum airborne concentration below which it is believed that nearly all individuals could be exposed for up to one hour without experiencing or developing life-threatening health effects.

Factors to consider when calculating a CEI are:

1. Credible scenario for a release
2. The rate at which toxic materials would be released in a scenario

When these two factors are considered together, a possible release rate can be calculated.

When considering release scenarios, the most hazardous unit in a plant should be chosen, based on inventory and process conditions. The idea is to imagine the release of material in the fastest way that is reasonably possible. The worst realistic scenario should be considered. This can be based on the outcome of a review, from a HAZOP study or a hazard analysis. The time a scenario will take is almost always considered to be continuous, because after a few minutes a stable dispersion distance exists. Making the time longer will not necessarily change the hazard distance.

Quantitative Tools for Risk Analysis

Quantitative Risk Analysis (QRA) QRA is a technique that provides advanced quantitative means to supplement other hazard identification, analysis, assessment, control, and management methods to identify the potential for such incidents and to evaluate risk reduction and control strategies. QRA identifies those areas where operation, engineering, or management systems may be modified to reduce risk and may identify the most economical way to do it. The primary goal of QRA is that appropriate management actions, based on results from a QRA study, help to make facilities handling hazardous chemicals safer. QRA is one component of an organization's total process risk management. It allows the quantitative assessment of risk alternatives that can be balanced against other considerations.

Fault Tree Analysis Fault tree analysis permits the hazardous incident (called the *top event*) frequency to be estimated from a logic model of the failure mechanisms of a system. The top event is traced downward to more basic failures using logic gates to determine its causes and likelihood. The model is based on the combinations of failures of more basic system components, safety systems, and human reliability. The underlying technology is the use of relatively simple logic gates (usually AND and OR gates) to synthesize a failure model of a plant. AND gates combine input events, all of which must exist simultaneously for the output to occur. OR gates also combine input events, but any one is sufficient to cause the output. The top event frequency or probability is calculated from failure data of more simple events. The top event might be a boiling liquid evaporating vapor explosion (BLEVE), a relief system discharging to the atmosphere, or a runaway reaction.

NFPA Standard System for Identification of Health, Flammability, Reactivity, and Related Hazards (NFPA 704, Chaps. 2–5, 1990. This printed 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.)

This is a brief summary of NFPA 704 which addresses hazards that may be caused by short-term, acute exposure to a material during handling under conditions of fire, spill, or similar emergencies. This standard provides a simple, easily recognized, easily understood system of markings. The objective is to provide on-the-spot identification of hazardous materials.

These markings provide a general idea of the hazards of a material and the severity of these hazards as they relate to handling, fire protection, exposure, and control. This standard is not applicable to transportation or to use by the general public. It is also not applicable to chronic exposure. For a full description of this standard, refer to NFPA 704. The system identifies the hazards of a material in four principal categories: health, flammability, reactivity, and unusual hazards such as reactivity with water.

The degree of severity of health, flammability, and reactivity is indicated by a numerical rating that rates from zero (no hazard) to four (severe hazard). The information is presented in a square-on-point (diamond) field of numerical ratings. Information is presented as follows:

- Health rating in blue at nine o'clock
- Flammability rating in red at twelve o'clock
- Reactivity hazard rating in yellow at three o'clock
- Unusual hazards at six o'clock

Materials that demonstrate unusual reactivity with water are identified as ~~W~~ and materials that possess oxidizing properties shall be identified by the letters OX. Other special hazard symbols may be used to identify radioactive hazards, corrosive hazards, substances that are toxic to fish, and so on.

The use of this system will provide a standard method of identifying the relative degree of hazard that is contained in various tanks, vessels, and pipelines. Suggested applications include:

- All storage tanks outside the block limits of a plant.
- Within block limits of a plant, tanks or process vessels with a capacity of more than 5000 gal (19 m^3).
- Process lines 3 in (7.62 cm) and larger, containing material with a health or reactivity rating of two, three, or four, or a flammability rating of three or four. Lines containing materials with lower ratings can also be marked if desired.

The name of the material contained in the pipelines should be placed on all lines at the point where they enter or leave the block and at road crossings. Block limit valves and emergency block valves should be painted yellow.

For a detailed description of the degrees of severity of the ratings, see NFPA 704. Table 26-4 shows the system for identification of hazards. Figures 26-1, 26-2, and 26-3 show examples of arrangements for display of the NFPA 704 Hazard Identification System.

RISK ANALYSIS

General References: *Guidelines for Chemical Process Quantitative Risk Analysis,* CCPS-AIChE, New York, 1989. Arendt, "Management of Quantitative Risk Assessment in the Chemical Process Industry," *Plant Operations Progress,* vol. 9, no. 4, AIChE, New York, October 1990. CMA, "A Manager's Guide to Quantitative Risk Assessment," Chemical Manufacturers' Association, December 1989. EFCE, "Risk Analysis in the Process Industries," European Federation of Chemical Engineering, Publication Series no. 45, 1985. Lees,

TABLE 26-4 System for Identification of Hazards

	Identification of health hazard. Color code: Blue		Identification of flammability. Color code: Red		Identification of reactivity (stability). Color code: Yellow
Signal	Type of possible injury	Signal	Susceptibility of materials to burning	Signal	Susceptibility to release of energy
4	Materials that on short exposure could cause death or major residual injury	4	Materials that will rapidly or completely vaporize at atmospheric pressure and normal ambient temperature, or that are readily dispersed in air and will burn readily	4	Materials that in themselves are readily capable of detonation or of explosive decomposition or reaction at normal temperatures and pressures
3	Materials that on short exposure could cause serious temporary or residual injury	3	Liquids or solids that can be ignited under almost all ambient temperature conditions	3	Materials that in themselves are readily capable of detonation or of explosive decomposition or reaction but require a strong initiating source or which must be heated under confinement before initiation or which react explosively with water
2	Materials that on intense or continued but not chronic exposure could cause temporary incapacitation or possible residual injury	2	Materials that must be moderately heated or exposed to relatively high ambient temperatures before ignition can occur	2	Materials that readily undergo violent chemical change at elevated temperatures and pressures or which react violently with water or which may form explosive mixtures with water
1	Materials that on exposure would cause irritation but only minor residual injury	1	Materials that must be preheated before ignition can occur	1	Materials that are normally stable, but which can become unstable at elevated temperatures and pressures
0	Materials that on exposure under fire conditions would offer no hazard beyond that of ordinary combustible material	0	Materials that will not burn	0	Materials that are normally stable, even under fire exposure conditions, and which are not reactive with water

SOURCE: Reprinted with permission from NFPA 704, *Standard System for the Identification of the Fire Hazards of Materials,* National Fire Protection Association, Quincy, Mass., 1990. This printed 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.

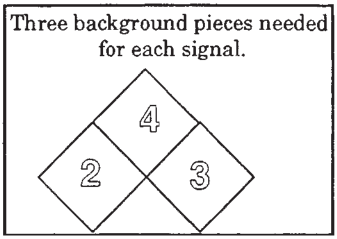


FIG. 26-1 For use where specified color background is used with numerals of contrasting colors. (*NFPA 704, 1990.*)

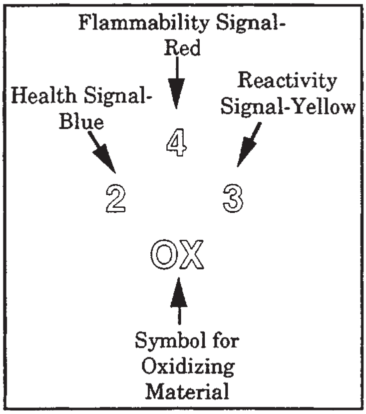


FIG. 26-2 For use where white background is used. (*NFPA 704, 1990.*)

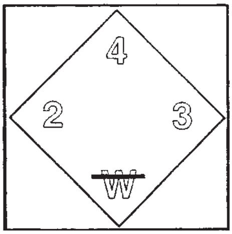


FIG. 26-3 For use where white background is used or for signs or placards. (*NFPA 704, 1990.*)

Loss Prevention in the Process Industries, Butterworths, Boston, 1980. World Bank, *Manual of Industrial Hazard Assessment Techniques,* Office of Environmental and Scientific Affairs, World Bank, Washington, D.C., 1985.

FREQUENCY ESTIMATION REFERENCES: *Guidelines for Process Equipment Reliability Data,* CCPS-AIChE, New York, 1989. Billington and Allan, *Reliability Evaluation of Engineering Systems: Concepts and Techniques,* Plenum Press, New York, 1983. Fussell, Powers, and Bennetts, "Fault Trees: A State of the Art Discussion," *IEEE Transactions on Reliability,* 1974. Roberts, N. H. et al., *Fault Tree Handbook,* NUREG-0492, Washington, D.C. Swain and Guttmann, *Handbook of Human Reliability Analysis with Emphasis on Nuclear Power Plant Applications,* NUREG/CR-1278, USNRC, Washington, D.C., 1983.

CONSEQUENCE ESTIMATION REFERENCES: *Guidelines for Use of Vapor Cloud Dispersion Models,* CCPS-AIChE, New York, 1987. TNO, *Methods for the Calculation of the Physical Effects of the Escape of Dangerous Materials: Liquids and Gases* ("The Yellow Book"), Apeldoorn, The Netherlands, 1979.

RISK ESTIMATION REFERENCES: Health and Safety Executive, *Canvey—An Investigation of Potential Hazards from the Operations in the Canvey Island/Thurrock Area,* HMSO, London, 1978. Rasmussen, *Reactor Safety Study: An Assessment of Accident Risk in U.S. Commercial Nuclear Power Plants,* WASH-1400 NUREG 75/014, Washington, D.C., 1975. Rijnmond Public Authority, *A Risk Analysis of 6 Potentially Hazardous Industrial Objects in the Rijnmond Area—A Pilot Study,* D. Reidel, Boston, 1982.

Introduction The previous sections dealt with techniques for the identification of hazards and methods for calculating the effects of accidental releases of hazardous materials. This section addresses the methodologies available to analyze and estimate risk, which is a function of both the consequences of an incident and its frequency. The application of these methodologies in most instances is not trivial. A significant allocation of resources is necessary. Therefore, a selection process or risk prioritization process is advised before considering a risk analysis study.

Important definitions are as follows.

Markov model A mathematical model used in reliability analysis. For many safety applications, a discrete-state (e.g., working or failed), continuous-time model is used. The failed state may or may not be repairable.

Probit model A mathematical model of dosage and response in which the dependent variable (response) is a probit number that is related through a statistical function directly to a probability.

risk A measure of economic loss or human injury in terms of both incident likelihood (frequency) and the magnitude of the loss or injury (consequence).

risk analysis The development of an estimate of risk based on engineering evaluation and mathematical techniques for combining estimates of incident consequences and frequencies. Incidents in the context of the discussion in this chapter are acute events which involve loss of containment of material or energy.

A typical hazard identification process, such as a hazard and operability (HAZOP) study, is sometimes used as a starting point for selection of potential major risks for risk analysis. Other selection or screening processes can also be applied. However major risks are chosen, a HAZOP study is a good starting point to develop information for the risk analysis study. A major risk may qualify for risk analysis if the magnitude of the incident is potentially quite large (high potential consequence) or if the frequency of a severe event is judged to be high (high potential frequency) or both. A flowchart which describes a possible process for risk analysis is shown in Fig. 26-4.

The components of a risk analysis involve the estimation of the frequency of an event, an estimation of the consequences (the extent of the material or energy release and its impact on population, property, or environment), and the selection and generation of the estimate of risk itself.

A risk analysis can have a variety of potential goals:

1. To screen or bracket a number of risks in order to prioritize them for possible future study
2. To estimate risk to employees
3. To estimate risk to the public
4. To estimate financial risk
5. To evaluate a range of risk reduction measures
6. To meet legal or regulatory requirements
7. To assist in emergency planning

The scope of a study required to satisfy these goals will be dependent upon the extent of the risk, the depth of the study required, and the level of resources available (mathematical models and tools and skilled people to perform the study and any internal or external constraints).

The objective of a risk analysis is to reduce the level of risk wherever practical. Much of the benefit of a risk analysis comes from the discipline which it imposes and the detailed understanding of the major contributors of the risk that follows. There is general agreement that if risks can be identified and analyzed, then measures for risk reduction can be effectively selected.

The expertise required in carrying out a risk analysis is substantial. Although various software programs are available to calculate the frequency of events or their consequences, or even risk estimates, engineering judgment and experience are still very much needed to produce meaningful results. And although professional courses are available in this subject area, there is a significant learning curve required not only for engineers to become practiced risk analysts, but

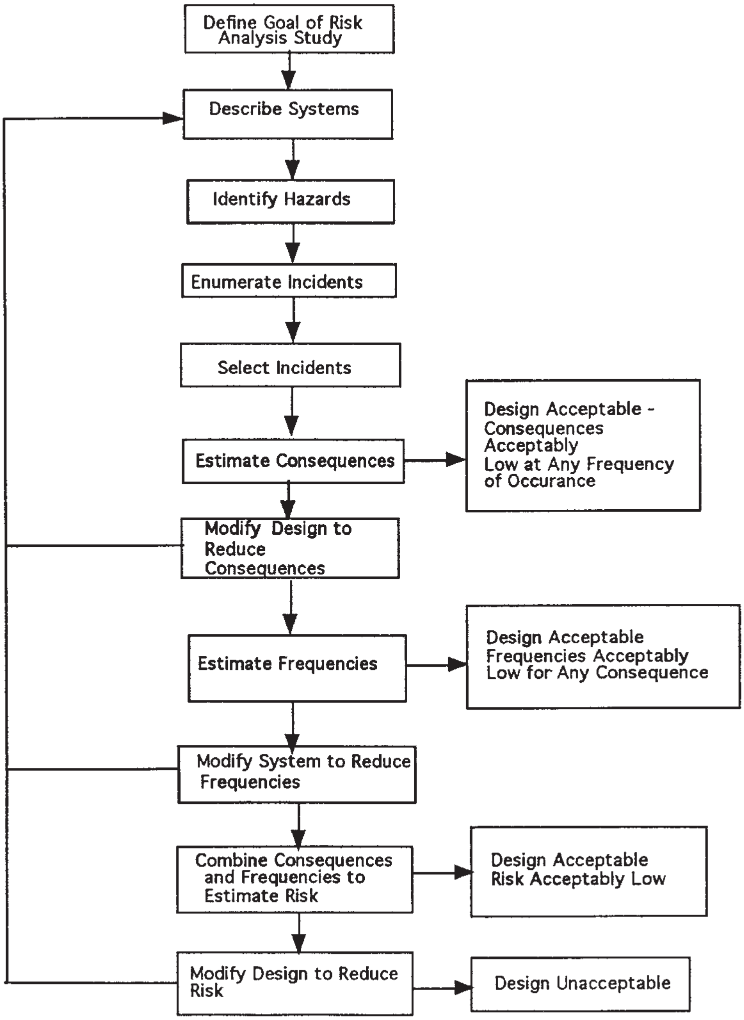


FIG. 26-4 One version of a risk analysis process. (*CCPS-AIChE, 1989, p. 13 by permission.*)

also for management to be able to understand and interpret the results. For these reasons, it may be useful to utilize a consultant organization in this field when a decision is made that a risk analysis is needed as a means to get started.

The analysis of a risk—that is, its estimation—leads to the assessment of that risk and the decision-making processes of selecting the appropriate level of risk reduction. In most studies this is an iterative process of risk analysis and risk assessment until the risk is reduced to some specified level. The subject of "acceptable" or "tolerable" levels of risk that could be applied to decision making on risks is a complex subject which will not be addressed in this section.

Frequency Estimation There are two primary sources for estimates of incident frequencies. These are historical records and the application of fault tree analysis and related techniques, and they are not necessarily applied independently. Specific historical data can sometimes be usefully applied as a check on frequency estimates of various subevents of a fault tree, for example.

The use of historical data provides the most straightforward approach to the generation of incident frequency estimates but is subject to the applicability and the adequacy of the records. Care should be exercised in extracting data from long periods of the historical record over which design or operating standards or measurement criteria may have changed.

An estimate of the total population from which the incident information has been obtained is important and may be difficult to obtain.

Fault tree analysis and other related event frequency estimation techniques, such as event tree analysis, play a crucial role in the risk analysis process. Fault trees are logic diagrams that depict how components and systems can fail. The undesired event becomes the top event and subsequent subevents, and eventually basic causes, are then developed and connected through logic gates. The fault tree is completed when all basic causes, including equipment failures and human errors, form the base of the tree. There are general rules for construction, which have been developed by practitioners, but no specific rules for events or gates to use. The construction of a fault tree is still more of an art than a science. Although a number of attempts have been made to automate the construction of fault trees from process flow diagrams or piping instrumentation diagrams, these attempts have been largely unsuccessful. (P. K. Andow, "Difficulties in Fault Tree Synthesis for Process Plant," *IEEE Transactions on Reliability* **R-29**(1): 2, 1980).

Once the fault tree is constructed, quantitative failure rate and probability data must be obtained for all basic causes. A number of equipment failure rate databases are available for general use. However, specific equipment failure rate data is generally lacking and, therefore, data estimation and reduction techniques must be applied to generic databases to help compensate for this shortcoming. Accuracy and applicability of data will always be a concern, but useful results from quantifying fault trees can generally be obtained by experienced practitioners.

Human error probabilities can also be estimated using methodologies and techniques originally developed in the nuclear industry. A number of different models are available (Swain, "Comparative Evaluation of Methods for Human Reliability Analysis," GRS Project RS 688, 1988). This estimation process should be done with great care, as many factors can affect the reliability of the estimates. Methodologies using expert opinion to obtain failure rate and probability estimates have also been used where there is sparse or inappropriate data.

In some instances, plant-specific information relating to frequencies of subevents (e.g., a release from a relief device) can be compared against results derived from the quantitative fault tree analysis, starting with basic component failure rate data.

An example of a fault tree logic diagram using AND and OR gate logic is shown in Fig. 26-5.

The logical structure of a fault tree can be described in terms of boolean algebraic equations. Some specific prerequisites to the application of this methodology are as follows.

- Equipment states are binary (working or failed).
- Transition from one state to another is instantaneous.
- Component failures are statistically independent.
- The failure rate and repair rate are consistent for each equipment item.
- After repair, the component is returned to the working state.

Minimal cut set analysis is a mathematical technique for developing and providing probability estimates for the combinations of basic component failures and/or human error probabilities, which are necessary and sufficient to result in the occurrence of the top event.

A number of software programs are available to perform these calculations, given the basic failure data and fault tree logic diagram (AIChE-CCPS, 1989). Other less well known approaches to quantifying fault tree event frequencies are being practiced, which result in gate-by-gate calculations using discrete-state, continuous-time, Markov models (Doelp et al., "Quantitative Fault Tree Analysis, Gate-by-Gate Method," *Plant Operations Progress* **4**(3): 227–238, 1984).

Identification and quantitative estimation of common-cause failures are general problems in fault tree analysis. Boolean approaches are generally better suited to mathematically handle common-cause failures.

Event tree analysis is another useful frequency estimation technique used in risk analysis. It is a bottom-up logic diagram, which starts with an identifiable event. Branches are then generated, which lead to specific chronologically based outcomes with defined probabilities. Event tree analysis can provide a logic bridge from the top event, such as a flammable release into specific incident outcomes (e.g., no ignition, flash fire, or vapor cloud explosion). Probabilities for each limb in the event tree diagram are assigned and, when multiplied by the starting frequency, produce frequencies at each node point for all the various incident outcome states. The probabilities for all of the limbs at any given level of the event tree must sum to 1.0. Event trees are generally very helpful toward the generation of a final risk estimate.

Consequence Estimation Given that an incident (release of material or energy) has been defined, the consequences can be estimated. The general logic diagram in Fig. 26-6 illustrates these calculations for the release of a volatile hazardous substance.

For any specific incident there will be an infinite number of incident outcome cases that can be considered. There is also a wide degree of consequence models which can be applied. It is important, therefore, to understand the objective of the study to limit the number of incident outcome cases to those which satisfy that objective. An example of variables which can be considered is as follows.

- Quality, magnitude, and duration of the release
- Dispersion parameters
  - wind speed
  - wind direction
  - weather stability
- Ignition probability (flammable releases)
  - ignition sources/location
  - ignition strength
- Energy levels contributing to explosive effects (flammable releases)
- Impact of release on people, property, or environment
  - thermal radiation
  - projectiles
  - shock-wave overpressure
  - toxic dosage
- Mitigation effects
  - safe havens
  - evacuation
  - daytime/nighttime populations

Probit models have been found generally useful to describe the effects of incident outcome cases on people or property for more complex risk analyses. At the other end of the scale, the estimation of a distance within which the population would be exposed to a concentration of ERPG-2 or higher may be sufficient to describe the impact of a simple risk analysis.

Portions or all of the more complex calculation processes, using specific consequence models, have been incorporated into a few commercially available software packages (AIChE-CCPS, 1989). These programs should be used by risk analysts with extensive engineering experience, as significant judgment will still be required.

The output of these calculation processes is one or more pairs of an incident or incident outcome case frequency and its effect (consequence or impact).

Risk Estimation There are a number of risk measures which can be estimated. The specific risk measures chosen are generally related to the study objective and depth of study, and any preferences or requirements established by the decision makers. Generally, risk measures can be broken down into three categories: risk indices, individual risk measures, and societal risk measures.

Risk indices are usually single-number estimates, which may be used to compare one risk with another or used in an absolute sense compared to a specific target. For risks to employees the *fatal accident rate* (FAR) is a commonly applied measure. The FAR is a single-number index, which is the expected number of fatalities from a specific event based on 10^8 exposure hours. For workers in a chemical plant, the FAR could be calculated as follows:

$$\text{FAR} = \frac{10^8}{8760} \times f \times \frac{D}{N} \tag{26-1}$$

where FAR = fatal accident rate, expected number of fatalities from a specific event based on 10^8 exposure hours
f = frequency of the event in years^{-1}
D = expected number of fatalities, given the event
N = average number of exposed individuals on each shift

References are available which provide FAR estimates for various occupations, modes of transportation, and other activities (Kletz, "The Risk Equations—What Risk Should We Run?," *New Scientist,* May 12, pp. 320–325, 1977).

Figure 26-7 is an example of an individual risk contour plot, which shows the expected frequency of an event causing a specified level of harm at a specified location, regardless whether anyone is present at that location to suffer that level of harm.

The total individual risk at each point is equal to the sum of the individual risks at that point from all incident outcome cases.

$$\text{IR}_{x,y} = \sum_{i=1}^{n} \text{IR}_{x,y,i} \tag{26-2}$$

where $\text{IR}_{x,y}$ = total individual risk of fatality at geographical location x,y
$\text{IR}_{x,y,i}$ = individual risk of fatality at geographical location x,y from incident outcome case i
n = total number of incident outcome cases

A common form of societal risk measure is an F-N curve, which is normally presented as a cumulative distribution plot of frequency F

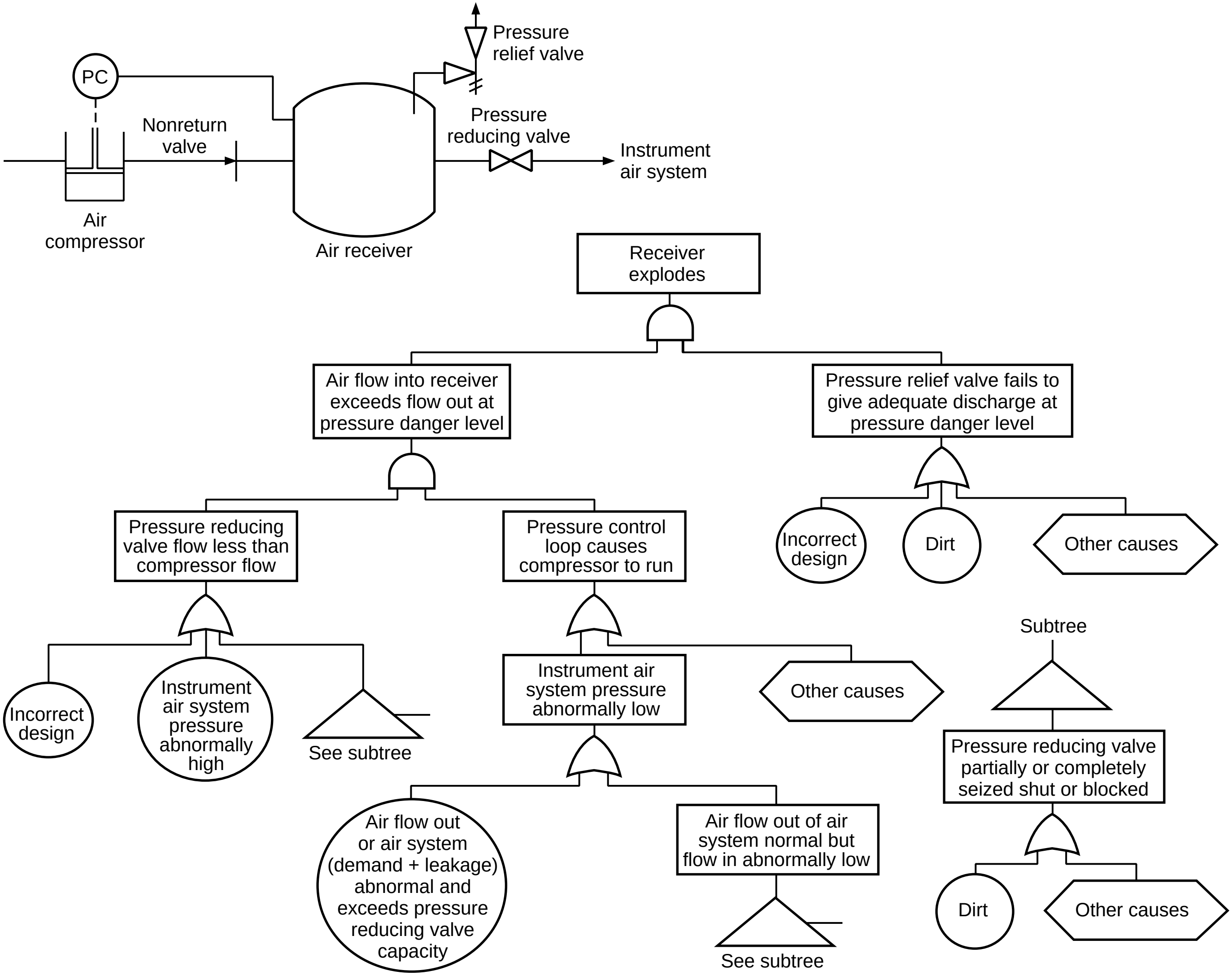


FIG. 26-5 Process drawing and fault tree for explosion of an air receiver. (*From Lees, 1980, pp. 200, 201, by permission.*)

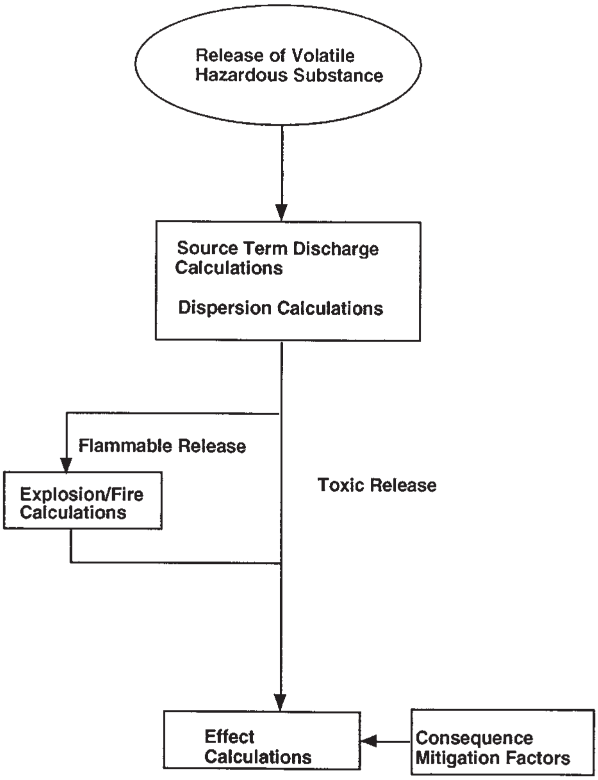


FIG. 26-6 Overall logic diagram for consequence analysis of volatile hazardous substances. (*CCPS-AIChE, 1989, p. 60.*)

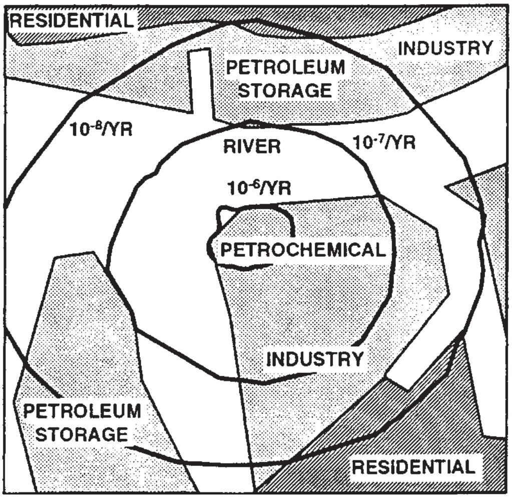


FIG. 26-7 Example of an individual risk contour plot. (*CCPS-AIChE, 1989, p. 269.*)

versus number of fatalities *N*. An example of this type of measure is shown in Fig. 26-8.

Any individual point on the curve is obtained by summing the frequencies of all events resulting in that number of fatalities or greater. The slope of the curve and the maximum number of fatalities are two key indicators of the degree of risk.

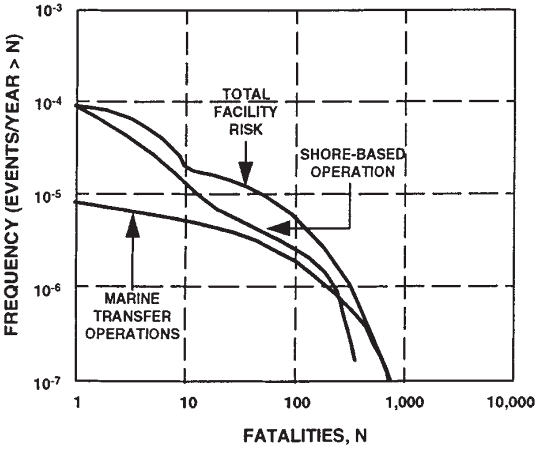


FIG. 26-8 Example of a societal risk F-N curve. (*AIChE-CCPS, 1989, p. 4.4.*)

For all risk measures it is possible to estimate the risk level of the current process as well as the risk levels from incorporation of various risk reduction alternatives. Management can then use this information as an important input in the final risk decision-making process.

GUIDELINES FOR ESTIMATING DAMAGE

Nomenclature

A	Projected area of fragment, breach area, or fragment cross-sectional area
a_a	Sound velocity in atmosphere
a_e	Sound velocity in high-pressure gas prior to vessel failure
B	Batch energy availability
d	Fragment diameter
E	Explosion energy available to generate blast and fragment kinetic energy, etc.
E_p	Critical perforation energy ($\frac{1}{2} MV_f^2$)
E_y	Young's modulus of elasticity
F	Dimensionless initial fragment acceleration
F	$P_eAR/Ma_e = P_eR/ma_e$ for vessel completely shattered into many small fragments
g	Acceleration due to gravity
h	Vessel wall thickness
k	Ratio of vessel outside diameter to internal diameter
L	Length of cylindrical vessel
M	Fragment mass
m	Mass per unit area of vessel shell
N	Length of cylindrical vessel forming rocketing tub fragment
N/m^2	Unit of pressure in SI system, N/m^2; also called pascal (Pa). One psi $= 6.89476 \times 10^3$ Pa or 6.89476 kPa.
P	Liquid pressure
P_a	Atmospheric pressure
P_b	Dynamic vessel burst pressure
P_c	Pressure at expanding gas contact surface
P_e	Pressure at vessel failure
P_{inc}	Incident (side-on) blast pressure
P_r	Normally reflected (face-on) blast pressure
R	Vessel radius
r	Fragment radius $= (A/\pi)^{0.5}$
R_g	Range of fragment
t	Steel target thickness
U	$U_f + U_m$
u	Ultimate tensile strength of target steel
U_f	Fluid compression energy
U_m	Elastic strain energy in vessel walls
V	Volume of gas
V_f	Fragment velocity
V_L	Liquid volume
W	Equivalent mass of TNT
w	Unsupported span of steel target
X	Distance from wall of vessel to target

Nomenclature (*Concluded*)

	Greek letters
β_T	Fluid compressibility
γ	Ratio of specific heats of gas C_p/C_v
ϕ_0	Standard steady-state availability
ν	Poisson's ratio of vessel steel
	Subscripts
0	Reference state
1	Initial state
a	Environmental state
$1 \rightarrow a$	Denotes the path from state 1 to the environmental ambient state a

General References: Baker, Cox et al., "Explosion Hazards and Evaluation," *Fundamental Studies in Engineering 5,* Elsevier Science Publishing, New York, 1983. Kinney and Graham, *Explosive Shocks in Air,* 2d ed., Springer-Verlag, New York, 1985. Petes, *Annals, New York Academy of Sciences 1968,* vol. 152, pp. 283–316. Holden, *Assessment of Missile Hazards: Review of Incident Experience Relevant to Major Hazard Plant,* UKAEA SRD/HSE/R477, November 1988. Lees, *Loss Prevention in the Process Industries,* Butterworths, London, 1996. Leslie and Birk, "State of the Art Review of Pressurized Liquefied Gas Container Failure Modes and Associated Projectile Hazards," *Journal of Hazard Materials* **28,** 1991, pp. 329–365. *ASCE Structural Analysis and Design of Nuclear Plant Facilities Manual and Reports on Engineering Practice* no. 58, 1980. Pritchard and Roberts, "Blast Effects from Vapour Cloud Explosions: A Decade of Progress," *Safety Science,* vol. 16 (3,4) 1993, pp. 527–548. "Explosions in the Process Industries," Major Haz. Monograph Series, *I. Chem. E.* (U.K.), 1994.

The availability of energy from an explosion can be approximately calculated in most cases but the method used depends upon the nature of the explosion.

Inert, Ideal Gas-Filled Vessels The energy available for external work following the rapid disintegration of the vessel is calculated by assuming that the gas within the vessel expands adiabatically to atmospheric pressure.

$$E = \frac{P_e V}{(g-1)}\left(\left[1-\left(\frac{P_a}{P_e}\right)^{(\gamma-1)/\gamma}\right] + (g-1)\left(\frac{P_a}{P_e}\right)\left[1-\left(\frac{P_a}{P_e}\right)^{-1/\gamma}\right]\right) \qquad (26\text{-}3)$$

See Nomenclature table for definitions of terms.

In the case of thick-walled HP vessels, the strain energy in the vessel shell can contribute to the available energy, but for vessels below about 20 MN/m^2 (200 barg) it is negligible and can be ignored. If a Mollier chart for the gas is available, the adiabatic energy can be measured directly. This is the preferred method, but in many cases the relevant chart is not available.

The available energy is dissipated in several ways, e.g., the strain energy to failure, plastic strain energy in the fragments, kinetic energy of the fragments, blast wave generation, kinetic energy of vessel contents, heat energy in vessel contents, etc. For damage estimation purposes, the energy distribution can be simplified to:

$$\underbrace{\hspace{1em}\text{30\% blast} \quad \text{40\% fragment kinetic energy} \quad \text{30\% other dissipative mechanisms}\hspace{1em}}_{}\;\; E\left(\int p\,dv\right)$$

Blast Characteristics Accurate calculation of the magnitude of the blast wave from an exploding pressure vessel is not possible, but it may be estimated from several approximate methods that are available.

One method of estimating the blast wave parameters is to use the TNT equivalent method, which assumes that the damage potential of the blast wave from a fragmenting pressure vessel can be approximated by the blast from an equivalent mass of trinitrotoluene (TNT). The method is not valid for the region within a few vessel diameters from the vessel. However, a rough approximation can be made outside this region by calculating an equivalent mass of TNT and utilizing its well-known blast properties. The term *equivalent mass* means the mass of TNT which would produce a similar damage pattern to that of the blast from the ruptured vessel. The energy of detonation of TNT is 4.5 MJ/kg (1.5 × 10^{-6} ft·lb/lb), so the TNT equivalent mass W is given by $W = 0.3E/4.5$ kg. Standard TNT data (Dept. of the Army, Navy, and Air Force, "Structures to resist the effects of accidental explosions," TM5-1300, NAVFAC P-397, AFM 88-22. U.S. Gov. Printing Office, vol. 2, November 1990, Figs. 2-7 and 2-15, or Kingery and Pannill, Memorandum Report No. 1518, Ballistic Research Laboratories, Aberdeen Proving Ground, U.S., April 1964) can then be used to determine the blast parameters of interest (Fig. 26-9). This method has limitations in the far field where the peak incident overpressure is less than 4 kN/m^2 (0.5 psi). In this region, local terrain and weather effects become significant.

The blast parameters also depend upon the physical location of the vessel. If the vessel is located close to or on the ground, then *surface-burst* data should be used. In other circumstances where the vessel is high in the air, either *free-air* or *air-burst* blast data may be used. These data are best presented in the form of *height-of-burst* curves (Petes, "Blast and Fragmentation Characteristics," *Ann. of New York Acad. of Sciences,* vol. 152, art. 1, fig. 3, 1968, p. 287). For incident blast pressures of 3 × 10^5 N/m^2 (3 bar) or less, using surface-burst data may overestimate the blast pressure by about 33 percent. Generally, pressure vessel ruptures rarely cause ground craters, so no allowance for cratering should be made.

Fragment Formation The way in which a vessel breaks up into several fragments as a consequence of an explosion or metal failure is impossible to predict. Consequently, in most cases it is necessary to assume several failure geometries and to assess the effect of each. The number of fragments formed is strongly dependent upon the nature of the explosion and the vessel design. For high-speed explosions—e.g., detonations or condensed phase explosions—the vessel frequently shatters into many fragments, but for slower-speed explosions—e.g., deflagrations and BLEVEs—generally fewer than ten fragments are formed, and frequently less than five. In the special case of pressurized liquefied gas vessels affected by fire, Holden and Reeves ("Fragment Hazards from Failures of Pressurized Liquefied Gas Vessels," *I. Chem. E. Sym. Series 93,* 1985, p. 213) suggest that with cylindrical vessels, up to four fragments could be projected and that greater fragmentation of spherical vessels occurred with the possibility that the number of fragments may increase with increasing vessel size.

Initial Fragment Velocity (V_f) The process of energy transfer from the expanding gas to the vessel fragments is not efficient and seldom exceeds 40 percent of the available energy. According to Baum ("The Velocity of Missiles Generated by the Disintegration of Gas Pressurized Vessels and Pipes," *Journal of Press. Vessel Technology,* Trans. ASME, vol. 106, November 1984, pp. 362–368), there is an

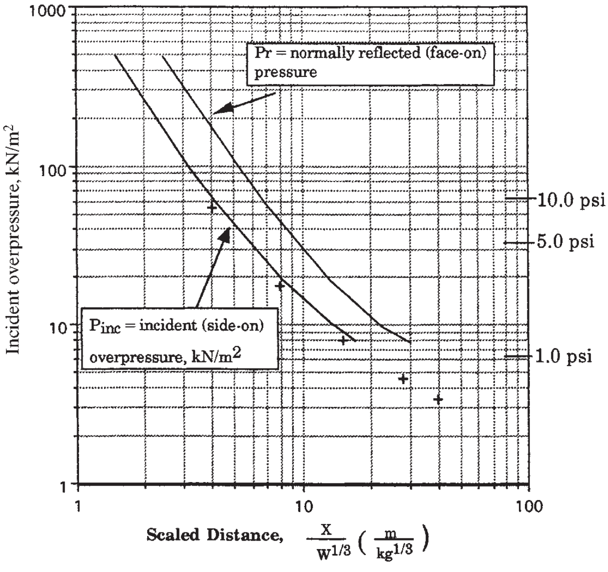


FIG. 26-9 Incident overpressure vs. scaled distance, surface burst. (*The "t" points are from Kingery and Pannill, Memo Report 1518 BRL. Adapted from Department of Army, Navy, and Air Force TM5-1300, NAVFAC P-397, AFM 88-22.*)

upper limit to the fragment velocity, which is taken to be the velocity of the contact surface between the expanding high-pressure gas and the surrounding atmospheric air. This is referred to as the *zero-mass* fragment velocity and, for most industrial low- to medium-pressure vessels, is less than about 1.3 Mach. It is calculated using ideal gas, one-dimensional shock tube theory and is given by the equation for the shock tube contact surface velocity (Wright, *Shock Tubes,* Methuen & Co., London, 1961).

$$\frac{V_f}{a_0} = -\frac{2}{(\gamma - 1)}\left[\left(\frac{P_c}{P_e}\right)^{(\gamma-1)/2\gamma} - 1\right] \tag{26-4}$$

where P_c is determined from the relationship:

$$\frac{a_a(1-\mu_a)\left(\dfrac{P_c}{P_a} - 1\right)}{a_e\left[(1+\mu_a)\left(\dfrac{P_c}{P_a} + \mu_a\right)\right]^{1/2}} = \frac{2}{(\gamma-1)}\left(1 - \left(\frac{P_a}{P_e}\cdot\frac{P_c}{P_a}\right)^{(\gamma-1)/2\gamma}\right) \tag{26-5}$$

and

$$\mu_a = \frac{\gamma_a - 1}{\gamma_a + 1} \tag{26-6}$$

where P_c = pressure at expanding gas contact surface
a_a = sound velocity at ambient conditions
a_e = sound velocity in gas prior to vessel failure

The value of a_e may be approximated using physical property data for the specific gas at the temperature and pressure at the start of the expansion. Equation (26-5) must be solved using a trial-and-error method. Most fragments never achieve the zero-mass velocity and their velocity can be assessed using the correlations of Baum ("Disruptive Failure of Pressure Vessels: Preliminary Design Guidelines for Fragments Velocity and the Extent of the Hazard Zone," *J. Pressure Vessel Technology,* Trans. ASME, vol. 110, May 1988, pp. 168–176; Baum, "Rupture of a Gas-Pressurized Cylindrical Pressure Vessel. The Velocity of Rocketing Fragments," *J. Loss Prev. Process Ind.,* vol. 4, January 1991, pp. 73–86; Baum, "Velocity of a Single Small Missile Ejected from a Vessel Containing High Pressure Gas," *J. Loss Prev. Process Ind.*, vol. 6, no. 4, 1993, pp. 251–264).

The Baum correlations for several vessel failure modes are given in Eqs. (26-7) to (26-16).

End-Cap Released from a Cylindrical Vessel Pressurized with an Inert Ideal Gas

$$\frac{V_f}{a_e} = 2F^{0.5} \tag{26-7}$$

where F is a dimensionless initial fragment acceleration given by

$$\frac{P_e A R}{M a_e} \tag{26-8}$$

and A = projected area of fragment
M = fragment mass
R = vessel radius

Rocket Fragment from a Cylindrical Vessel Pressurized with an Inert Ideal Gas

$$\frac{V_f}{a_e} = 2.18\left[F\left(\frac{L}{R}\right)^{0.5}\right]^{2/3} \tag{26-9}$$

where L = length of vessel and F is calculated using the area of the open end. For a more precise result, a correction factor to allow for the vessel opening time should be made (Baum, 1991).

Rocket Fragment from a Cylindrical Missile Pressurized with a Liquid at a Temperature Such That Rupture Initiates Flash Evaporation

$$\frac{V_f}{a_e} = 0.2\left(\frac{2E}{M}\right)^{0.5} \tag{26-10}$$

Range of experimental data:

$$\text{Water, } T_{\text{sat}} \sim 320°\text{C, } 145 \le \frac{P_e}{P_a} \le 155,\ N/L = 1.0,\ 12 \le L/R \le 24$$

The vessel is completely full of liquid and N is the length of the vessel forming the rocket fragment, with limited data.

Whole Vessel Driven by an Inert Ideal Gas Escaping through Axial Split

$$\frac{V_f}{a_e} = 0.17\left(\frac{2E}{M}\right)^{0.5} \tag{26-11}$$

Range of experimental data:

$$10 < \frac{P_e}{P_a} < 63,\ \gamma = 1.4,\ 4 < L/R < 6$$

Large, Single Fragment Ejected from Cylindrical Vessel Pressurized with an Inert Ideal Gas

$$\frac{V_f}{a_e} = 2F^{0.5} \tag{26-12}$$

Range of experimental data:

$$\frac{P_e}{P_a} = 100,\ \gamma = 1.4,\ L/R = 13.5,\ \text{A}^{0.5} > R$$

based upon two points only. End-cap equation (26-5) is probably adequate.

Single Small Fragment Ejected from a Cylindrical Vessel Pressurized with an Inert Ideal Gas

$$\frac{V_f}{a_e} = \left[2F\left(\frac{h}{R}\right)\right]^{0.5} + 0.96\left[F\left(\frac{r}{R}\right)\right]^{0.25} \tag{26-13}$$

where h = wall thickness
r = fragment radius, i.e., $r = (A/\pi)^{0.5}$

Range of experimental data:

$$20 < \frac{P_e}{P_a} < 300,\ \gamma = 1.4,\ r < 0.3\,R,\ h < 0.1\,R$$

Fragments Generated by Disintegration of a Cylindrical Vessel Pressurized with an Inert Ideal Gas

$$\frac{V_f}{a_e} = 0.88\,F^{0.55} \tag{26-14}$$

Experimental data show no strong dependence on P_e/P_a or L/R.

Hemispherical Fragment Released from a Spherical Vessel Pressurized with a Liquid at a Temperature That on Rupture Initiates Flash Evaporation

$$\frac{V_f}{a_e} = 0.16\left(\frac{2E}{M}\right)^{1/2} \tag{26-15}$$

Range of experimental data:

$$\text{Water } T_{\text{sat}} \sim 230°\text{C, } 49.5 \le \frac{P_e}{P_a} \le 60.5$$

Limited data, vessel full of water.

Fragments Generated by Complete Shattering of Spherical Vessel Pressurized by an Inert Ideal Gas

$$\frac{V_f}{a_e} = 0.88\,F^{0.55} \tag{26-14}$$

Vessel Filled with Reactive Gas Mixtures Most cases of damage arise not from the vessel failing at its normal operating pressure but because of an unexpected exothermic reaction occurring within the vessel. This usually is a decomposition, polymerization, deflagration, runaway reaction, or oxidation reaction. In assessing the damage potential of such incidents, the peak explosion or reaction pressure can often be calculated, and if this peak pressure P_e is then inserted into Eq. (26-3), the available energy can be assessed and the blast and fragment hazard determined. Where the expected peak explosion pressure P_e is greatly in excess of the vessel dynamic burst pressure, it is sufficient to increase the burst pressure to allow for the increase in vessel pressure during the period necessary for both the vessel to rupture and the fragments to be removed from the path of the expanding vessel contents. Where the gas pressure in the vessel is rising rapidly, the gas may reach a much higher pressure than the estimated dynamic burst pressure of the vessel. This effect is similar to the accumulation on a relief valve. It is, therefore, conservative to assume that the gas reaches the pressure calculated on the assumption of complete reaction. The reaction is assumed to go to completion before the containing vessel fails. However, there are reactions where it is simpler to calculate the energy availability using thermodynamic methods. The maximum energy released in an explosion can be assessed from the change in the Helmholz free energy ($-\Delta H = -\Delta E + T\Delta S$), but if the required data is not available, it may be necessary to use the Gibbs free energy ($\Delta F = \Delta H - T\Delta S$), which—especially in the case of reactions with little or no molal change, e.g., hydrocarbon/air oxidation—is similar to the Helmholz energy. It may sometimes be more convenient to calculate the batch energy availability [$B = \phi_0 + \Delta\phi_{1\rightarrow a} + \Delta(PV)_{1\rightarrow a} - P_a\Delta V_{1\rightarrow a}$] (Crowl, "Calculating the Energy of Explosion Using Thermodynamic Availability," *J. Loss Prev. Process Ind.*, **5,** no. 2, 1992, p. 109), which for an ideal gas becomes

$$B_1 = f_0 + f_{1\rightarrow a} + nRT_1\left[\left(\frac{P_a}{P_1}\right) - 1\right] \qquad (26\text{-}16)$$

The energy partition between blast wave energy and fragment kinetic energy is as described in paragraph 1.

Vessels Completely Filled with an Inert High-Pressure Liquid A typical example is the pressure testing of vessels with water. The energy available to cause damage is the sum of the liquid compression energy and the strain energy in the vessel shell. The sudden release of this energy on vessel failure generally creates flying fragments but rarely any significant blast effects.

The fluid compression energy up to about 150 MN/m² (22,000 psig) can be estimated from $U_f = \frac{1}{2}\beta_T P^2 V_L$, where β_T is the liquid bulk compressibility, P is the liquid pressure, and V_L is the liquid volume. At higher pressure, this simple equation becomes too conservative and more complex methods of calculating the fluid compression energy are required. The elastic strain energy for cylindrical vessels, ignoring end closures, can be estimated from:

$$U_m = \frac{P^2 V_L}{2E(k^2 - 1)}[3(1 - 2\nu) + 2k^2(1 + \nu)] \qquad (26\text{-}17)$$

where P = pressure of liquid
V_L = volume of liquid
E_y = Young's modulus of elasticity
ν = Poisson's ratio

Energy available $U = U_f + U_m$.

Only a small fraction of U is available to provide kinetic energy to the fragments. There are few data available, but in five incidents analyzed by High (unpublished data), no fraction was greater than 0.15. The fragment initial velocity can be assessed from $0.15\ U = \frac{1}{2}MV_f^2$.

Distance Traveled by Fragments There is no method available to estimate the distance traveled by an irregularly shaped, possibly tumbling, subsonic fragment projected at an unknown angle. A conservative approach is to assume that all the fragments are projected at an angle of 45° to the horizontal and to ignore the aerodynamic effects of drag and/or lift. The range R_g is then given by $R_g = V_f^2/g$, where g = gravitational acceleration.

This is too conservative to provide anything more than an upper bound. Some limited guidance is given by Scilly and Crowther ("Methodology for Predicting Domino Effects from Pressure Vessel Fragmentation," *Proc. Hazards Ident. and Risk Anal., Human Factors and Human Reliability in Process Safety*, Orlando, Fla., 15 Jan 1992, p. 5, sponsored by AIChE and HSE), where the range, for vessels with walls less than 20 mm (0.79 in), is 2.8 P_b with the range in meters and P_b as the vessel burst pressure in bars. Other sources are Baker (*Explosion Hazards and Evaluation,* Elsevier, 1983, p. 492) and Chemical Propulsion Information Agency (*Hazards of Chemical Rockets and Propellants Handbook,* vol. 1 NTIS, Virginia, May 1972, pp. 2-56, 2-60).

Fragment Striking Velocity It is generally impossible to assess the fragment velocity, trajectory, angle of incidence, and fragment attitude at the moment of striking a target; consequently, the conservative view is taken that the fragment strikes the target at right angles, in the attitude to give the greatest penetration, with a velocity equal to the initial velocity.

Damage Potential of Fragments In designing protection for fragment impact, there are two failure modes to be considered: local response and overall response. Local response includes penetration/perforation in the region of the impact. Overall response includes the bending and shear stresses in the total target element; i.e., will the whole target element fail regardless of whether the element is penetrated or perforated?

Local Failure The penetration or perforation of most industrial targets cannot be assessed using theoretical analysis methods, and recourse is made to using one of the many empirical equations. In using the equations, it is essential that the parameters of the empirical equation embrace the conditions of the actual fragment.

The penetrability of a fragment depends on its *kinetic energy density* (KED), given by

$$\text{KED} = \frac{1}{2}\frac{MV_f^2}{A} \qquad (26\text{-}18)$$

where A is the fragment cross-sectional area. The KED is a useful comparative measure of a fragment's penetrability when comparing like with like. Several equations are given in the following sections.

Ballistics Research Laboratory (BRL) Equation for Steel Targets

$$E_p = 1.4 \times 10^9\ (dt)^{1.5} \qquad (26\text{-}19)$$

where d is the fragment diameter, t is the steel target plate thickness, and E_p is the critical perforation energy in SI units (kg, m, m/s, J), when applied to fragments between 1 kg and 19.8 kg, impacting targets 1 mm to 25 mm (1 in) thick plate with velocities from 10 m/s to 100 m/s. Neilson (*Procedures for the Design of Impact Protection of Off-shore Risers and ESV's,* U.K. AEA [ed.], 1990) found a large scatter in the results, but most were within ±30 percent.

Stanford Research Institute (SRI) Equation for Steel Targets

$$E = \frac{dut^2}{10.3}\left(42.7 + \frac{w}{t}\right) \qquad (26\text{-}20)$$

where, with the same notation as Eq. (26-14), w is the unsupported span of the target plate (m) and u the ultimate tensile strength of the target steel (N/m²). The parameters for this equation are given by Brown ("Energy Release Protection for Pressurized Systems," part II, "Review of Studies into Impact/Terminal Ballistics," *Applied Mechanics Review,* vol. 39, no. 2, 1986, pp. 177–201) as $0.05 \le d \le 0.25m$, $414 \le u \le 482$ MN/m² for a fragment mass between 4.5 and 50 kg.

Overall Response The transition from local to overall response is difficult to define. High-velocity impact implies that the boundary conditions of the target have little influence on the local response (excluding reflected shock waves). If the fragment is small relative to the target, local response will dominate, but fragments that are of the same order of size as the target will produce an overall response. It is often necessary to consider both overall and local response. Low values of KED are associated with overall response. Design methods for dynamically applied loads are given by Newark ("An Engineering Approach to Blast Resistant Design," ASCE New York, 1953), Baker (see General References), or ASCE (*Manual and Reports on Engineering Practice,* no. 58, 1980).

Response to Blast Waves The effect of blast waves upon equipment and people is difficult to assess because there is no single blast wave parameter which can fully describe the damage potential of the blast. Some targets respond more strongly to the peak incident overpressure and others to the impulse ($\int p\,dt$) of the blast. The blast parameters are usually based on the conservative assumption that the blast strikes the target normal to its surface, so that normal reflection parameters are used.

The pressure exerted by the blast wave on the target depends upon the orientation of the target. If the target surface faces the blast, then the target will experience the reflected or face-on blast pressure P_r, but if the target surface is side-on to the blast, then the target will experience the incident or side-on blast pressure P_{inc}. The reflected blast pressure is never less than double the incident pressure and can, for ideal gases, be as high as eight times the incident pressure. For most industrial targets where the incident pressure is less than about 17 kN/m^2 (25 psi), the reflected pressure is not more than 2.5 times the incident pressure.

Response of Equipment The response of equipment to blast is usually a combination of two effects: one is the displacement of the equipment as a single entity and the other is the failure of the equipment itself. The displacement of the equipment is an important consideration for small, unsecured items—e.g., empty drums, gas cylinders, empty containers. Most damage results from the failure in part or totally of the equipment or containing structure itself.

The blast parameters are usually based on the conservative assumption that the blast strikes the target normal to its surface, so that normal reflection parameters may be used.

The response of a target is a function of the ratio of the blast wave duration and the natural period of vibration of the target (T/T_n). Neither of these parameters can be closely defined.

Calculating the specific response of a specific target can generally be done only approximately. Accuracy is not justified when the blast properties are not well defined. A guide to the damage potential of condensed phase explosive blast is given in Table 26-5 (Scilly and High, "The Blast Effect of Explosions," *Loss Prevention and Safety Promotion in the Process Industries,* European Fed. of Chem. Eng., 337 Event, France, September 1986, table 2). Nuclear data is available (Table 26-6) (Walker, "Estimating Production and Repair Effort in Blast-damaged Petroleum Refineries," *Stanford Research Inst.,* July 1969, fig. 5, p. 45), which is based upon long positive-duration blast (±6 s). This suggests that the Walker data will be conservative for the much shorter duration blast from accidental industrial explosions.

A blast incident overpressure of 35 kN/m^2 (5 psi) is often used to define the region beyond which the damage caused will be minor and not lead to significant involvement of plant and equipment beyond the 35 kN/m^2 boundary.

Response of People The greatest hazard to people from blast is generally from the deceleration mechanism after people have been blown off their feet and they become missiles. This occurs at an incident overpressure of about 27 kN/m^2 (4.0 psi) for long positive-duration nuclear weapon blasts. People have more blast resistance than most equipment and can survive incident overpressures of 180 kN/m^2 (27 psi) (Bowen, Fletcher, and Richmond, DASA-2113, Washington, D.C., October 1968), even for long-duration blasts.

TABLE 26-5 Damage Effects

Incident, psi	Pressure, kPa	Damage effects
10	70	Damage to most refineries would be severe, although some pumps, compressors, and heat exchangers could be salvaged. All conventional brick buildings would be totally destroyed. Rail wagons (rail cars) overturned. Storage tanks ruptured. Fatalities certain.
5.0	34	Brick buildings severely damaged, 75% external wall collapse. Fired heaters badly damaged. Storage tanks leak from base. Threshold for eardrum damage to people. Domino or knock-on radius. Pipe bridges may move.
2.0	14	Doors and windows removed. Some frame distortion to steel frame buildings and cladding removed. Some electrical/instrument cables broken.[*]
1.0	7	Lethal glass fragments. Limit for public housing, schools, etc.
0.3	2	About 50% domestic glass broken.

[*] 1% probability electrical cables broken at 2.0 psi inc. 99% probability electrical cables broken at 3.6 psi inc.

PROJECT REVIEW AND AUDIT PROCESSES

General References: Center for Chemical Process Safety (CCPS), *Guidelines for Hazard Evaluation Procedures, Second Edition with Worked Examples,* AIChE, September 1992. CCPS, *Guidelines for Technical Management of Chemical Process Safety,* AIChE, 1989. CCPS, *Guidelines for Auditing Process Safety Management Systems,* AIChE, 1993.

Introduction Review and audit processes are used in the chemical process industry to evaluate, examine, and verify the design of process equipment, operating procedures, and management systems. These processes assure compliance with company standards and guidelines as well as government regulations. Reviews and audits can encompass the areas of process and personnel safety, environmental and industrial hygiene protection, quality assurance, maintenance procedures, and so on.

To distinguish between a review and an audit, some definitions will be provided. A review is a critical examination or evaluation of any operation, procedure, condition, event, or equipment item. Reviews can take many forms and be identified as project reviews, design reviews, safety reviews, pre-start-up reviews, and so on. The following discussion of the review process will deal with project reviews associated with capital projects and focus on the area of process safety.

An audit is a formal, methodical examination and verification of an operation, procedure, condition, event, or series of transactions. The verification element of an audit makes it distinctive from a review. A project review will *recommend* design, procedural, maintenance, and management practices to minimize hazards and reduce risk while meeting company standards and government regulations. An audit will *verify* that the design, the procedures, and the management systems are actually in place, and are being maintained and used as intended. In fact, it is not uncommon for an audit to be done on a review process, which is a management system, to verify that the elements of the review process are being followed.

The following sections will describe the project review and audit processes separately, addressing the why, when, and how for each process.

Project Review Process The scope of capital projects can be large, involving the construction of new plants with new technologies and products, or small, involving minor changes to existing facilities. In either case, project safety reviews can be used to evaluate and examine the process design, operating procedures, and process control scheme for process hazards, conformance to company standards and guidelines, and compliance with government regulations. Some objectives of the review process (CCPS, 1992, p. 53) are: (1) identify equipment or process changes that could introduce hazards, (2) evaluate the design basis of control and safety systems, (3) evaluate operating procedures for necessary revisions, (4) evaluate the application of new technology and any subsequent hazards, (5) review the adequacy of maintenance and safety inspections, and (6) evaluate the consequences of process deviations and determine if they are acceptable (CCPS, 1989, p. 46).

The project review process should be integrated with the development of the project from the conceptual stage to the start-up stage (CCPS, 1989, p. 46). Figure 26-10 depicts the various stages of a capital project. The size and complexity of a project will determine if the project progresses through all these stages and, in the same manner, determine the number and type of reviews that are needed. The earlier in a project that a review can be used to identify required changes, the less costly the change will be to implement. For example, reviews held at the research stage of a project can be beneficial in choosing the least hazardous technology and contribute to an inherently safer process design that needs fewer add-on safety systems.

As the project progresses, more information is available; therefore, the review technique used can be different at each stage of the project. The use of various hazard evaluation techniques, such as checklist analyses, relative rankings, what-if analyses, and hazard and operabil-

TABLE 26-6 Blast Overpressure Effects on Vulnerable Refinery Parts

	Overpressure (psi)																								
Equipment	0.5	1.0	1.5	2.0	2.5	3.0	3.5	4.0	4.5	5.0	5.5	6.0	6.5	7.0	7.5	8.0	8.5	9.0	9.5	10.0	12.0	14.0	16.0	18.0	20.0	>20.0
Control house: steel roof	*a*	*c*	*d*				*h*																			
Control house: concrete roof	*a*	*e p*	*d*				*n*													*e*						
Cooling tower	*b*		*f*				*o*																			
Tank: cone roof		*d*				*k*							*u*													
Instrument cubicle			*a*			*i m*						*t*														
Fired heater				*g*	*i*					*t*																
Reactor: chemical				*a*				*i*					*p*					*t*								
Filter				*h*					*i*										*v*		*t*					
Regenerator						*i*				*i p*					*t*											
Tank: floating roof						*k*							*u*												*d*	
Reactor: cracking							*i*							*i*							*t*					
Pipe supports							*p*					*s o*														
Utilities: gas meter									*q*																	
Utilities: electric transformer									*h*						*l*					*t*						
Electric motor										*h*								*l*								*v*
Blower										*q*										*t*						
Fractionation column											*r*			*t*												
Pressure vessel: horizontal												*p i*						*t*								
Utilities: gas regulator												*i*								*m q*						
Extraction column													*i*							*v*	*t*					
Steam turbine															*l*						*m*	*s*				*v*
Heat exchanger															*i*			*t*								
Tank: sphere																*i*						*i*	*t*			
Pressure vessel: vertical																					*i*	*t*				
Pump																					*i*		*v*			

CODE:

a	Windows and gauges break.
b	Louvers fall at 0.3–0.5 psi.
c	Switchgear is damaged from roof collapse.
d	Roof collapses.
e	Instruments are damaged.
f	Inner parts are damaged.
g	Brick cracks.
h	Debris-missile damage occurs.
i	Unit moves and pipes break.
j	Bracing fails.
k	Unit uplifts (half-filled).
l	Power lines are severed.
m	Controls are damaged.
n	Block walls fail.
o	Frame collapses.
p	Frame deforms.
q	Case is damaged.
r	Frame cracks.
s	Piping breaks.
t	Unit overturns or is destroyed.
u	Unit uplifts (0.9 filled).
v	Unit moves on foundation.

SOURCE: F. E. Walker, “Estimating Production and Repair Effort in Blast Damaged Petroleum Refineries,” *SRI,* July 1969.

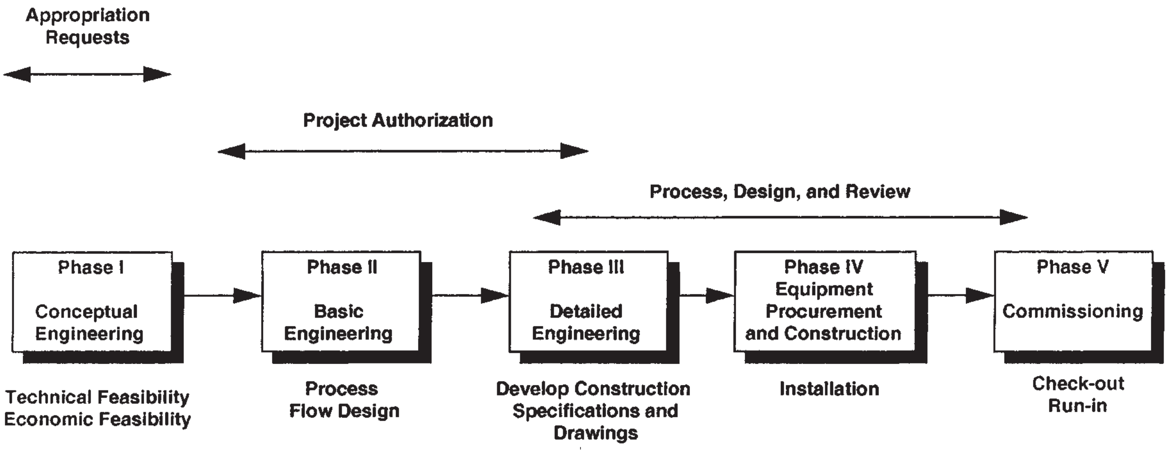


FIG. 26-10 The phases of a capital project. (*CCPS, 1989 by permission of AIChE.*)

ity studies, is documented in *Guidelines for Hazard Evaluation Procedures: Second Edition with Worked Examples* (CCPS, 1992). The need to use more quantitative techniques for hazard evaluation may be identified during these reviews, and become an action item for the project team.

The project review process involves multiple steps that should be defined in management guidelines (CCPS, 1993, pp. 57–61). The steps include: (1) review policy, (2) review scheduling, (3) review technique, (4) review team representation, (5) review documentation, (6) review follow-up, (7) review follow-up verification, and (8) review procedures change management. These steps define how a review, whether it be a safety review, environmental review, pre-start-up review, or whatever, is conducted and how closure of review action items is achieved.

Review Policy The review policy should establish when project safety reviews should be done. All capital projects, large or small, should have one or more safety reviews during the course of the project. The number and types of review should be stated in a management policy. Any reasons for exceptions to the policy should be documented as well. The policy should address not only projects internal to a company, but also any joint ventures or turnkey projects by outside firms.

Review Scheduling A review scheduling procedure should be established that documents who is responsible for initiating the review and when the review(s) should occur during the project. The scheduling needs to balance availability of process information, review technique used, and the impact of potential review action items on project costs (i.e., early enough to minimize the cost of any potential changes to the process). The actual amount of time needed for the review should also be stated in the procedure. On the basis of the number of project reviews required and the estimated time needed for each review, the project cost estimate should include the cost for project reviews as part of the total cost for the project.

Review Team The project review should be conducted by a functionally diverse team. The team should consist of a team leader to organize and lead the team review, a scribe or secretary to record and issue a review summary with action items, and functional experts in fields relevant to the project such as safety, environmental, and industrial hygiene (CCPS, 1993, p. 58). The team leader should be experienced in the use of the selected review technique with leadership skills and no direct involvement with the project under review. The review procedure should address the minimum requirements for team leaders and team members. Some typical requirements could be years of experience, educational background, and training in the review technique. Responsibilities should be clearly defined for initiating the review, assigning the review team, recording the team findings, and monitoring follow-up of team recommendations.

Review Techniques The review techniques used at the various stages of a project should be selected based on the amount of process information and detail available. Figure 26-11 depicts some typical review techniques at the various stages of a capital project. A detailed description, including the type and amount of process information required, for each review technique can be found in *Guidelines for Hazard Evaluation Procedures: Second Edition with Worked Examples* (CCPS, 1992). The process information required for the review should be defined and documented in the review guidelines. Up-to-date and accurate process information is essential to conducting a successful review.

Review Documentation The project review team leader has the ultimate responsibility for documenting the results of the project review. This responsibility may be delegated to a team scribe or secretary to record the review minutes and issue a summary report with listed action items. The action items could address exceptions to company or industry standards and government regulations, review team recommendations based on experience and knowledge, and further issues for study that could not be resolved during the review session.

The summary report should have a standard format and could contain a short project scope summary, a listing of review team members by function, a listing of project team members present, a meeting agenda or checklist of topics reviewed by the team, and a list of concerns and action items for project team follow-up. The distribution list for the summary report should be established and include the review team, project team, and any personnel outside the project team who have follow-up responsibilities for any of the action items. Also, include on the distribution list any appropriate management personnel, whether they be project team supervisors, manufacturing managers, or engineering managers. The documentation for the review should be archived in a process plant file with the appropriate records retention time (e.g., the life of the plant).

Review Follow-up An important element (maybe the most important) of the review process is the follow-up to action items. The project review will result in a list of potential concerns and action items, but, without follow-up, the issues will never be resolved and implemented. A person(s) should be assigned to each action item, preferably at the time of the project review. The person(s) assigned should have a combination of knowledge, resources, and authority to do a proper job in following up on the action items (CCPS, 1993, p. 59). The total action item list should not be assigned to one person, since it may overwhelm one individual. Depending on the number of action items generated, prioritizing the action item list may be helpful and a responsibility the review team can assume.

Progress on the action items should be documented in periodic progress reports to the review team leader or others assigned that functional responsibility. If no one is assigned the responsibility of tracking this progress, completion of the action list will probably be relegated to a lower priority and not be done.

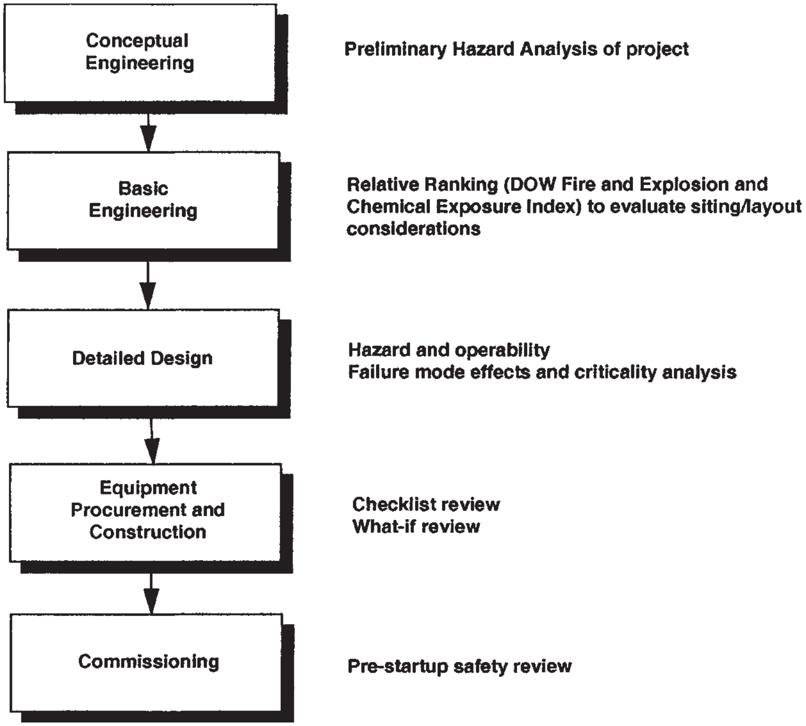


FIG. 26-11 Hazard evaluation at various project stages. (*CCPS, 1993, by permission of AIChE.*)

Changes made to the process as a result of the project review may require a similar review before implementation, especially if the change is significant.

Review Follow-up Verification In addition to someone tracking the follow-up through progress reports, responsibility should be assigned to verify that any process changes were actually made in the field. This verification can be done by a review team as part of a process pre-start-up review. It could also be part of the project team management responsibility or assigned to a particular functional (i.e., safety and loss prevention) representative. The closure of the review process is complete once implementation is verified.

On rare occasions, the resolution of project review concerns or action items is a point of contention between review team and project team members. In such a case, a management structure must be in place to arbitrate such disputes.

Review Procedure Change Management The project review process can require changes in policy and procedures at certain times. Therefore, the procedures should provide a management-of-change mechanism for suggesting changes and assign a person responsible for initiating and implementing any necessary changes.

Audit Process Audits in the chemical process industry can be focused on process safety, process safety management, environmental, and health areas. The discussion in this section will focus on the process safety and process safety management area, but it should be recognized that the process can be applied to the other areas as well. "Process safety audits are intended to provide management with increased assurance that operating facilities and process units have been designed, constructed, operated, and maintained such that the safety and health of employees, customers, communities, and the environment are being properly protected" (CCPS, 1989, p. 133). Process safety management system audits "provide increased assurance that operating units have appropriate systems in place to manage process risk" (CCPS, 1989, p. 130). The audit process described in the following can be used to verify the implementation of equipment designs, operating and maintenance procedures, control systems, and management systems to meet the previously stated intentions.

The key steps in the audit process are outlined according to preaudit activities, audit activities, and postaudit activities in Fig. 26-12. These activities are described in detail in *Guidelines for Auditing Process Safety Management Systems* (CCSP, 1993) and will be only briefly discussed in this section.

Preaudit Process Prior to the actual on-site audit, some preliminary activities should take place. These activities include selecting the facilities to be audited, scheduling the audit, selecting the audit team, and planning the audit. The selection criteria may be random, based on potential hazards of the facilities or the value of the facilities from a business standpoint. Audit scheduling must account for the availability of key facility personnel and audit team members, operational mode of the facility (i.e., it should be in normal operation), and the lead time required to obtain background information that may require advance visits to the facility and preaudit interviews. The audit team members should possess the technical training and experience to understand the facilities being audited. They should be knowledgeable in the auditing process and in the appropriate regulations and standards that will apply to the facilities. They should also be impartial and objective about audit findings. The audit plan should define the audit scope (what parts of the facility will be covered, what topics, who will do it, etc.), develop an audit protocol that is a step-by-step guide to how the audit is performed, identify any priority topics for coverage, and develop an employee interview schedule.

On-Site Audit Process An opening meeting with key facility personnel is held at which the audit team covers the objectives and approach for the audit, and the facility personnel provide an overview of the site operations including site safety rules and a site tour. The on-site audit process should then follow five basic steps that include: (1) understanding management systems, (2) evaluating management systems, (3) gathering audit information, (4) evaluating audit information, and (5) reporting audit findings (CCSP, 1993, p. 17).

An understanding of the management systems in place to control and direct the process safety of the facility can be obtained from reading engineering and administrative standards, guidelines, and procedures that should be available in the background information supplied

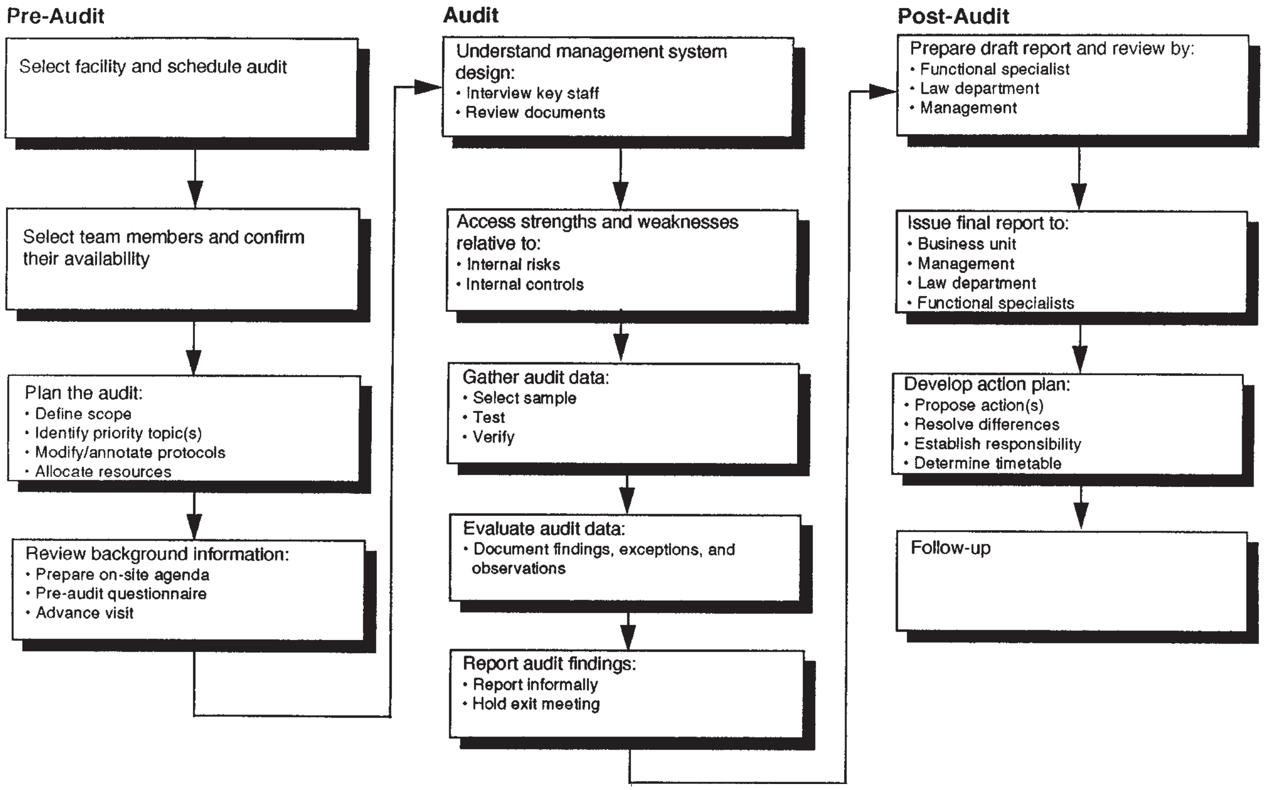


FIG. 26-12 Typical steps in the process safety management audit process. (*CCSP, 1993, by permission of AIChE.*)

prior to the on-site audit. Informal procedures and guidelines used by the facility may only be discovered in interviews with staff management and operations management. This understanding of the formal and informal management systems is a critical step in the audit process.

The next process step evaluates the process safety management systems to determine if they are adequate to achieve the desired results, and if they are used as intended. This evaluation is highly subjective on the auditor's part. This step sets the stage for the rest of the audit, guiding the auditor's information gathering and focusing attention on critical areas.

Gathering audit data can be accomplished through observations, documents, and interviews. The data obtained is used to verify and validate that the process safety management systems are implemented and functioning as designed. Data gathering can be aided by the use of audit samples, where a representative number of items are audited to draw a conclusion, and by using self-evaluation questionnaires.

The audit data can now be evaluated, resulting in audit findings (i.e., conclusions both positive and negative). The audit team should confirm that sufficient data has been collected to support each finding. Additional data may need to be gathered if the team decides a preliminary finding needs to be strengthened. The conclusions drawn from the data evaluation should be a team consensus.

The reporting step of the on-site audit should be planned to avoid any surprises to facility personnel. Reporting sessions should be held at the end of each audit day to inform facility personnel of the findings, clear up any misunderstandings of the data, and help redirect the audit team, if necessary. The on-site audit should end with a well-planned exit or closeout meeting between the audit team and facility personnel. All the findings of the audit team should be presented at this meeting. This verbal report is the opportunity for clarification of any ambiguities and determination of the final disposition of the findings (written audit report, for local attention only, etc.).

Postaudit Process The postaudit process consists of preparation of a draft report, preparation of a final report, development of action plans, and follow-up. A draft report of the audit findings should be prepared shortly after the completion of the on-site audit. The draft report usually undergoes review and comment by facility personnel involved with the audit, experienced auditors not involved with the subject audit, functional specialists, and attorneys. The review of the draft report is done to assure that a clear, concise, and accurate report is issued, and not to modify or change the findings. Once this review procedure is completed, a final report can be issued and distributed based on a distribution list provided by the facility personnel. The final audit report should be issued in a timely manner and meet the time requirement specified in the audit plan.

An action plan should be developed by the appropriate personnel of the audited facility to address any deficiencies stated in the audit report. Action plans should state what is to be done, who is responsible for getting it done, and when it is to be completed. Rationale for not taking any action for any of the stated deficiencies should also be documented. The action plan is an important step in closing the audit process.

It would not be unusual for some action plans to take a long time to complete. When extended implementation time is necessary, a follow-up mechanism should be used to document progress and show that an effort is being made to resolve the issues. Periodic (i.e., quarterly, semiannually) progress reports should be used as a follow-up method to ensure implementation. Future audits of the facility should include confirmation of the implementation of previous audit action plans.

The final audit report, action plans, progress reports, and any closure report should be retained by the facility based on the facility record retention policy. Typically, these items will be retained until future audit documentation replaces them. In some cases, audit records are retained for the life of the plant.

SAFETY DEVICES

PRESSURE RELIEF SYSTEMS

Nomenclature

C_p	Liquid heat capacity, Btu/lb-°F
Critical (or choked) condition	Maximum flow condition for compressible fluids
D	Duct diameter
F	Inlet mass flow rate, lb/min
f	Friction factor
G	Mass flux
g	Acceleration due to gravity
L	Flow length
M	Total mass in the equipment
P	Stream pressure
P_0	Stagnation pressure of the fluid (i.e., pressure under no-flow conditions)
P_1	Flowing pressure
Q	Heat input rate, Btu/min
R_v	Volume generation rate, ft^3/min
t	Time
v	Specific volume of stream
v_f, v_g	Specific volumes of liquid and gas phases in the equipment
V_g, V_l	Specific volumes of gas and liquid phases, ft^3/lb
V_r	Total equipment volume
W	Mass flow rate, lb/min
X_0	Quality, weight fraction vapor
X_r	Overall weight fraction vapor in the equipment
Greek letters	
β	Volumetric expansion coefficient, ft^3/lb-°F
γ	C_p/C_v
ϕ	Angle of inclination from vertical
λ	Heat of vaporization, Btu/lb
ρ_f	Stream density entering the protected equipment, lb/ft^3
ρ_w	Stream density entering the relief system, lb/ft^3

Introduction All process designs should attempt to arrive at an inherently safe facility; that is, one from which a worst-case event cannot cause injury to personnel, damage to equipment, or harm to the environment. Incorporating safety features that are intrinsic (built-in) rather than extrinsic (added-on) to the basic design, together with the use of high-integrity equipment and piping, provide the first lines of defense against the dramatic, often catastrophic, effects of an overpressure and subsequent rupture. 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 provides yet another layer of safety. However, regardless of the number of lines of defense and depressuring systems in place, overpressure protection must still be provided. Emergency pressure relief systems are intended to provide the last line of protection and thus must be designed for high reliability, even though they will have to function infrequently.

Self-actuated pressure relief systems must be designed to limit the pressure rise which can occur as a result of overcompressing, overfilling, or overheating either an inert or a chemically reactive medium in a closed system. Pressure generation is usually the result of either expansion of a single-phase medium (by material addition and/or heating) or a shift of the phase equilibrium in a multiphase medium (as a result of composition and/or temperature changes). These mechanisms of pressure generation differ from what is commonly referred to as *explosion venting.* Events such as dust explosions and flammable vapor deflagrations propagate nonuniformly from a point of initiation, generating pressure or shock waves. Such venting problems are not included in these discussions.

Relief System Terminology Specific terminology has been developed for the various components which compose an emergency relief system. The American National Standards Institute (ANSI) definitions pertaining to relief devices themselves are listed as follows. Special care is required to avoid confusion on the following terms:

relief valve A pressure relief valve set up for liquid flow. This device opens gradually over a pressure range to avoid “hammer.”

safety (pop) valve A pressure relief valve set up for gas or vapor flow. This device opens over a narrow pressure range, with an initial “pop” action.

safety relief valve A pressure relief valve with mechanical design or adjustments to allow either relief or safety service.

backpressure Pressure existing at the outlet of a relief device. The value under no-flow conditions is *superimposed* backpressure. The value under flowing conditions consists of both superimposed backpressure and built-up pressure due to piping pressure drop.

conventional vs. balanced valves In conventional valves, the downstream side of the closing mechanism is exposed to the backpressure of the flowing fluid; in balanced valves, the closing mechanism is isolated from the fluid and open to atmosphere.

set point The inlet gauge pressure at which a device will start to open (or a rupture disk will burst) under service conditions of temperature and backpressure.

differential set pressure The difference between the upstream and downstream pressures at the set point.

blowdown The reduction in flowing pressure below the set point required for a device to close.

overpressure The rise of inlet pressure above the set point during relief flow, usually expressed as a percentage of the differential set pressure.

maximum allowable working pressure (MAWP) The maximum allowed pressure at the top of the vessel in its normal operating position at the operating temperature specified for that pressure.

Accumulation The rise of pressure above the MAWP of the protected system, usually expressed as a percentage of the gauge MAWP. *Note:* The **MAWP** and **accumulation** terms are not included in the ANSI definitions since they relate to the protected system instead of the relief device.

Codes, Standards, and Guidelines Industry practice is to conform to the applicable regulations, codes, and recommended practices. In many cases, these will provide different guidelines. A suggested approach would be to review all applicable codes, standards, and recommended practices prior to choosing a design basis. In addition to currently available material, the Center for Chemical Process Safety (CCPS), formed by the American Institute of Chemical Engineers, is continually developing guidelines and conducting research to further the general knowledge in emergency relief system design. The Design Institute for Emergency Relief Systems (DIERS) was established by AIChE to address sizing aspects of relief systems for two-phase, vapor-liquid flashing flow regimes. The DIERS Project Manual (Emergency Relief System Design Using DIERS Technology—1992) is the generally accepted industry standard for two-phase relief venting.

NFPA 30 and API Standard 2000 provide guidance for design of overpressure protection involving storage tanks that operate at or near atmospheric pressure. In particular, NFPA 30 focuses on flammability issues, while API 2000 addresses both pressure and vacuum requirements. The ASME code (Sections I and VIII) and API RP 520 are the primary references for pressure relief device sizing requirements.

Designers of emergency pressure relief systems should be familiar with the following list of regulations, codes of practice, and industry standards and guidelines.

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, 3d ed., November 1988. American Petroleum Institute, Washington, D.C.

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

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

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

CCPS. 1993. *Engineering Design for Process Safety.* American Institute of Chemical Engineers, New York.

DIERS. 1992. *Emergency Relief System Design Using DIERS Technology, DIERS Project Manual.* American Institute of Chemical Engineers, New York.

National Board of Boiler and Pressure Vessel Inspectors. 1992. *Pressure Relieving Device Certification (Red Book),* National Board of Boiler and Pressure Vessel Inspectors, Columbus, Ohio.

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

Relief Design Scenarios The most difficult part of designing an adequate emergency pressure relief system is determining the emergency events (credible design scenarios) for which to design. The difficulty arises primarily because the identification of credible design scenarios usually involves highly subjective judgments, which are often influenced by economic situations. Unfortunately, there exists no universally accepted list of credible design scenarios. Relief systems must be designed for the credible chain of events that results in the most severe venting requirements (worst credible scenario). Credibility is judged primarily by the number and the time frame of causative failures required to generate the postulated emergency. Only totally independent equipment or human failures should be considered when judging credibility. A failure resulting from another failure is an effect, rather than an independent causative factor. A suggested guideline for assessing credibility as a function of the number and time frames of independent causative events is:

- Any single failure is *credible.*
- Two or more simultaneous failures are *not credible*
- Two events in sequence are *credible.*
- Three or more events in sequence are *not credible.*

The first step in scenario selection is to identify all the credible emergencies using the preceding guidelines (or a similar set). This is perhaps best accomplished by identifying all the possible sources of pressure and vacuum. Table 26-7 lists a number of commonly existing pressure and vacuum sources.

Fire The main consequence of fire exposure is heat input causing thermal expansion, vaporization, or thermally induced decomposition resulting in a pressure rise. An additional result of fire exposure is the possibility of overheating the wall of the equipment in the vapor space where the wall is not cooled by the liquid. In this case, the vessel wall may fail due to the high temperature, even though the relief system is operating. Guidelines for estimating the heat input from a fire are found in API recommended practices, NFPA 30 (for bulk storage tanks), OSHA 1910.106, and corporate engineering standards. In determining the heat input from fire exposure, NFPA allows credit for application of water spray to a vessel; API allows no such credit.

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, or remote-controlled depressuring devices. Plant layout should consider spacing requirements, such as those set forth by NFPA, API, Industrial Risk Insurers, or Factory Mutual, and must include accessibility for fire-fighting personnel and equipment. Several pieces of equipment located adjacent to each other that cannot be isolated by shutoff valves can be protected by a common relief device, providing the interconnecting piping is large enough to handle the required relief load.

TABLE 26-7 Common Sources of Pressure and Vacuum

Heat Related
- Fire
- Out-of-control heaters and coolers
- Ambient temperature changes
- Runaway chemical reactions

Equipment and Systems
- Pumps and compressors
- Heaters and coolers
- Vaporizers and condensers
- Vent manifold interconnections
- Utility headers (steam, air, water, etc.)

Physical Changes
- Gas absorption (e.g., HCl in water)
- Thermal expansion
- Vapor condensation

Operational Failures A number of scenarios of various operational failures may result in the generation of overpressure conditions:

- *Blocked outlet.* Operation or maintenance errors (especially following a plant turnaround) can block the outlet of a liquid or vapor stream from a piece of process equipment, resulting in an overpressure condition.
- *Opening a manual valve.* Manual valves which are normally closed to isolate two or more pieces of equipment or process streams can be inadvertently opened, causing the release of a high-pressure stream or resulting in vacuum conditions. Other effects may include the development of critical flows, flashing of liquids, or the generation of a runaway chemical reaction.
- *Cooling water failure.* The loss of cooling water is one of the more commonly encountered causes of overpressurization. Two examples of the critical consequences of this event are the loss of condensing duty in column 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 failure affects a single piece of equipment (or process unit) or is plantwide.
- *Power failure.* The loss of power will shut down all motor-driven rotating equipment, including pumps, compressors, air coolers, and vessel agitators. As with cooling water failure, power failure can have a negative cascading effect on other equipment and systems throughout the plant.
- *Instrument air failure.* The consequences of the loss of instrument air should be evaluated in conjunction with the failure mode of the control valve actuators. It should not be assumed that the correct air failure response will occur on these control valves, as some valves may stick in their last operating position.
- *Thermal expansion.* Equipment and pipelines which are liquid-full under normal operating conditions are subject to hydraulic expansion if the temperature increases. Common sources of heat that can result in high pressures due to thermal expansion include solar radiation, steam or other heated tracing, heating coils, and heat transfer from other pieces of equipment.
- *Vacuum.* Vacuum conditions in process equipment can develop due to a wide variety of situations including:

Instrument malfunction
Draining or removing liquid with venting
Shutting off purge steam without pressuring with noncondensable vapors
Extreme cold ambient temperatures resulting in subatmospheric vapor pressures
Water addition to vessels that have been steam-purged

If vacuum conditions can develop, then either the equipment must be designed for vacuum conditions or a vacuum relief system must be installed.

Equipment Failure Most equipment failures that can lead to overpressure situations involve the rupture or break of internal tubes inside heat exchangers and other vessels and the failure of valves and regulators. Heat exchangers and other vessels should be protected with a relief system of sufficient capacity to avoid overpressure in case of internal failure. Characterization of the types of failure and the design of the relief system 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 likely. In cases involving the failure of control valves and regulators, it is important to evaluate both the fail-open and fail-closed positions.

Runaway Reactions Runaway temperature and pressure in process vessels can occur as a result of many factors, including loss of cooling, feed or quench failure, excessive feed rates or temperatures, contaminants, catalyst problems, and agitation failure. Of major concern is the high rate of energy release and/or formation of gaseous products, which may cause a rapid pressure rise in the equipment. In order to properly assess these effects, the reaction kinetics must either be known or obtained experimentally.

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 a containment vessel, a disposal system, or directly to the atmosphere (Fig. 26-13). Table 26-8 summarizes some of the device characteristics and the advantages.

Safety Relief Valves *Conventional* safety relief valves (Fig. 26-14) are used in systems where built-up backpressures typically do not exceed 10 percent of the set pressure. The spring setting of the valve is reduced by the amount of superimposed backpressure expected. Higher built-up backpressures 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; however, the manufacturer should be consulted for specific details.

Balanced safety relief valves may be used in systems where built-up and/or superimposed backpressure is high or variable. In general, the capacity of a balanced valve is not significantly affected by backpressures below 30 percent of set pressure. Most manufacturers recommend keeping the backpressure on balanced valves below 45 to 50 percent of the set pressure.

Pilot-Operated Relief Valves In a pilot-operated relief valve, the main valve is combined with and controlled by a smaller, self-actuating pressure relief valve. 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. 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 and in services where a large relieving area at high set pressures is required. The set pressure of this type of valve can be close to the operating pressure. Pilot-operated valves are frequently chosen when operating pressures are within 5 percent of set pressures and a close tolerance valve is required.

TABLE 26-8 Summary of Device Characteristics

	Reclosing devices		Nonreclosing devices
	Relief valves	Disk-valve combinations	Rupture disks
Fluid above normal boiling point	+	+	−
Toxic fluids	+	+	−
Corrosive fluids	−	+	+
Cost	−	−	+
Minimum pipe size	−	−	+
Testing and maintenance	−	−	+
Won't fatigue and fail low	+	+	−
Opens quickly and fully	−	−	+

NOTE: + indicates advantageous
− indicates disadvantageous

Rupture Disks A rupture disk is a device designed to function by the bursting of a pressure-retaining disk (Fig. 26-15). This assembly consists of a thin, circular membrane usually made of metal, plastic, or graphite that is firmly clamped in a disk holder. When the process reaches the bursting pressure of the disk, the disk ruptures and releases the pressure. Rupture disks can be installed alone or in combination with other types of devices. Once blown, rupture disks do not reseat; thus, the entire contents of the upstream process equipment will be vented. Rupture disks are commonly used in series (upstream) with a relief valve to prevent corrosive fluids from contacting the metal parts of the valve. In addition, this combination is a reclosing system.

The burst tolerances of rupture disks are typically about ±5 percent for set pressures above 40 psig.

Pressure-Vacuum Relief Valves For applications involving 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 a single assembly that mounts on a nozzle on top of the tank and are usually sized to handle the normal in-breathing and out-breathing requirements. For emergency pressure relief situations (e.g., fire), ERVs are used. API RP 520 and API STD 2000 can be used as references for sizing.

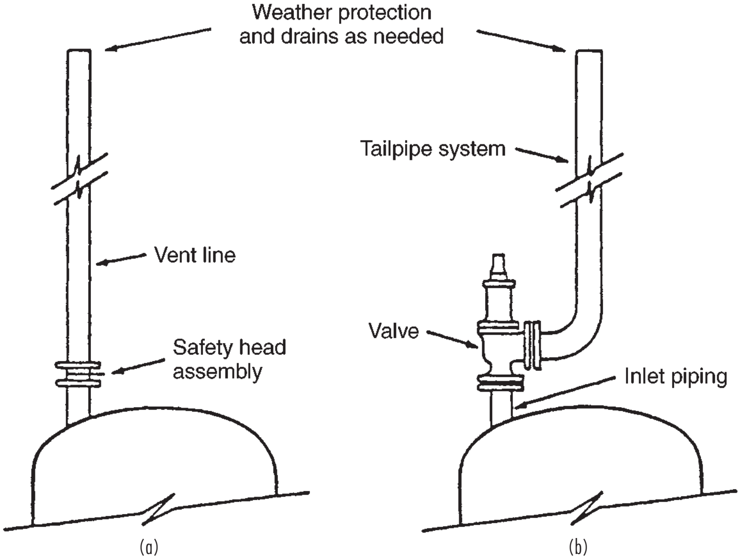


FIG. 26-13 Typical pressure relief system configurations: (*a*) rupture disk system; (*b*) pressure relief valve system.

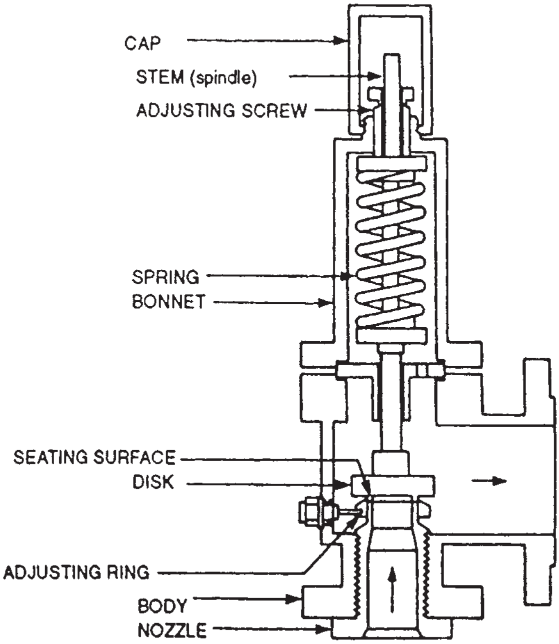


FIG. 26-14 Typical conventional pressure relief valve.

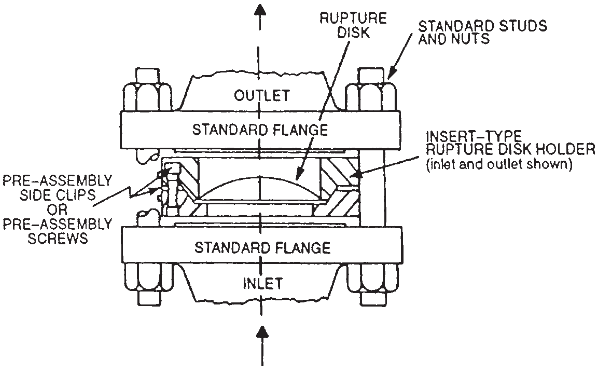


FIG. 26-15 Typical rupture disk assembly.

Sizing of Pressure Relief Systems A critical point in design is determining whether or not the relief system must be sized for single-phase or two-phase relief flow. Two-phase flow frequently occurs during a runaway reaction, but it can also occur in nonreactive systems such as vessels with gas-spargers, vessels experiencing high heat input rates, or systems containing known foaming agents such as latex. In 1976, the Design Institute for Emergency Relief Systems (DIERS) was formed to develop methods for the design of emergency relief systems to handle runaway reactions. The DIERS group consisted of a consortium of 29 companies under the auspices of the American Institute of Chemical Engineers. Of particular interest were the prediction of when two-phase flow venting would occur and the applicability of various sizing methods for two-phase vapor-liquid flashing flow situations. The most significant theoretical and experimental finding of the DIERS program is 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. The DIERS methodology is important as a means of addressing situations, such as two-phase flow, not covered adequately by ASME and API methods. The *DIERS Project Manual* (DIERS, 1992) is the best source of detailed information on these methods.

Required Relief Rate The required relief rate is the venting rate required to remove the volume being generated within the protected equipment when the equipment is at its highest allowed pressure:

$$W_{\text{required}} = \frac{\text{net volume generation rate}}{\text{specific volume of vent stream}} \tag{26-21}$$

The required relief rate is constant only if both the numerator and denominator in Eq. (26-21) are constant. If the conditions within the protected equipment (temperature, composition, etc.) or the composition and/or quality of the vent stream are changing, then the required relief rate as defined above represents the instantaneous required relief rate. For steady-state design scenarios, the required relief rate, once determined, provides the capacity information that is required to properly size the relief device and associated piping. For situations that are transient in nature (e.g., the venting of a vessel exposed to fire), the required relief rate will be continually changing as the equipment is emptied. In these situations the design should be done based on finding the required vent area that will keep the pressure in the protected equipment at (or below) the maximum allowed accumulation during the entire venting period. These cases will require the simultaneous solution of the applicable material and energy balances around the protected equipment.

Constant Flow into Protected Equipment For the steady-state design scenario with a constant, steady flow of fluid from a pressure source that is above the maximum allowed pressure in the protected equipment, volume is being generated within the equipment at a rate $RV = F/\rho_f$. Substituting into Eq. (26-21) and noting that the specific volume of the vent stream is $1/\rho_w$ gives the required mass flow rate:

$$W = \frac{F\rho_w}{\rho_f} \tag{26-22}$$

where W = required mass flow rate, lb/min
F = inlet mass flow rate, lb/min
ρ_w = stream density entering the relief system, lb/ft^3
ρ_f = stream density entering the protected equipment, lb/ft^3

Constant Energy Input into Protected Equipment If the design scenario involves a constant flow of energy (heat) into the protected equipment, then the required flow rate calculation involves determining whether or not a phase change (boiling) is occurring. If the addition of heat to the equipment does not cause the fluid to boil, then the volume generation rate is the thermal expansion rate of the fluid:

$$R_v = \frac{\beta Q}{C_p} \tag{26-23}$$

where R_v = volume generation rate, ft^3/min
β = volumetric expansion coefficient, ft^3/lb-°F
Q = heat input rate, Btu/min
C_p = liquid heat capacity, Btu/lb-°F

Combining Eqs. (26-23) and (26-22) gives the required relief rate:

$$W = \frac{\rho_w \beta Q}{C_p} \tag{26-24}$$

If the fluid is at its boiling point, then volume is generated through the phase change that occurs upon vaporization:

$$R_v = \frac{[Q(V_g - V_l)]}{\lambda} \tag{26-25}$$

where V_g, V_l = specific volumes of gas and liquid phases, ft^3/lb
λ = heat of vaporization, Btu/lb

As before, the required relief rate becomes:

$$W = \frac{[\rho_w Q(V_g - V_l)]}{\lambda} \tag{26-26}$$

Transient Material and Energy Balances The relief rate requirement at any instant during any event is developed on the basis that the total volume of vapor plus liquid is just equal to the vessel volume. In differential form, this condition is equivalent to setting the volumetric vent rate equal to the rate of volume increase in the protected equipment at any instant. The development of the relief rate criterion, which relates the rate of vapor generation to the venting rate, is based on the assumption that the equipment geometry is such that the temperature and pressure will be reasonably uniform throughout the contents, with negligible composition gradients within the phases. In addition, the time scale of the relief event is assumed to be small enough that influence of any feed streams is insignificant relative to the venting stream. Under these assumptions the material balance around the protected equipment is given by:

$$\frac{dX_r}{dt} = \frac{\left(\dfrac{WV_r}{M^2} - (1 - X_r)\dfrac{dv_f}{dt} - X_r\dfrac{dv_g}{dt} \right)}{v_g - v_f} \tag{26-27}$$

where V_r = total equipment volume
X_r = overall weight fraction vapor in the equipment
M = total mass in the equipment
v_f, v_g = specific volumes of liquid and gas phases in the equipment
W = mass vent rate
t = time

The energy balance on the equipment is developed for conditions under which thermal mixing within the vessel is sufficient to allow the properties of all portions of the liquid and vapor phases to be characterized adequately by a single value of temperature. It is assumed also that pressure gradients within the vessel are small with respect to the pressure level so that a single value of pressure may be assigned to the contents. The resulting expression for the incompressible liquid–ideal gas case is given by Huff ("Emergency Venting Requirements," *Plant/Operations Progress,* October 1982, p. 212):

$$\begin{aligned} \frac{dT}{dt}\left[X_r(C_{pg} - R) + (1 - X_r)\left(C_{pf} - T\,\frac{dv_f}{dT}\,\frac{dP}{dT} \right) \right] \\ = Q - [\lambda - P(v_g - v_f)]\,\frac{dX_r}{dt} - \frac{W}{M}\,\{[X_0 - X_r][\lambda - P(v_g - v_f)] \\ + P[X_0 v_g + (1 - X_0)v_f]\} \end{aligned} \tag{26-28}$$

where T and P are the temperature and pressure of the contents, C_{pg} and C_{pf} are the gas and liquid specific heats, λ is the latent heat of vaporization, R is the universal gas constant, and Q is the rate of heat addition to the equipment contents. The solution of Eq. (26-28) requires a value of the quality of the vent stream as it leaves the protected equipment (X_0). Limiting cases are $X_0 = 1$ (all-vapor venting) and $X_0 = 0$ (all-liquid venting). If the venting process is such that no vapor-liquid disengagement occurs, then the criterion for top venting becomes $X_0 = X_r$, where X_r is the mass fraction vapor in the equipment.

The time-dependent nature of the emergency pressure relieving event is obtained by the simultaneous solution of Eqs. (26-27) and (26-28). Generally, the only unknown parameters in these two equations are the venting rate W and the vent stream quality (X_0). The vent rate W at any instant is a function of the upstream conditions and the relief system geometry.

Vessel Flow Models and the Coupling Equation In order to evaluate the quantity of vapor entering the vent system at any instant (X_0), one must consider the dynamics of vapor disengagement that occur in the top of the protected equipment. Based on experience gained in the DIERS program, a number of vapor-liquid disengagement models have been formulated. These models estimate the liquid swell (i.e., the degree of vapor-liquid disengagement) as a function of vapor throughput. The key model parameters include 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 listed as follows in order of increasing vapor-liquid disengagement.

Homogeneous Vessel Model This model assumes that no vapor-liquid disengagement occurs in the protected equipment; thus, the vapor mass fraction entering the vent system (X_0) will be the same as the average vapor mass fraction in the equipment (X_r). This model is used to approximate the vessel conditions when the vessel contents are extremely viscous or foamy. The specification $X_0 = X_r$ has come into rather wide use as a conservative but realistic basis for taking account of the two-phase venting phenomena.

Bubbly Vessel Model The bubbly vessel model assumes uniform vapor generation throughout the liquid with limited disengagement in the vessel. In this model, the liquid phase is continuous with discrete bubbles.

Churn-Turbulent Vessel Model The churn-turbulent vessel model is also based on uniform vapor generation throughout the liquid but with considerable vapor-liquid disengagement. The liquid phase is continuous with coalesced vapor regions of increased size relative to the bubble vessel model.

Nonboiling Height Model This model applies the churn-turbulent assumptions to only a top portion of the fluid in the protected equipment. Below this portion, boiling does not occur and there is no liquid swell. The location of this nonboiling height is estimated from a balance of the hydrostatic effects and the recirculation effects.

The coupling equation is a vapor mass balance written at the vent system entrance and provides a relationship between the vent rate W and the vent system inlet quality X_0. The relief system flow models described in the following section provide a second relationship between W and X_0 to be solved simultaneously with the coupling equation. Once W and X_0 are known, the simultaneous solution of the material and energy balances can be accomplished. For all the preceding vessel flow models and the coupling equations, the reader is referred to the *DIERS Project Manual* for a more complete and detailed review.

Vent System Flow Capacity The mass flow rate W through a given vent system geometry, in general, requires a trial-and-error approach when the system configuration contains more than a single diameter. The generalized approach is to assume a flow rate W and calculate the resulting pressure profiles down the system until the final discharge pressure matches the specified value. If choked flow is encountered at any point in the system, then the system must be broken into two or more separate systems and each treated independently while preserving the mass flow rate through each.

The presence of both liquid and vapor phases in the vent stream is normally treated as a vapor-liquid mixture at equilibrium conditions. The adiabatic flashing of the stream as the pressure falls along the flow path is usually computed by conventional flash distillation methods. In principle, the flash path should be isentropic for flow in devices exhibiting low friction losses (nozzles and short pipes). For friction flow, the sum of the stream enthalpy, kinetic energy, and potential energy is held constant along the path. In practice, little error is introduced by carrying out the flash computations at constant enthalpy. With this simplification, the flash temperature-pressure-composition history can be established before starting the actual flow calculations, thus eliminating the need for repetitive flash calculations at each step in the integration.

The treatment of vent flow calculations in most typical relief system configurations involves two classes of computational models: flow in low-friction geometries such as nozzles and frictional flow in pipes and fittings.

Ideal (Frictionless) Flow in Nozzles The flow path in well-formed nozzles follows smoothly along the nozzle contour without separating from the wall. The effects of small imperfections and small frictional losses are accounted for by correcting the ideal nozzle flow by an empirically determined coefficient of discharge. The acceleration of a fluid initially at rest to flowing conditions in an ideal nozzle is given by:

$$-\frac{G^2 v^2}{2} = \int_{P_0}^{P_1} v\,dP \tag{26-29}$$

where P_0 is the stagnation pressure of the fluid (i.e., the pressure under no-flow conditions), P_1 is the flowing pressure, G is the mass flux, and v is the fluid specific volume. If the fluid is compressible, the flow will increase to a maximum value as the downstream pressure P_1 is reduced and any further decrease in the downstream pressure will not affect the flow. This maximum flow condition is referred to as the *critical* (or *choked*) condition. At this condition, the maximum mass flux is

$$G_{\max} = \sqrt{\frac{-1}{dv/dp}} \tag{26-30}$$

Pipe Flow For steady-state flow through a constant diameter duct, the mass flux G is constant and the governing steady-state momentum balance is:

$$vdP + G^2\left[vdv + \left(\frac{4fv^2}{2D}\right)dL\right] + g \cos \phi dL = 0 \tag{26-31}$$

where G = mass flux
v = specific volume of stream
P = stream pressure
f = friction factor
D = duct diameter
L = flow length
g = acceleration due to gravity
ϕ = angle of inclination from vertical

Equation (26-31) can be integrated directly to yield the mass flux G, provided that D, L, f, and ϕ are known, as well as the relationship between pressure and volume. For all-vapor cases, the expansion of the vapor is usually assumed to follow the form Pv^γ = constant ($\gamma = C_p/C_v$) and thus the momentum equation can be analytically integrated. Similarly, for all-liquid (nonflashing) flow, the stream specific volume is usually assumed to be constant, thus also providing a direct analytical integration of Eq. (26-31). For two-phase flashing flow, the requisite p-v relationship is usually obtained from flash calculations, and normally requires a numerical integration of Eq. (26-31). In addition to calculating the flow rates through sections of piping in the relief system, there may also exist additional pressure drop constraints in both the inlet and outlet piping if the relief device is a PRV. The designer is referred to the ASME and API references for further information.

A number of papers have explored methods for the solution of Eqs. (26-29) and (26-31), especially for the two-phase conditions. The reader is referred to the *DIERS Project Manual* for a more detailed review and list of appropriate references and available computer programs.

EMERGENCY RELIEF DEVICE EFFLUENT COLLECTION AND HANDLING

Nomenclature (consistent English or SI units)

A_v	Vapor flow area, ft^2
C_q	Specific heat of the quench fluid
C_R	Specific heat of the reactants
D	Drum diameter, ft
G_v	Superficial vapor mass flux, lb/s · ft^2
k	Capacity coefficient
L	Drum length, ft
M	Molecular weight of vapor
m_o	Mass of reactants
P	Pressure in the drum, psia
Q_v	Vapor flow rate, ft^3/s
r	Volumetric vapor flow rate/volumetric liquid flow rate
T	Temperature of the vapor, °R
T_a	Allowable temperature following complete quench
T_o	Initial temperature of the quench fluid
T_R	Temperature of reactants at relief set pressure
U_a	Allowable vapor velocity, ft/s
V_L	Drum liquid volume, ft^3
V_v	Superficial velocity, ft/s
W	Vapor flow rate, lb/h
Greek letters	
ρ_L	Liquid density, lb/ft^3
ρ_v	Vapor density, lb/ft^3

GENERAL REFERENCES: API Report 521, *Guide for Pressure Relieving and Depressurizing Systems,* American Petroleum Institute, Washington, D.C., March 1997. AIChE-CCPS, *Guidelines for Pressure Relief and Effluent Handling Systems,* AIChE, New York, 1997. DIERS, *Emergency Relief System Design Using DIERS Technology,* AIChE, New York, 1992. Fthenakis, *Prevention and Control of Accidental Releases of Hazardous Gases,* Van Nostrand-Reinhold, New York, 1993. Grossel and Crowl, *Handbook of Highly Toxic Materials Handling and Management,* Marcel Dekker, New York, 1995. Grossel, *Journal of Loss Prevention in the Process Industries* **3**(1): 112–124, 1990. Grossel, *Plant/Operations Progress* **5**(3): 129–135, 1986. Keiter, A. G., *Plant/Operations Progress* **11**(3): 157–163, 1992.

Introduction In determining the disposal of an effluent vent stream from an emergency relief device (safety valve or rupture disk), a number of factors must be considered, such as:

1. Is the stream single-phase (gas or vapor) or multiphase (vapor-liquid or vapor-liquid-solid)?
2. Is the stream flammable or prone to deflagration?
3. Is the stream toxic?
4. Is the stream corrosive to equipment or personnel?

Some vent streams, such as light hydrocarbons, can be discharged directly to the atmosphere even though they are flammable and explosive. This can be done because the high-velocity discharge entrains sufficient air to lower the hydrocarbon concentration below the lower explosive limit (API RP 521, 1997). Toxic vapors must be sent to a flare or scrubber to render them harmless. Multiphase streams, such as those discharged as a result of a runaway reaction, for example, must first be routed to separation or containment equipment before final discharge to a flare or scrubber.

These matters are organized into three major divisions: the types of equipment, the criteria employed in the selection of equipment, and the sizing and design of the equipment.

Types of Equipment The three most commonly used types of equipment for handling emergency relief device effluents are *blowdown drums* (also called *knockout drums* or *catch tanks*), *cyclone vapor-liquid separators,* and *quench tanks* (also called *passive scrubbers*). These are described as follows.

Horizontal Blowdown Drum/Catch Tank This type of drum, shown in Fig. 26-16, combines both the vapor-liquid separation and holdup functions in one vessel. Horizontal drums are commonly used where space is plentiful, such as in petroleum refineries and petrochemical plants. The two-phase mixture usually enters at one end and the vapor exits at the other end. For two-phase streams with very high vapor flow rates, inlets may be provided at each end, with the vapor outlet at the center of the drum, thus minimizing vapor velocities at the inlet and aiding vapor-liquid separation.

Cyclone Separator with Separate Catch Tank This type of blowdown system, shown in Fig. 26-17 and 26-18, is frequently used in chemical plants where plot plan space is limited. The cyclone performs the vapor-liquid separation, while the catch tank accumulates the liquid from the cyclone. This arrangement allows location of the cyclone knockout drum close to the reactor so that the length of the relief device discharge line can be minimized. The cyclone has internals, vital to its proper operation, which will be discussed in the following sections.

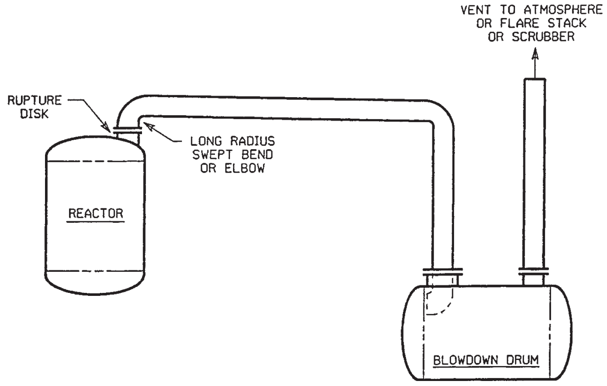


FIG. 26-16 Horizontal blowdown drum.

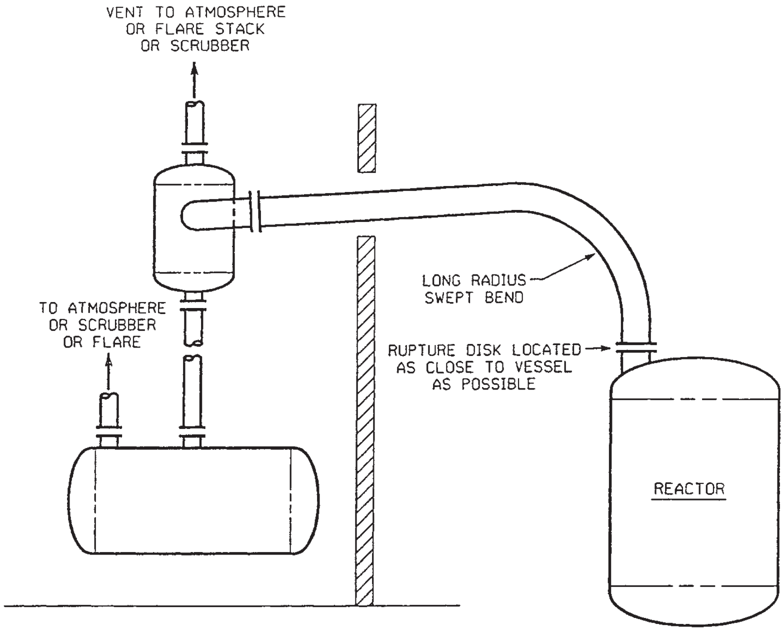


FIG. 26-17 Cyclone separator with separate liquid catch tank.

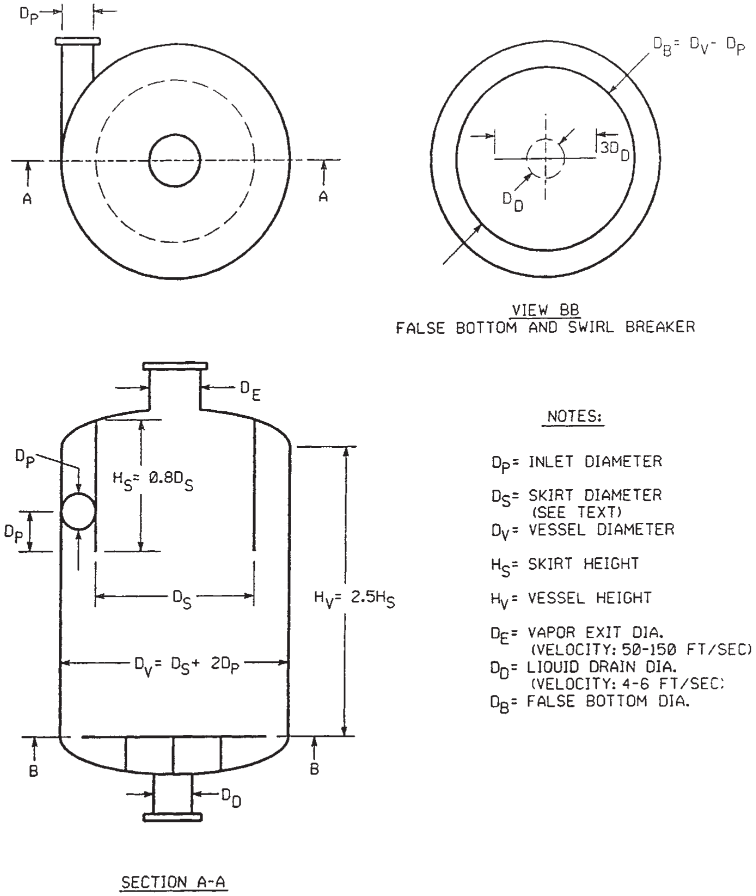


FIG. 26-18 Cyclone separator design details.

Cyclone Separator with Integral Catch Tank This type of containment system, depicted in Fig. 26-19, is similar to the aforementioned type, except that the knockout drum and catch tank are combined in one vessel shell. This design is used when the vapor rate is quite high so that the knockout drum diameter is large.

Quench Tank/Catch Tank This type of system, as shown in Figs. 26-20 and 26-21, is used when it is desired to remove condensable vapors from a flammable or toxic vent mixture by passing them through a pool of liquid in a vessel. This arrangement often obviates the need for a subsequent scrubber and/or flare stack. The design of the quencher arm is critical to efficient condensation and avoidance of water hammer. Figure 26-20 is the more conventional passive-type quenching pool used in the chemical and nuclear industry. The type shown in Fig. 26-21, with a superimposed baffle-plate section, is used when complete condensation of the incoming vapors is not expected. The exiting vapors are usually cooled to 150 to 200°F in the baffle plate section. This type is often used in petroleum refineries.

Multireactor Knockout Drum/Catch Tank This interesting system, depicted in Fig. 26-22, is sometimes used as the containment vessel for a series of closely spaced reactors (Speechly et al., "Principles of Total Containment System Design," presented at *I. Chem. E North West Branch Meeting*, 1979). By locating the drum as shown in Fig. 26-22, minimum-length vent lines can be routed directly to the vessel without any bends.

Equipment Selection Criteria and Guidelines A number of factors should be considered in order to determine when to select a blowdown drum, cyclone separator, or quench tank to handle a multiphase stream from a relief device. Among these are the plot plan space available, the operating limitations of each type, and the physicochemical properties of the stream.

The criteria for application and performance characteristics of blowdown drums, cyclone separators, and quench tanks are discussed as follows.

Horizontal Blowdown Drums (Catch Tanks)

Applications:

1. Inlet liquid loading is greater than 20 wt % based on gas flow rate.
2. They can be used for viscous and/or fouling service.

Performance Characteristics:

1. Residual entrainment is in the range of tenths to a few percent.
2. Pressure drop is usually very low.
3. Efficiency of separation is weakly dependent on the size of the vessel.
4. They are usually able to separate droplets 300 μm and larger.

Cyclones

Applications:

1. They can handle liquids with low to moderate viscosity.
2. Some fouling is acceptable.
3. Inlet liquid loading is generally less than 20 wt % based on the gas flow rate, but higher loadings are sometimes possible.

Performance Characteristics:

1. They have higher separation efficiency than a horizontal knockout drum.
2. Pressure drop is higher than that of a horizontal knockout drum.

Quench Tanks

Applications:

1. They can handle liquids with low to high viscosity.
2. They can handle liquids with moderate solids loading.
3. They can handle high liquid loading—actually no limit, as vessel can be sized to contain all the liquid.

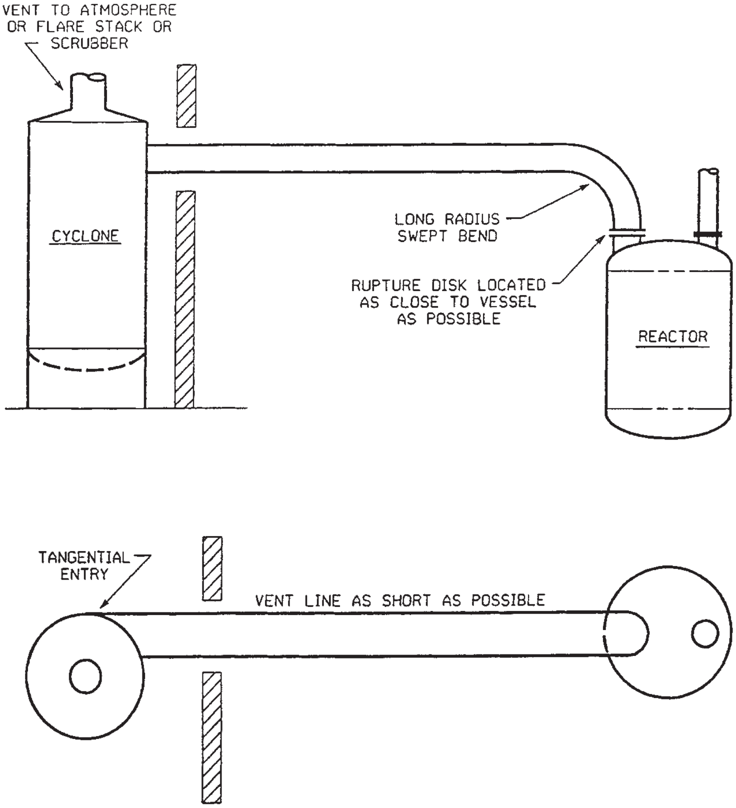


FIG. 26-19 Cyclone separator with integral catch tank.

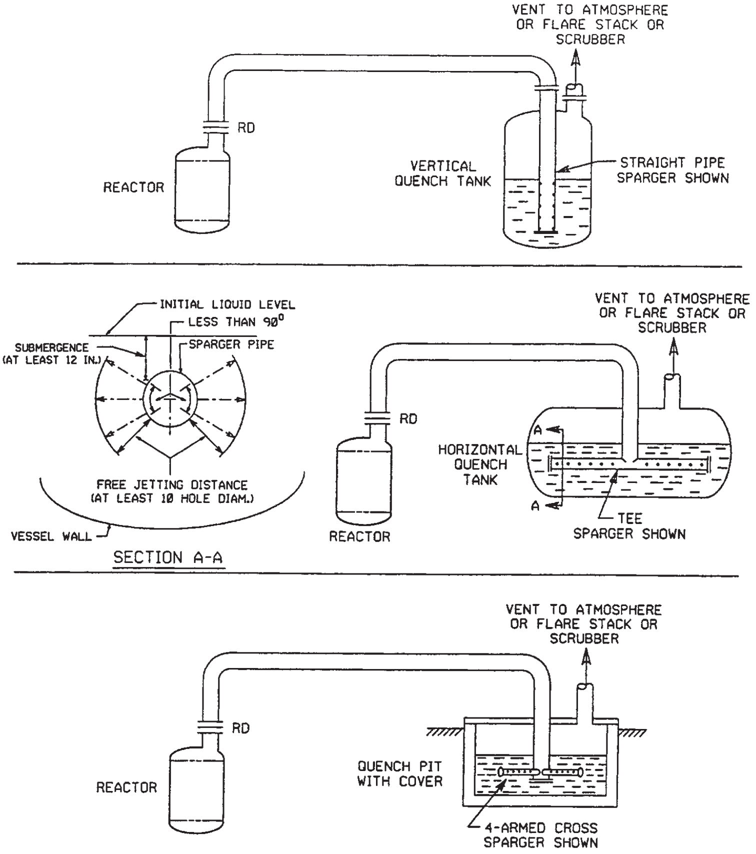


FIG. 26-20 Quench tank/catch tank.

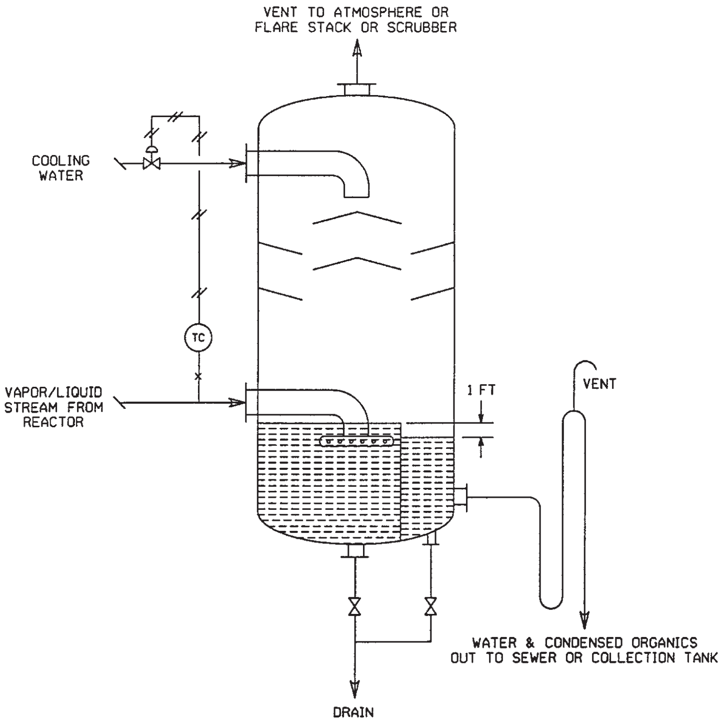


FIG. 26-21 Quench tank with direct-contact baffle tray section.

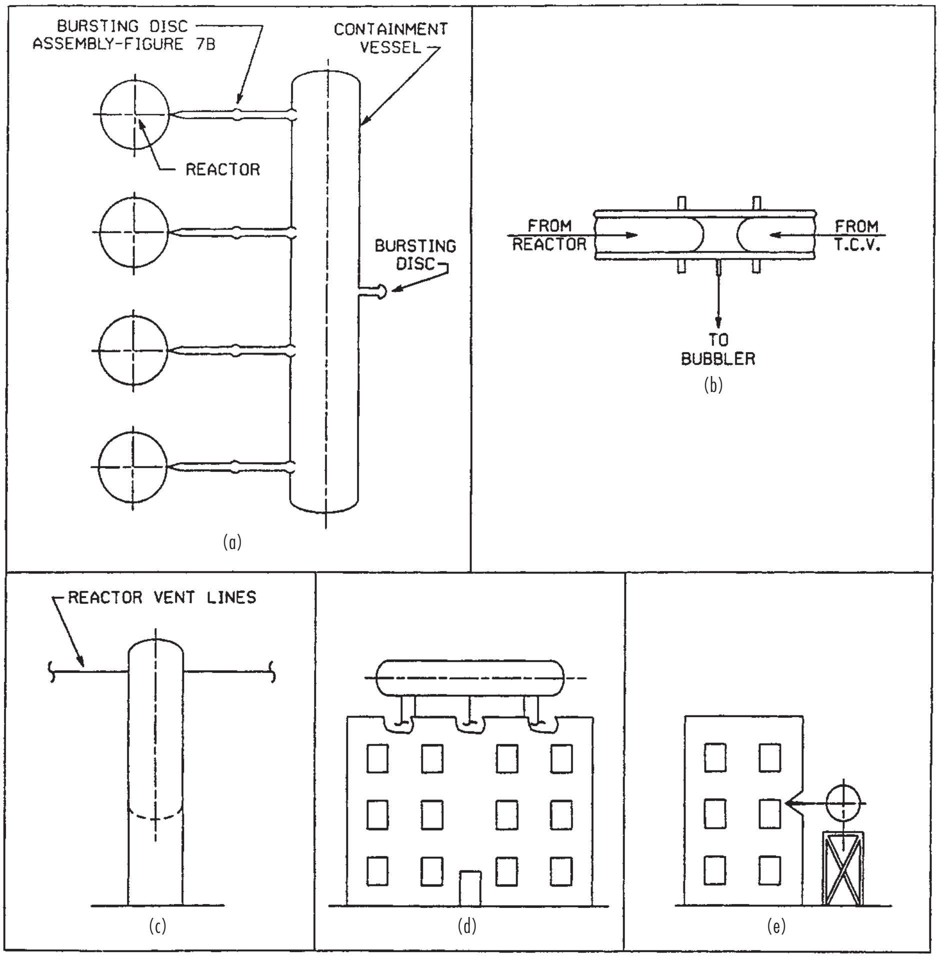


FIG. 26-22 Multireactor knockout (K-O) drum/catch tank: (*a*) plan view of reactors connected to horizontal containment vessel; (*b*) back-to-back bursting disc assembly; (*c*) elevation of self-supporting vessel; (*d*) elevation of horizontal vessel on roof of building; (*e*) elevation of horizontal vessel on side of building.

Performance Characteristics:

Quenching only saturated vapors with no inerts:

Cold quench liquid:

1. Sparging will condense the vapors effectively.
2. Sudden vapor condensation in the pool may cause water hammer if the holes are too big and the pressure drop is too low. Sonic hole velocity is desirable to avoid this problem.

Hot, nearly saturated quench liquid:

1. Sparging may not condense all the vapor. The injection of cold liquid spray in the vapor space should be considered.
2. Sudden vapor condensation in the pool is a minor problem.

Quenching only saturated vapors with some inerts:

1. Sparging may be ineffective in condensing all the condensable vapor.
2. A mass transfer device, such as a packed or trayed contact section, should be considered (see Fig. 26-21).

Quenching two-phase mixtures:

High volumetric vapor/liquid ratios ($r > 10$): where r = volumetric vapor flow rate/volumetric liquid flow rate.

1. The sparger design can be based on all vapor flow, but the heat balance must include the liquid.

Moderate volumetric vapor liquid ratios ($1 < r < 10$):

1. The liquid may inhibit the mass transfer rates needed to condense the vapors; sparging may, therefore, be less effective.
2. Sudden vapor condensation is of less concern.

Low volumetric vapor/liquid ratios ($r < 1$):

1. The mixture acts like a liquid and the vapor condensation is dependent on jet mixing. This will require a different type of sparger design.

Sizing and Design of Equipment The information in the following sections that pertain to the sizing and design of blowdown drums (catch tanks) and cyclone separators are for normal liquid-vapor systems (low-viscosity and nonfoamy or unstable foams). They are not applicable to high-viscosity (newtonian and non-newtonian) liquids and/or systems which exhibit surface-active foaming behavior, as no information is available at the present time as to the separation efficiency for these types of equipment. Quench tanks can usually handle high-viscosity liquids as well as stable foams.

Horizontal Blowdown Drum (See Fig. 26-16.) The two main criteria used in sizing horizontal blowdown drums or catch tanks are as follows.

1. The diameter must be sufficient to effect good vapor-liquid separation.
2. The total volume must be sufficient to hold the estimated amount of liquid carryover from the reactor. For a foamy discharge,

the holding volume should be greater than the reactor liquid volume (to be discussed further). One design method for sizing a horizontal blowdown drum is presented in API RP521 (1997). This may require a trial-and-error design procedure to arrive at an optimum drum size. Another procedure, which has been used in the industry by many companies, may be used to size horizontal blowdown drums more directly and is as follows:

1. Calculate the allowable vapor velocity U_a

$$U_a = k\sqrt{\frac{\rho_L - \rho_v}{\rho_v}} \qquad (26\text{-}32)$$

where U_a = allowable vapor velocity, ft/s
ρ_L = liquid density, lb/ft^3
ρ_v = vapor density, lb/ft^3
k = capacity coefficient

Values of k reported in the technical literature have ranged from 0.157 to 0.40. A k value of 0.27 has resulted in conservatively sized blowdown drums, able to separate liquid droplets 300 μm in diameter and larger.

2. Calculate the vapor flow area A_v

$$A_v = \frac{Q_v}{U_a} \qquad (26\text{-}33)$$

where A_v = vapor flow area, ft^2
Q_v = vapor flow rate, ft^3/s

3. Assume A_v occupies half of the drum area, so that the drum diameter is:

$$D_d = \sqrt{\frac{2A_v}{0.785}},\ \text{ft} \qquad (26\text{-}34)$$

4. Determine the drum volume occupied by liquid V_L based on the following criteria:

a. For nonfoaming systems, V_L should be equal to the maximum working volume of the reactor.

b. For mildly foaming systems, which rapidly defoam, V_L should be a minimum of 1.5 times the maximum working volume of the reactor. Experimental data may indicate that V_L has to be even larger than this.

5. Ignoring both heads, calculate the drum length L:

$$L = \frac{2V_L}{0.785D_d^2} \qquad (26\text{-}35)$$

where V_L = drum liquid volume, ft^3
L = drum length, ft

6. If the drum length is less than two to three times the diameter, the design is satisfactory. If L is greater than $3D_d$, assume a larger diameter and repeat the calculation until a satisfactory L/D_d ratio is achieved.

Another equation for quick sizing of horizontal knockout drums/catch tanks is presented by Tan (*Hydrocarbon Processing*, October 1967, p. 149). He recommends the following equation for calculating the drum diameter:

$$W = 360D^2\sqrt{(\rho_L - \rho_v)\frac{MP}{T}} \qquad (26\text{-}36)$$

where W = vapor flow rate, lb/h
D = drum diameter, ft
ρ_L = liquid density, lb/ft^3
ρ_v = vapor density, lb/ft^3
M = molecular weight of vapor
P = pressure in the drum, psia
T = temperature of the vapor, °R

The author states that this equation is valid for the design of knockout drums which can separate liquid droplets of 400 μm and larger.

Cyclone Separator with Separate Catch Tank (See Figs. 26-17 and 26-18.) The sizing of a cyclone knockout drum for emergency relief systems is somewhat different from sizing a cyclone separator for normal process service for the following reasons:

1. In normal process service, the superficial vapor velocity at the inlet of tangential-entry vapor-liquid separators is limited to about 120 to 150 ft/s. Higher velocities may lead to:
   - Excessive pressure drop in the separator and in the inlet piping
   - Generation of fine mist in the inlet piping, which escapes collection in the separator
2. Inlet velocity restrictions do not apply in the design of separators for emergency relief systems because:
   - Pressure drop is usually not a penalty.
   - Escape of fine mist can usually be tolerated.

Sizing Procedure The cyclone is sized by choosing a superficial F-factor for the skirt in the range of 5.0 to 8.0. The higher value may be used for waterlike liquids; the lower value for liquids like molasses. If design F-factors exceed the range of 5 to 8, the liquid draining down the skirt is entrained and escapes with the vapor. These F-factors were determined in small-scale lab experiments using water and a high-polymer solution as the test liquids. The high-polymer solution had a viscosity that was molasses-like, probably in the range of 1500 cP. There were no liquids of intermediate viscosity used in the tests.

The F-factors of 5.0 and 8.0 are conservative in the opinion of the researcher who performed the experiments (private communication from E. I. du Pont de Nemours Co., Inc., to the DIERS Project).

The F-factor is defined as follows:

$$F = V_v\sqrt{\rho_v} \qquad (26\text{-}37)$$

or

$$F = \frac{G_v}{\sqrt{\rho_v}} \qquad (26\text{-}38)$$

where V_v = superficial velocity, ft/s
ρ_v = vapor density, lb/ft^3
G_v = superficial vapor mass flux, lb/s·ft^2

The design procedure is as follows:

1. Calculate G_v

$$G_v = F\sqrt{\rho_v},\ \text{lb/s·ft}^2 \qquad (26\text{-}39)$$

2. Calculate the skirt flow area

$$A_S = \frac{W}{3600G_v},\ \text{ft}^2 \qquad (26\text{-}40)$$

where W = vapor flow rate, lb/h

3. Calculate skirt diameter

$$D_S = \sqrt{\frac{A_S}{0.785}},\ \text{ft} \qquad (26\text{-}41)$$

4. Calculate all the other separator dimensions from the relationships given in Fig. 26-18.

When the pressure relief device is set to open at greater than 15 psig (critical flow will result), it is normally not necessary to be concerned about the pressure drop in the separator. If the liquid is to be drained from the separator during the emergency blowdown, a vortex breaker and false bottom should be used (Fig. 26-18, view BB).

If the liquid contents of the vented vessel are to be retained in the separator for subsequent disposition, the holdup capacity may be increased by increasing the height of the vessel to increase the total volume by an amount equal to the vented liquid volume.

Cyclone Separator with Integral Catch Tank (See Fig. 26-19.) The diameter of the knockout drum is calculated by the criteria given in the preceding section and Fig. 26-18. Since the liquid is also to be retained in the vessel, extend the shell height below the normal bottom tangent line to increase the total volume by an amount equal to the volume of the liquid carried over.

Quench Tank (See Figs. 26-20 and 26-21.)

General In comparison with design information on blowdown drums and cyclone separators, there is very little information in the open technical literature on the design of quench tanks in the chemical industry. What is available deals with the design of quench tanks (also called *suppression pools*) for condensation of steam or steam-water mixtures from nuclear reactor safety valves. Information and criteria from quench tanks in the nuclear industry can be used for the design of quench tanks in the chemical industry. There have been several articles in recent years which provide more data for chemical industry quench tank design (AIChE-CCPS, 1997). The following sections summarize some of this information.

Design Criteria Pertinent criteria for quench tank sizing and design are presented below:

OPERATING PRESSURE There are three modes of operation of a quench tank: atmospheric pressure operation, nonvented operation, and controlled venting operation. Atmospheric operation is usually feasible when the effluent being emitted has a bubble point well above the maximum ambient temperature. A very small quantity of vapor escapes with the air that is displaced as the tank fills with the emergency discharge (typically about 0.2 percent of the reactor contents). Depending on the toxic or flammable properties of the vapor, the vent from the quench tank can be routed to the atmosphere or must be sent to a scrubber or flare.

In nonvented operation, no material is vented to the atmosphere, and this design is used when complete containment of the discharge is required. It is also used when the discharge mixture bubble point is close to or below the maximum ambient temperature and the concentration of noncondensable gas in the feed stream is very low. The tank design pressure is relatively high since the initial air in the tank is compressed by the rising liquid level, adding to the vapor pressure. The designer must take into consideration that the quench tank backpressure must be limited so as not to adversely affect the reactor relief system.

In controlled venting operation, the quench tank pressure is maintained at a desired level by a pressure controller/control valve system or pressure relief valve. This mode of operation is used when the discharge mixture bubble point is close to or below the maximum ambient temperature, and it is desired to limit the maximum quench tank pressure.

QUENCH LIQUID SELECTION The choice of the appropriate quench liquid depends on a number of factors. Water is usually the first quench liquid to consider, since it is nontoxic, nonflammable, compatible with many effluent vapors, and has excellent thermal properties. If water is selected as the quench liquid, the tank should be located indoors, if possible, to avoid freezing problems. If the tank has to be located outdoors in a cold climate, the addition of antifreeze is preferable to heat-tracing the tank, since overheating the tank can occur from tracing, thus reducing its effectiveness.

If other quench liquids are required, the liquid should have as many of the following properties as possible: compatibility with the discharge effluent, low vapor pressure, high specific heat, low viscosity, low flammability, low freezing point, high thermal conductivity, immiscibility with the discharge effluent, low cost, and ready availability.

QUENCH LIQUID QUANTITY A good discussion of the factors determining the quantity of quench liquid required is presented by CCPS (AIChE-CCPS, 1995).

When water is used as the quench medium and the effluent stream is a hydrocarbon or organic, separate liquid phases are often formed. In this case, heat transfer is the predominating mechanism during the quench. To achieve effective heat transfer, there must be a sufficient difference between the quench liquid temperature and the bubble point of the incoming effluent stream. The minimum temperature difference occurs at the end of the discharge, when the quench pool temperature is highest. A rule of thumb, from industry practice, is to allow a 10 to 20°C (18 to 36°F) ΔT. For atmospheric tank operation, the final quench liquid temperature is then set 10 to 20°C (18 to 36°F) below the normal boiling point of the final quench pool mixture. For nonvented or controlled venting operation, the final boiling point is elevated, permitting a greater design temperature rise and the use of less quench liquid. Therefore, the quench pool final temperature must be set 10 to 20°C (18 to 36°F) lower than the saturated temperature of the discharge effluent at the design maximum quench tank pressure.

The minimum capacity of quench liquid can be estimated by a heat balance, knowing the final quench pool temperature. The following equation given by Fauske (*International Symposium on Multi-Phase Transport and Particulate Phenomena,* December 15–17, 1986) can be used to calculate the minimum amount of quench liquid:

$$M = \frac{m_o(T_R - T_a)C_R}{(T_a - T_o)C_q} \tag{26-42}$$

where m_o = mass of reactants
T_R = temperature of reactants at relief set pressure
T_a = allowable temperature following complete quench
T_o = initial temperature of the quench fluid
C_q = specific heat of the quench fluid
C_R = specific heat of the reactants
(consistent English or SI units)

The preceding equation assumes the reaction is completely quenched immediately after the relief point is reached. This behavior is closely approximated if the reaction stops in the quench pool and the reactor empties quickly and thoroughly. If the reaction continues in the quench pool, the temperature T_R should be increased to the maximum adiabatic exotherm temperature. An equation is presented by CCPS (AIChE-CCPS, 1997) that includes the heat of reaction. In some cases, an experiment is necessary to confirm that the reaction indeed stops in the quench pool.

It is good practice to provide 10 to 20 percent more quench liquid than the minimum amount calculated.

QUENCH TANK VOLUME The total volume of the quench tank should be equal to the sum of the following volumes:

Quench liquid required
Liquid entering in the multiphase effluent stream
Liquid condensed from vapors in entering the effluent stream
Freeboard for noncondensables (a minimum of 10 percent is recommended)

QUENCH TANK GEOMETRY Quench tanks can have any of the following three types of geometry:

- Horizontal cylindrical vessel
- Vertical cylindrical vessel
- Concrete pit (usually rectangular)

Usually, the geometry is determined by space limitations. Both horizontal or vertical cylindrical vessels are designed as pressure vessels, and for pressures up to 50 psig, an L/D ratio of 2 to 3 results in an economic design.

SPARGER DESIGN The effluent stream should be discharged into the quench liquid by means of a sparger, which breaks it up into small jets to provide good heat and mass transfer. The sparger design must also incorporate the following capabilities:

- Maximize momentum-induced recirculation in the quench pool
- Provide adequate flow area (cross section for pressure relief without imposing high backpressure)
- Minimize shock due to vapor bubble collapse
- Minimize unbalanced momentum forces

Figure 26-20 shows conventional quench tank sparger arrangements. As can be seen in this figure, the sparger can be of the following types:

- Vertical straight pipe sparger
- Tee sparger
- Four-armed cross sparger

The following design criteria are recommended:

1. For effluent streams consisting of only liquid and vapor, hole diameters ranging from ⅛ to ½ in are recommended. Larger hole diameters (up to 2 in) may be required if the blowdown stream contains solids (polymers and/or catalyst). However, the violently collapsing vapor bubbles create a water hammer effect which increases in severity with hole size.

2. Sonic hole velocity is desirable in smaller holes and is essential in ½- to 2-in holes. A minimum sparger pressure drop of 10 psi should be used.

3. The number of holes should provide at least 0.2 holes per square foot of pool cross-sectional area. The flow area of the manifold and/or distributor piping should be at least 2 times the total area of the sparger holes. This generally ensures that the pressure drop across the holes will be at least 10 times the pressure drop in the distributor.

4. To balance high-velocity momentum forces, a symmetrical sparger design must be used. This can be a vertical straight pipe, a tee-shaped, or a cross-shaped quencher arm configuration with rows of holes on opposite sides of the pipe, which helps to balance piping forces (see Fig. 26-20). This arrangement also enhances the momentum-induced recirculation of quench liquid and maximizes the temperature difference for heat transfer. A center-to-center hole spacing

of at least two to three hole diameters is recommended, which will minimize the coalescence of the discharging jets into larger, less effective jets.

The quencher arm should be anchored to prevent pipe whip. It should also extend to the length (for horizontal vessels) or the height (for vertical vessels) of the vessel to evenly distribute the vapors in the pool.

When quenching effluents discharged by safety valves, it is preferable to use a straight, vertical sparger with holes in the end cap as well as in the pipe side walls. This is recommended to minimize the possibility of liquid hammer, which can occur more readily in horizontal spargers. The liquid hammer usually occurs for the following reasons: as the relief valve opens for the first time, the pressure spike is cushioned by the air trapped in the vent line. This air is blown out. If the valve recloses, the line may cool, causing slugs of condensate to accumulate. When the valve reopens, the slugs will accelerate to very high velocities and impact any elbows and end caps of the sparger. In severe cases, the sparger-arm end caps can be knocked off. The preceding recommendation avoids turns and the holes in the end cap provide some relief from the pressure spike.

Mass-Transfer Contact Section Where there is a strong possibility that not all of the incoming vapors will be condensed in the pool, a direct-contact mass-transfer section is superimposed on the quench tank. This can be a baffle-tray section (as shown in Fig. 26-21) or a packed column section.

The design of direct-contact mass-transfer columns is discussed in detail by Scheiman (*Petro Chemical Engr.* **37**(3): 29–33, 1965; ibid. **37**(4): 75, 78–79) and Fair (*Chem. Eng.*, June 12, 1972).

Multireactor Knockout Drum/Catch Tank (See Fig. 26-22.)

Vessel Sizing The area needed for vapor disengaging is calculated by the equations given earlier in the section on horizontal blowdown drums.

The diameter and length (or height) are determined by considering a number of factors as follows:

1. The length should be sufficient to extend beyond the locations of the reactors discharging into the vessel so as to simplify discharge pipe runs (for a horizontal vessel).
2. The height should not greatly exceed the height of the building (for vertical vessels).
3. The diameter should be sufficient to allow attenuation of the shock wave leaving the deflector plate.
4. The diameter should be sufficient to allow installation of the pipes and deflector plates in such a way as not to interfere directly with one another (particularly important for vertical vessels).
5. The cost of pressure vessels increases as the diameter increases.
6. An upper limit to the diameter is set by the need to transport complete cylindrical sections from manufacturer to site.
7. The volume of liquid in the reactor or reactors (assuming more than one vents at the same time) must be determined.

Mechanical Design Considerations The paper by Speechly et al., (“Principles of Total Containment System Design,” presented at *I. Chem. E. Northwestern Branch Meeting,* 1979) discusses a number of pertinent design features, as follows:

1. Each vent device discharge pipe is extended into the vessel and its end is fitted with a deflector device. This disperses the jet stream of solids (catalyst) and liquids discharged and dissipates this force, which should otherwise be exerted on the vessel wall immediately opposite.
2. The deflector device (baffle plate) must be carefully designed as described by Woods (*Proc. Inst. Mech. Engrs.* **180,** part 3J: 245–259, 1965–1966).
3. Isolate the catch tank from both reaction loads and forces generated by thermal expansion of the pipes; the pipes can be designed to enter the vessel through a sliding gland. Depending on layout, vessels which tend to have shorter, stiffer pipes between the building and the vessel may also require flexible bellows to be incorporated in the pipes.
4. There are usually several reactors linked to a single catch tank. To ensure that rupture of a disk on one reactor does not affect the others, each reactor is fitted with a double-rupture-disk assembly. The use of double rupture disks in this application requires installation of a leak detection device in the space between the two disks, which must also prevent a pressure buildup from occurring within this space. Otherwise, under some circumstances it is possible for a pinhole-type leakage in one disk to cause a pressure to be retained in the space between the two disks. In this event, the pressure at which the disks would rupture could be increased significantly. This condition could therefore render ineffective the protection of the reactor system itself.

For additional details on the design of blowdown drums, cyclone separators, and quench tanks, such as mechanical design, thrust forces, ancillary equipment, and safety considerations, refer to the books and articles listed in the General References.

FLAME ARRESTERS

General References: “Deflagration and Detonation Flame Arresters,” *Guidelines for Engineering Design for Process Safety,* chap. 13, CCPS-AICE, 1993. Ibid., chap. 15, “Effluent Disposal Systems.” Howard, W. B., “Flame Arresters and Flashback Preventers,” *Plant/Operations Progress,* vol. 1, no. 4, 1982. Howard, “Precautions in Selection, Installation and Use of Flame Arresters,” *Chem. Eng. Prog.*, April 1992. Piotrowski, “Specification of Flame Arresting Devices for Manifolded Low Pressure Storage Tanks,” *Plant/Operations Progress,* vol. 10, no. 2, April 1991. Roussakis and Lapp, “A Comprehensive Test Method for In-Line Flame Arresters,” *Plant/Operations Progress,* vol. 10, no. 2, April 1991. NFPA 497A, *Recommended Practice for Classification of Class I Hazardous (Classified) Locations for Electrical Installations in Chemical Process Areas*, 1997.

General Considerations Flame arresters are passive devices designed to prevent propagation of gas flames through pipelines. Typical applications are to prevent flames entering a system from outside (such as via a tank vent) or propagating within a system (such as from one tank to another). Flame arrestment is achieved by a permeable barrier, usually a metallic matrix containing narrow channels, which removes heat and free radicals from the flame fast enough to both quench it within the matrix and prevent reignition of the hot gas on the protected side of the arrester. These metallic matrices are known as *elements.* Some preliminary considerations for arrester selection and placement are:

1. Identify the at-risk equipment and the potential ignition sources in the piping system to determine where arresters should be placed and what general type (deflagration or detonation, unidirectional or bidirectional) are needed.
2. Determine the worst-case gas mixture combustion characteristics, system pressure, and permissible pressure drop across the arrester, to help select the most appropriate element design. Not only does element design impact pressure drop, but the rate of blockage due to particle impact, liquid condensation, and chemical reaction (such as monomer polymerization) can make some designs impractical even if in-service and out-of-service arresters are provided in parallel.
3. The possibility of a stationary flame residing on the arrester element surface should be evaluated, and so should the need for additional safeguards, should such an event occur (see “Endurance Burn” section).
4. Consider any material of construction limitations due to reactive or corrosive stream components.
5. Consider upset conditions that could exceed the test conditions at which the arrester was certified. These include the gas composition with regard to concentration of sensitive constituents such as ethylene or hydrogen, maximum system pressure during an emergency shutdown, and maximum temperature. Under certain upset conditions such as a high-pressure excursion, there may be no flame arrester available for the task.
6. Consider the type and location of the arrester with respect to ease of maintenance, particularly for large in-line arresters.

These questions address the type of arrester needed, the appropriate location, and the best design with respect to flow resistance, maintainability, and cost. It should be recognized that while flame arrester effectiveness is high, it is not 100 percent. To maximize effectiveness, attention should be given to proper selection, application, and maintenance of the device. In the case of marine vapor control systems in the United States, the testing and application of flame arresters is regulated by the U.S. Coast Guard. In other cases, recent testing protocols have been developed to address most adverse conditions encountered. Some arresters, such as hydraulic arresters and in-line types used to stop decomposition flames, have specialized applications for which general design and testing information are scarce. Where flame arresters are impractical, alternative strategies such as fast-acting valves, vapor suppression, and flammable mixture control should be considered.

Combustion: Deflagrations and Detonations A deflagration is a combustion wave propagating at less than the speed of sound as measured in the unburned gas immediately ahead of the flame front. Flame speed relative to the unburned gas is typically 10–100 m/s, although, owing to expansion of hot gas behind the flame, several hundred meters per second may be achieved relative to the pipe wall. The combustion wave propagates via a process of heat transfer and species diffusion across the flame front, and there is no coupling in time nor space with the weak shock front generated ahead of it. Deflagrations typically generate maximum pressures in the range 8–12 times the initial pressure. The pressure peak coincides with the flame front, although a marked pressure rise preceeds it; thus, the unburned gas is compressed as the deflagration proceeds, depending on the flame speed and vent paths available. The precompression of gas ahead of the flame front (also known as "cascading" or "pressure piling") establishes the gas conditions in the arrester when the flame enters it and hence affects both the arrestment process and the maximum pressure generated in the arrester body. A severe deflagration arrestment test involves placing a restricting orifice behind the arrester, which increases the degree of precompression. This is known as "restricted-end" deflagration testing.

As the deflagration flame travels through piping, its speed increases due to flow-induced turbulence and compressive heating of the unburned gas ahead of the flame front. Turbulence is especially enhanced by flow obstructions such as valves, elbows, and tees. Once the flame speed has attained the order of 100 m/s, a deflagration-to-detonation transition (DDT) can occur, provided that the gas composition is within the detonatable limits, which lie inside the flammable limits. The travel distance for this to occur is referred to as the *run-up* distance for detonation. This distance varies with the gas mixture sensitivity and increases with pipe diameter. Tabulated run-up distances are generally for straight pipe runs, and DDT can occur for much smaller distances in pipe systems containing flow obstructions. At the instant of transition, a transient state of *overdriven detonation* is achieved and persists for a distance of a few pipe diameters. Overdriven detonations propagate at speeds greater than the speed of sound (as measured in the burned gas immediately behind the flame front), and side-on pressure ratios (at the pipe wall) in the range 50 to 100 have been measured. The peak pressure is variable, depending on the amount of precompression during deflagration. A severe test for detonation-type flame arresters is to arrange for the arrester to encounter a series of overdriven detonations.

After the abnormally high velocities and pressures associated with DDT have decayed, a state of stable detonation is attained. A detonation is a combustion-driven shock wave propagating at the speed of sound, as measured in the burned gas immediately behind the flame front. Since the speed of sound in this hot gas is much larger than in the unburned gas or the ambient air, and the flame front speed is augmented by the burned gas velocity, stable detonations propagate at supersonic velocities relative to an external fixed point. The wave is sustained by chemical energy released by shock compression and ignition of the unreacted gas. The flame front is coupled in space and time with the shock front, with no significant pressure rise ahead of the shock front. The high velocities and pressures associated with detonations require special element design to quench the high-velocity flames plus superior arrester construction to withstand the associated impulse loading. Since this entails narrower and/or longer element channels plus bracing of the element facing, both inherent pressure drop and the possibility of fouling of detonation arresters should be considered.

The problem of flame arrestment, either of deflagrations or detonations, depends on the properties of the gas mixture involved plus the initial temperature and pressure. Gas mixture combustion properties cannot be quantified for direct use in flame arrester selection and only general characteristics can be assigned. For this reason, flame arrester performance must be demonstrated by realistic testing. Such testing has demonstrated that arresters capable of stopping even overdriven detonations may fail under restricted-end deflagration test conditions. It is important to understand the significance of the test conditions addressed and their possible limitations.

Combustion: Gas Characteristics and Sensitivity Combustion thermodynamic calculations allow determination of peak deflagration and detonation pressures, plus stable detonation velocity. The peak pressure calculation may be used to determine combustion product venting requirements, although a conservative volume increase of 9:1 may be used for essentially closed systems. Other relevant gas characteristics are entirely experimental. The sensitivity to detonation depends on the detonatable range and fundamental burning velocity, although no specific correlations or measures of sensitivity exist based on fundamental properties. It is often considered that detonation sensitivity and the degree of difficulty in arresting flames increase with lower National Electrical Code (NEC) Groupings. Hence, Group A gases (acetylene) will be most sensitive and Group D gases (such as saturated hydrocarbons) will be least sensitive. This empirical method of characterizing gases is typically used in selecting deflagration arresters, where successful testing using one gas in an NEC electrical group is assumed to apply for other gases in that group. It is cautioned that, where the maximum experimental safe gaps (MESGs) of two gases within a single NEC group are significantly different, the assumption of equivalent sensitivity is dubious. Regulations applying to detonation arresters in vapor control systems under the authority of the U.S. Coast Guard (USCG) provide that MESGs be solely used to characterize gases, under the assumption that mixtures with smaller MESGs are more difficult to stop. See "Deflagration and Detonation Flame Arresters," (1993) for a discussion of MESG plus tabulated values.

Corrosion Consideration should be given to possible corrosion of both the element material and the arrester housing, since corrosion may weaken the structure, increase the pressure drop, and decrease the effectiveness of the element. While the housing might be designed to have a corrosion allowance, corrosion of the element must be avoided by proper material specification. Common materials of construction include aluminum, carbon steel, ductile iron, and 316 stainless steel housings and aluminum or 316 stainless steel elements. While special materials such as Hastelloy might be used for situations such as high HCl concentrations it may be more cost effective to use a hydraulic arrester in such applications.

Directionality To select an arrester for any service, the potential sources of ignition must be established in relation to the pipe system and the equipment to be protected. The pipe connecting an arrester with an identified ignition source is the *unprotected side* of the arrester. The pipe connecting the arrester with at-risk equipment is the *protected side.* If the arrester will encounter a flame arriving only from one direction, a *unidirectional* arrester can be used. If a flame may arrive from either direction, a *bidirectional* arrester is needed. The latter are either symmetrically constructed or are certified by testing. Back-to-back use of unidirectional arresters will not usually be cost effective unless testing reveals a specific advantage such as increased allowable operating pressure during restricted-end deflagration testing.

Endurance Burn Under certain conditions, a successfully arrested flame may stabilize on the unprotected side of an arrester element. Should this condition not be corrected, the flame will eventually penetrate the arrester as the channels become hot. An endurance burn time can be determined by testing, which specifies that the arrester has withstood a stabilized flame without penetration for a given period. The test should address either the actual or worst-case geometry, since heat transfer to the element will depend on whether the flame stabilizes on the top, bottom, or horizontal face. In general, the endurance burn time identified by test should not be regarded as an accurate measure of the time available to take remedial action, since test conditions will not necessarily approximate the worst possible practical case. Temperature sensors may be incorporated at the arrester to indicate a stabilized flame condition and either alarm or initiate appropriate action, such as valve closure.

Installation End-of-line arresters should be protected using appropriate weather hoods or cowls. In-line arresters (notably detonation arresters) must be designed to withstand the highest line pressure that might be seen, including upset conditions. The design should be verified by hydrostatic and pneumatic pressure tests. The piping system should be designed with adequate supports and should allow routine access to the arrester for inspection and maintenance.

Maintenance It is important to provide for arrester maintenance, both by selection of the most suitable arrester type and judicious location. Inspection and maintenance should be performed on a regular basis, depending on experience with the particular arrester in the service involved. It should also be carried out after successful function of the arrester. Some in-line designs allow removal, inspection, and cleaning of the element without the need to expand the line. Unit designs featuring multiple elements in parallel can reduce downtime by extending the period between cleaning. For systems which cannot be shut down during maintenance, parallel arresters incorporating a three-way valve may be used. Detonation arrester elements are especially prone to damage during dismantling, cleaning, and reassembly. Maintenance must be carefully done, avoiding sharp objects that could disable the delicate channels in the element. Spare elements should be available to reduce downtime and provisions made for storing, transporting, and cleaning the elements without damage.

Monitoring The differential pressure across the arrester element can be monitored to determine the possible need for cleaning. The pressure taps must not create a flame path around the arrester. It can be important to provide temperature sensors, such as thermocouples, at the arrester to detect flame arrival and stabilization. Since arrester function may involve damage to the arrester, the event of successful function (flame arrival) may be used to initiate inspection of the element for damage. If the piping is such that flame stabilization on the element is a realistic concern, action must be taken immediately upon indication of such stabilization (see also "Endurance Burn"). Such action may involve valve closure to shut off gas flow.

Operating Temperature and Pressure Arresters are certified subject to maximum operating temperatures and absolute pressures normally seen at the arrester location. Arrester placement in relation to heat sources, such as incinerators, must be selected so that the allowable temperature is not exceeded, with due consideration for the detonation potential as run-up distance is increased.

If heat tracing is used to prevent condensation of liquids, the same temperature constraint applies. In the case of in-line arresters, there may be certain upset conditions that produce unusually large system pressures outside the stipulated operating range of the arrester. Since the maximum operating pressure for a detonation arrester may be in the range of 16 to 26 psia, depending on the gas sensitivity and arrester design, it may be impossible to find a suitable arrester to operate during such an upset. The situation may be exacerbated by pressure drop across the device, caused by high flow and/or fouling.

Pressure Drop Flow resistance depends on flame arrester channel arrangement and on a time-dependent fouling factor due to corrosion or accumulation of liquids, particles, or polymers, depending on the system involved. Monomer condensation is a difficult problem, since inhibitors will usually be removed during monomer evaporation and catalysis might occur over particulates trapped in the element. Pressure drop can be a critical factor in operability, and cleaning may represent a large hidden cost.

Fouling may be mitigated in a number of ways. First, the least-sensitive element design can be selected, and in the case of end-of-line arresters, weather hoods or cowls can be used to protect against water or ice accumulation. Second, a fouling factor (20 percent or greater) might be estimated and an element with a greater tested flow capacity selected to reduce the pressure drop. This should be further increased if liquid condensation might occur. It is important that certified flow curves for the arrester be used rather than calculated curves, since the latter can be highly optimistic. Condensation and polymerization may be mitigated by geometry (minimizing liquid accumulation in contact with the element) and provision for drainage. Alternatively, the arrester may be insulated and possibly heat traced. Drains should not provide flame paths around the arrester or leak in either direction when closed. If heat tracing is used, the temperature must be limited to the certified operating range of the arrester.

In addition to using an arrester element with greater flow capacity, it is common to use two arresters in parallel where frequent cleaning is required, with one arrester in standby. A three-way valve can be used to allow uninterrupted operation during changeover. Where elements have an intrinsically high pressure drop, such as sintered metal elements used in acetylene service, multiple parallel elements can be used.

Deflagration Arresters The two types of deflagration arrester normally considered are the *end-of-line arrester* (Figs. 26-23 and 26-24) and the *tank vent deflagration arrester*. Neither type of arrester is designed to stop detonations. If mounted sufficiently far from the atmospheric outlet of a piping system, which constitutes the unprotected side of the arrester, the flame can accelerate sufficiently to cause these arresters to fail. Failure can occur at high flame speeds even without a run-up to detonation.

If atmospheric tanks are equipped with flame arresters on the vents, fouling or blockage by extraneous material can inhibit gas flow to the degree that the tank can be damaged by underpressure. API standards allow the use of pressure-vacuum (P/V) valves without flame arresters for free venting tanks on the basis that the high vapor velocity in the narrow gap between pressure pallet (platter) and valve body will prevent flashback. However, it is important to ensure that the pallet is not missing or stuck open, since this will remove the protection. Absence of the pallet was a listed factor in the 1991 Coode Island fire (State Coroner Victoria, Case No. 2755/91, Inquest into Fire at Coode Island on August 21 and 22, 1991, Finding). Whether flame arresters are used, proper inspection and maintenance of these vent systems is required.

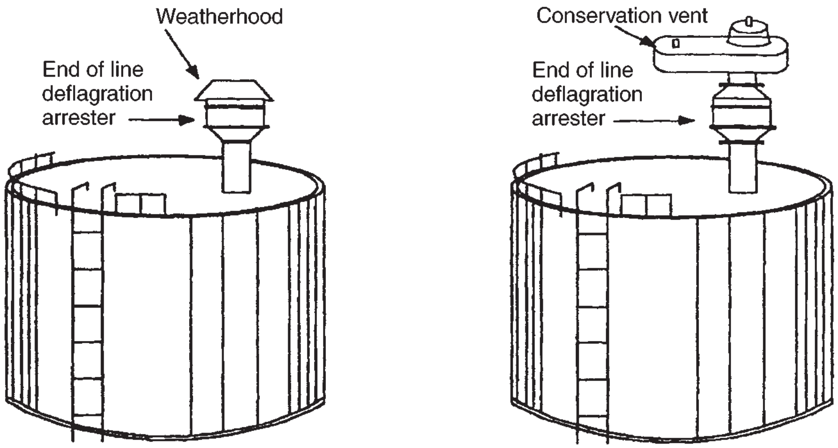


FIG. 26-23 Typical deflagration arrester installations.

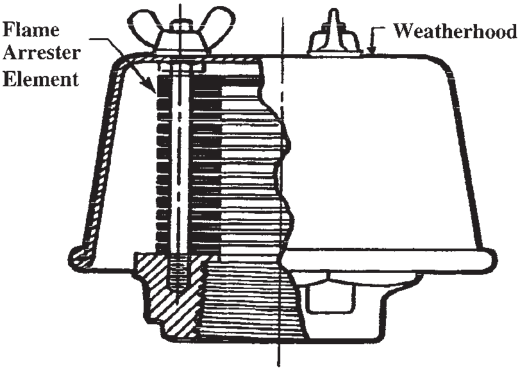


FIG. 26-24 Typical deflagration arrester design (end-of-line type).

End-of-line arresters are mounted at the outlet of a pipe system and go directly to the atmosphere, so there is no potential for significant flame acceleration in the pipe. Tank vent deflagration arresters are strictly limited by the approval agency, but for Group D gases they are typically mounted no more than 20 ft from the end of a straight pipe that vents directly to the atmosphere. The allowed distance must be established by proper testing with the appropriate gas mixture and the pipe diameter involved. Turbulence-promoting irregularities in the flow (bends, tees, elbows, valves, etc.) cannot be used unless testing has addressed the exact geometry. It is essential that run-up to detonation cannot occur in the available piping system, and run-up distance can be less than 2 ft for some fast-burning gases such as hydrogen in air (Group B). Thus the NEC Grouping of the gas mixture must be considered. More important, it must be emphasized that even if run-up to detonation does not occur, a deflagration arrester can fail if the flame speed is great enough. Thus the run-up distance is not an adequate criterion for acceptable location and this limitation can be determined only by realistic testing. A number of explosions have occurred due to misapplication of deflagration arresters where detonation arresters should have been used.

In certain exceptional cases, a specially designed deflagration arrester may be mounted in-line without regard to run-up distance. This can be done only where the system is known to be incapable of detonation. An example is the decomposition flames of ethylene, which are briefly discussed under “Special Arrester Types and Alternatives.”

Detonation and Other In-Line Arresters If the point of ignition is remote from the arrester location, the arrester is an in-line type such as might be situated in a vapor collection system connecting several tanks (Fig. 26-25). Due to the possibility of DDT, most in-line arresters are designed to stop both deflagrations and detonations (including overdriven detonations) of the specified gas mixture. These are known as *detonation arresters.* Figure 26-26 shows a typical design. In some cases, in-line arresters need to stop deflagrations only. However, in such cases it must be demonstrated that detonations cannot occur in the actual pipework system; unless the gas mixture is intrinsically not capable of detonation, this requires full-scale testing using the exact pipe geometry to be used in practice, which must not be changed after installation.

Detonation arresters are typically used in conjunction with other measures to decrease the risk of flame propagation. For example, in vapor control systems, the vapor is often enriched, diluted, or inerted, with appropriate instrumentation and control (see “Effluent Disposal Systems,” 1993). In cases where ignition sources are present or predictable (such as most vapor destruct systems), the detonation arrester is used as a last-resort method anticipating possible failure of vapor composition control. Where vent collection systems have several vapor/oxidant sources, stream compositions can be highly variable and

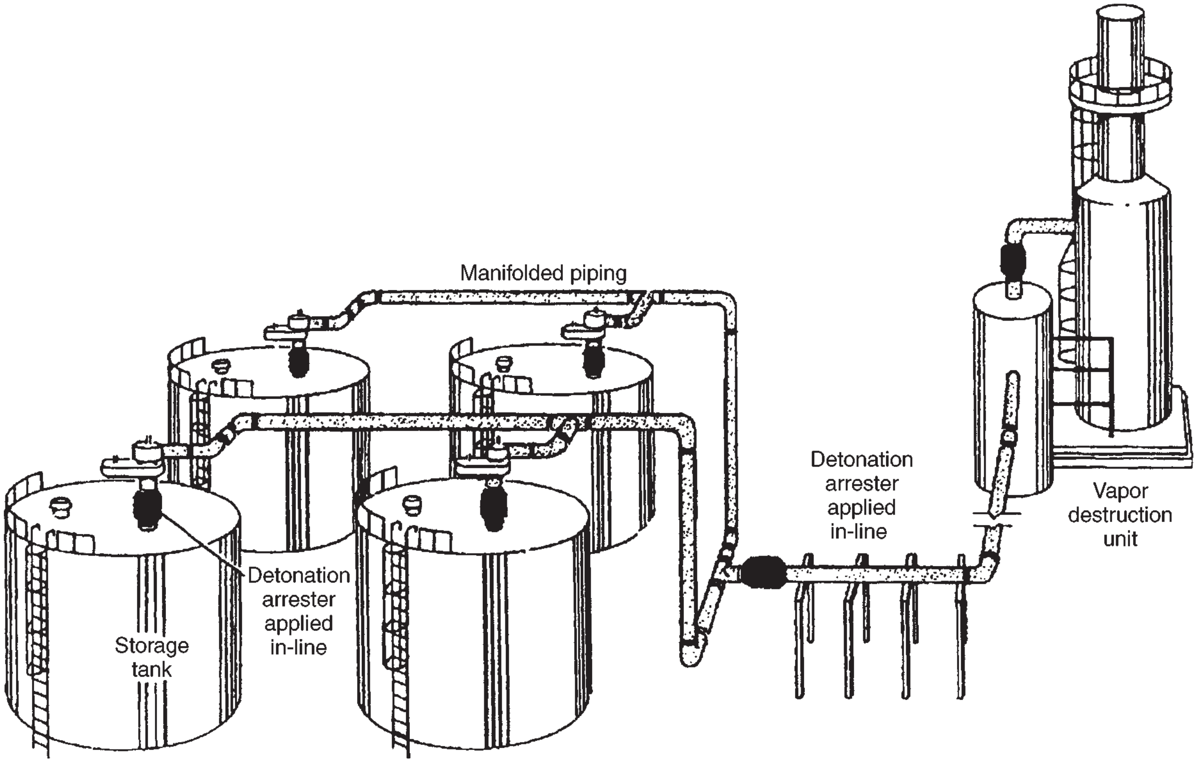


FIG. 26-25 Possible positions at which flame arresters may be placed (vapor control system).

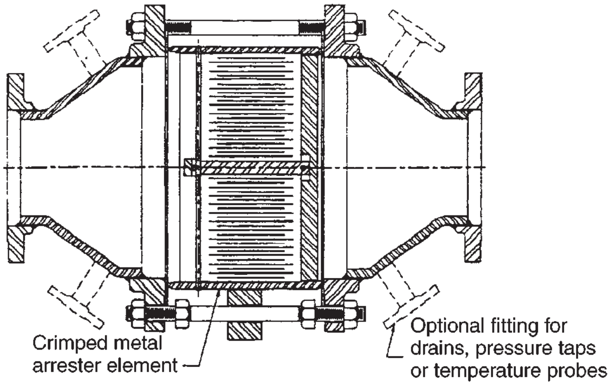


FIG. 26-26 Typical detonation arrester design (crimped-ribbon type).

this can be additionally complicated when upset conditions are considered. It is often cost effective to perform hazard analyses, such as fault tree analysis, to determine whether such vent streams can enter the flammable region and, if so, what composition corresponds to the worst credible case. Such an analysis is also suitable to assess alternatives to arresters.

Effect of Pipe Diameter Changes Arrester performance can be impaired by local changes in pipe diameter. It was shown that a minimum distance of 120 pipe diameters should be allowed between the arrester and any increase in pipe diameter, otherwise a marked reduction in maximum allowable operating pressure would occur. This impairment was observed during detonation testing but was most pronounced during restricted-end deflagration testing (Lapp and Vickers, *Int. Data Exchange Symp. on Flame Arresters and Arrestment Technology,* Banff, Alberta, October 1992). As a rule, arresters should be mounted in piping either equal to or smaller than the nominal size of the arrester.

Venting of Combustion Products As gas deflagrates or detonates in the piping system, there is a volume expansion of the products and an associated pressure increase. In some instances where the pipe system volume involved is relatively large, a significant overpressure might be developed in the vapor spaces of connected tanks, especially when vapor space is minimal due to high liquid level. It can be assumed that all the gas on the unprotected side of the arrester is converted to equilibrium products; the pressure is relieved via gas expansion into the entire system volume and to the atmosphere via any vent paths present. If heat losses are neglected by the assumption of high flame speeds or detonation and atmospheric venting paths are neglected, a conservative approach is that storage vessels be designed with a capacity to handle nine times the pipe volume on the unprotected side of the arrester. With regard to the high pressures associated with detonations, it has been shown (Lapp, *Independent Liquid Terminal Association Conference,* Houston, June 23, 1992) that detonation arresters attenuate the peak detonation pressure by up to 96 percent, depending on the arrester design, and therefore protect from much of the pressure pulse. To further reduce the pressure pulse, relief devices may be provided at the arrester.

Arrester Testing and Standards Regulatory and approval agencies and insurers impose acceptance testing requirements, sometimes as part of certification standards. The user may also request testing to demonstrate specific performance needs, just as the manufacturer can help develop standards. These interrelationships have resulted in several new and updated performance test procedures. *Listing* of an arrester by a testing laboratory refers only to performance under a defined set of test conditions. The flame arrester user should develop specific application requirements based on the service involved and the safety and risk criteria adopted.

A variety of test procedures and use guidelines have been developed. In addition, companies or associations may develop internal standards. The Federal Register, 33 CFR, Part 154, contains the USCG requirements for detonation arresters in marine vapor control systems. Other U.S. procedures are given in ASTM F 1273-91, UL 525, FM Procedure Classes 6061 and 7371, and API Publications 2028 and 2210. Outside the United States, procedures are given in Canada's CSA Standard Z 343, Rev. 12, 1993, the United Kingdom's British Standard BS 7244, Germany's DIN/CEN Draft Standard of the DAbF Subcommittee on Standardization, June 1991 (developed through the Federal Physical Technical Institute, PTB), and the International Maritime Organization (IMO) Standard MS/Circ. 373, Rev. 1, 1988. For U.S. mining applications, the Mine Safety and Health Administration (MSHA) provides regulation and guidance—for example, in CFR Title 30, Part 36.

Deflagration Arrester Testing For end-of-line and tank vent flame arresters, approval agencies may require manufacturers to provide users with data for flow capacity at operating pressures, proof of success during an endurance burn or continuous flame test, evidence of flashback test results (for end-of-line arresters) or explosion test results (for in-line or tank vent arrester applications), hydraulic pressure test results, and results of a corrosion test.

Endurance burn testing generally implies that the ignited gas mixture and flow rate be adjusted to give the worst-case heating (based on temperature observations on the protected side of the element surface), that the burn continue for a specified duration, and that flame penetration not occur. Continuous flame testing implies that a gas mixture and flow rate be established at specified conditions and burn on the flame arrester for a specified duration. The endurance burn test is usually a more severe test than the continuous burn. In both cases the flame arrester attachment configuration and any connecting piping or valves should be installed as in the plant design.

Flashback tests incorporate a flame arrester on top of a tank, with a large plastic bag surrounding the flame arrester. A specific gas mixture (for example, propane, ethylene, or hydrogen at the most sensitive composition in air) flows through and fills the tank and the bag. Deflagration flames initiated in the bag (three at different bag locations) must not pass through the flame arrester into the tank. On the unprotected side, piping and attachments such as valves are included as intended for installation; a series of tests—perhaps ten—is conducted.

Whatever the application, a user should be aware that not all test procedures are the same, are of the same severity, or use the same rating designations. Therefore, it is important to review the test procedure and determine whether the procedure used is applicable to the intended installation and potential hazard the flame arrester is meant to prevent.

Detonation Arrester Testing Requirements are described by various agencies in the aforementioned documents (UL 525, etc.). For installations governed by the USCG in Appendix A of 33 CFR, Part 154 (Marine Vapor Control Systems), the USCG test procedures must be followed. These are similar but not identical to those of other agencies listed (for a discussion of differences, see "Deflagration and Detonation Flame Arresters," 1993).

Detonation arresters are extensively tested for proof of performance against deflagrations, detonations, and endurance burns. In the United States, arrester manufacturers frequently test detonation arresters according to the USCG protocol; other test standards might alternatively or additionally be met. Under this protocol, the test gas must be selected to have either the same or a lower MESG than the gas in question (MESG means *maximum experimental safe gap*). Typical MESG benchmark gases are stoichiometric mixtures of propane, hexane, or gasoline in air to represent Group D gases having an MESG equal to or greater than 0.9 mm and ethylene in air to represent Group C gases with an MESG no less than 0.65 mm. Commercially available arresters are typically certified for use with one or another of these benchmark gas types. An ethylene-type arrester is selected should the gas in question have an MESG less than 0.9 mm but not less than 0.65 mm. Five low- and five high-overpressure deflagration tests are required with and without a flow restriction on the protected side. Of these 20 tests, the restricted-end condition is usually the more severe and often limits the maximum initial pressure at which the arrester will be suitable. Five detonation tests and five overdriven detonation tests are also required, which may involve additional run-up piping and turbulence promoters in order to achieve DDT at the arrester. If these tests are successful, an endurance burn test is required. This test does not use propane for

Group D gases, but hexane or gasoline, owing to their lower autoignition temperatures. For Group C tests, ethylene can be used for all test stages.

Shortcomings in the use of MESG to characterize gases, in the use of stoichiometric compositions for deflagration tests, and nonoptimization of test geometry have been recognized ("Deflagration and Detonation Flame Arresters," 1993). The user has the option to request additional tests to address such concerns and may wish to test actual stream compositions rather than simulate on the basis of MESG values.

Special Arrester Types and Alternatives Several types of *unlisted* arresters (water seals, packed beds, velocity-type devices, and fast-acting valves) mentioned in API 2028 are described more fully in Howard (1982). There are few design or test data for hydraulic and packed-bed arresters; some types are designed and used by individual companies for specific applications, while others are commercially available. Figure 26-27 shows some special arrester types.

Decomposition Flame Arresters Above certain minimum pipe diameters, temperatures, and pressures, some gases may propagate decomposition flames in the absence of oxidant. Special in-line arresters have been developed (Fig. 26-27). Both deflagration and detonation flames of acetylene have been arrested by hydraulic valve arresters, packed beds (which can be additionally water-wetted), and arrays of parallel sintered metal elements. Information on hydraulic and packed-bed arresters can be found in the Compressed Gas Association Pamphlet G1.3, "Acetylene Transmission for Chemical Synthesis." Special arresters have also been used for ethylene in 1000- to 1500-psi transmission lines and for ethylene oxide in process units. Since ethylene is not known to detonate in the absence of oxidant, these arresters were designed for in-line deflagration application.

Alternatives to Arresters Alternatives to the use of flame arresters include fast-acting isolation valves, vapor suppression systems, velocity-type devices in which gas velocity is designed to exceed flashback velocity, and control of the flammable mixture (NFPA 69 standard, "Explosion Prevention Systems"). The latter alternative frequently involves reduction of oxygen concentration to less than the limiting oxygen concentration (LOC) of the gas stream.

STORAGE AND HANDLING OF HAZARDOUS MATERIALS

GENERAL REFERENCES: *Air Quality Handbook,* ENSR Consulting and Engineering, Acton, Mass., June 1988. ANSI/API-620-1986, American National Standards Institute, New York, 1986. AP-40, *Air Pollution Engineering Manual,* 2d ed., U.S. Environmental Protection Agency, Office of Air Quality Planning and Standards, 1973. AP-42, *Compilation of Emission Factors for Stationary Sources,* U.S. Environmental Protection Agency, Office of Air Quality Planning and Standards, 1985. *API Standards,* American Petroleum Institute, Washington, D.C. Arthur D. Little, Inc., and LeVine, *Guidelines for Safe Storage and Handling of High Toxic Hazard Materials,* CCPS, AIChE, New York, 1986. *ASME Boiler and Pressure Vessel Code; ASME Code for Pressure Piping; ASME General and Safety Standards; ASME Performance Test Codes,* American Society of Mechanical Engineers, New York. *Chemical Exposure Index, Second Edition,* AIChE, New York, 1994. *Clean Air Act Amendments Bulletin Board System,* U.S. Environmental Protection Agency, Office of Air Quality Planning and Standards, 1200–9600 baud, April 1992. *Code of Federal Regulations,* Protection of Environment, Title 40, Parts 53 to 80, Office of the Federal Register, National Archives and Records Administration, July 1991. Englund, "Opportunities in the Design of Inherently Safer Chemical Plants," in J. Wei et al., ed., *Advances in Chemical Engineering,* vol. 15, Academic Press, 1990. Englund, "Design and Operate Plants for Inherent Safety," *Chem. Eng. Prog.*, parts 1 and 2, March and May 1991. Englund, Mallory, and Grinwis, "Preventing Backflow," *Chem. Eng. Prog.*, February 1992. Englund and Grinwis, "Redundancy in Control Systems," *Chem. Eng. Prog.*, October 1992. Englund and Holden, "Storage of Toxic Materials," in Grossel and Crowl, *Handbook of Highly Toxic Materials Handling and Management,* Marcel Dekker, New York, 1995. *Guidelines for Chemical Process Quantitative Risk Analysis,* CCPS, AIChE, New York, 1989. Hendershot, "Alternatives for Reducing the Risks of Hazardous Material Storage Facilities," *Environmental Progress,* 7 August 1988, pp. 180ff. Kletz, *An Engineer's View of Human Error,* Institution of Chemical Engineers, VCH Publishers, New York, 1991. Kletz, "Friendly Plants," *Chem. Eng. Prog.*, July 1989, pp. 18–26. Kletz, *Plant Design for Safety: a User Friendly Approach,* Hemisphere Publishing, London, 1991. Lees, *Loss Prevention in the Chemical Industries,* Butterworths, London, 1980. Prokop, "The Ashland Tank Collapse," *Hydrocarbon Processing,* May 1988. *Refrigerated Liquid Chlorine Storage,* Pamphlet 78, Edition 1, The Chlorine Institute, New York, July 1984. Russell and Hart, "Underground Storage Tanks, Potential for Economic Disaster," *Chemical Engineering,* March 16, 1987, pp. 61–69. *Ventsorb for Industrial Air Purification,* Bulletin 23-56c, Calgon Carbon Corporation, Pittsburgh, Pa., 1986. White and Barkley, "The Design of Pressure Swing Adsorption Systems," *Chem. Eng. Prog.*, January 1989.

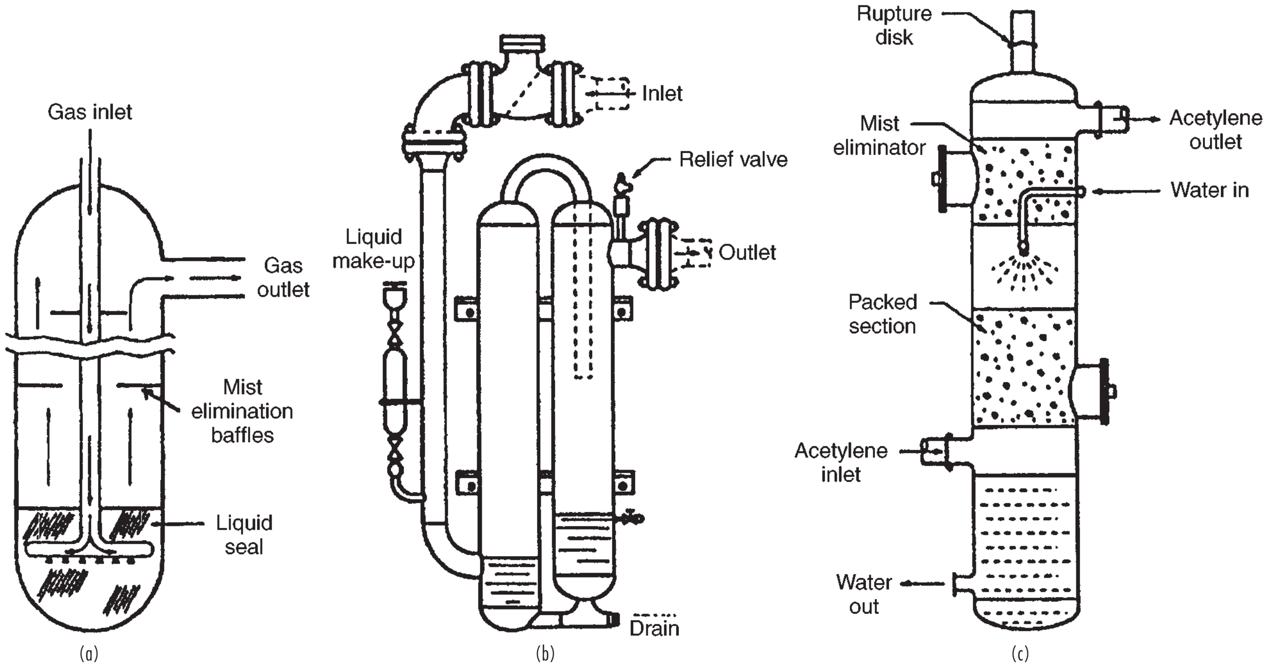


FIG. 26-27 Some special arrester designs: (*a*) liquid seal arrester; (*b*) Linde hydraulic seal arrester; (*c*) wetted packed-bed acetylene decomposition arrester. (*Howard, 1982.*)

Introduction The storage and handling of toxic materials involve risks that can be reduced to very low levels by good planning, design, and management practices. Facilities that handle toxic materials typically represent a variety of risks, ranging from small leaks, which require prompt attention, to large releases, which are extremely rare in well-managed facilities but which have the potential for widespread impact (Arthur D. Little, Inc., and LeVine, 1988, p. 5ff, by permission).

It is essential that good techniques be developed for identifying significant hazards and mitigating them where necessary. Hazards can be identified and evaluated using approaches discussed in the section on hazard and risk analysis.

Loss of containment due to mechanical failure or misoperation is a major cause of chemical process accidents. The design of storage systems should be based on minimizing the likelihood of loss of containment, with the accompanying release of hazardous materials, and on limiting the amount of the release. An effective emergency response program that can reduce the impacts of a release should be available.

Toxicity and Toxic Hazard There is a difference between toxicity and toxic hazard:

- Toxicity is the ability to cause biological injury.
- Toxicity is a property of all materials—even salt, sugar, and water.
- Toxicity is related to dose and degree of hazard associated with a material. Dose is time- and duration-dependent, in that dose is a function of exposure (concentration) times duration.

Toxic hazards may be caused by chemical means, radiation, and noise. Routes of exposure are: (1) eye contact, (2) inhalation, (3) ingestion, (4) skin contact, and (5) ears (noise). An *Industrial Hygiene Guide* (IHG) is based on exposures for an 8-h day, 40-h week, and is not to be used as a guide in the control of health hazards. It is not to be used as a fine line between safe and dangerous conditions.

A material that has a high toxicity does not necessarily present a severe toxic hazard. For example, a ton of lead arsenate spilled in a busy street is unlikely to poison members of the public just a short distance from the spill, because it is not mobile. It could be carefully recovered and removed and would present a low risk to the general public, even though it is extremely toxic. On the other hand, a ton of liquefied chlorine spilled on the same street could become about 11,000 ft^3 of pure gas. The IDLH for chlorine is 25 ppm. This is a concentration such that immediate action is required. Thus, the one ton of chlorine, if mixed uniformly with air, could create a cloud of considerable concern, having a volume of about 4.4×10^8 ft^3 or a sphere 770 ft in diameter. This could quickly spread over downwind areas and prove fatal to people near the spill site, causing toxic effects among hundreds of others in the downwind direction.

Measures of inhalation toxicity include ERPG, TLV, TLV-STEL, TLV-TWA, PEL, and IDLH.

- ERPG is defined in the section on hazard and risk analysis.
- TLV means *threshold limit value* (established by the American Conference of Government Industrial Hygienists, or ACGIH). TLV-C is the concentration in air that should not be exceeded during any part of the working exposure.
- TVL-STEL is a 15-min, time-weighted average concentration to which workers may be exposed up to four times per day with at least 60 min between successive exposures with no ill effect if the TLV-TWA is not exceeded (developed by the ACGIH).
- TLV-TWA is the time-weighted average concentration limit for a normal 8-h day and 40-h workweek, to which nearly all workers may be repeatedly exposed, day after day, without adverse effect (developed by the ACGIH).
- PEL means *permissible exposure level* (similar to TLV but developed by the National Institute for Occupational Safety and Health, or NIOSH).
- IDLH means *immediately dangerous to life and health.* This is a concentration at which immediate action is required. The exact effect on an individual depends on the individual's physical condition and susceptibility to the toxic agent involved. It is the maximum airborne contamination concentration from which one could escape within 30 min without any escape-impairing symptoms or irreversible health effects (developed by NIOSH).

Storage

Storage Facilities The Flixborough disaster (Lees, 1980) occurred on June 1, 1974, and involved a large, unconfined vapor cloud explosion (or explosions—there may have been two) and fire that killed 28 people and injured 36 at the plant and many more in the surrounding area. The entire chemical plant was demolished and 1821 houses and 167 shops were damaged.

The results of the Flixborough investigation made it clear that the large inventory of flammable material in the process plant contributed to the scale of the disaster. It was concluded that "limitations of inventory should be taken as specific design objectives in major hazard installations." It should be noted, however, that reduction of inventory may require more frequent and smaller shipments and improved management.

There may be more chances for errors in connecting and reconnecting with small shipments. Quantitative risk analysis of storage facilities has revealed solutions that may run counter to intuition (Schaller, *Plant/Operations Progress,* **9**(1), 1990). For example, reducing inventories in tanks of hazardous materials does little to reduce risk in situations where most of the exposure arises from the number and extent of valves, nozzles, and lines connecting the tank. Removing tanks from service altogether, on the other hand, helps. A large pressure vessel may offer greater safety than several small pressure vessels of the same aggregate capacity because there are fewer associated nozzles and lines. Also, a large pressure vessel is inherently more robust, or it can economically be made more robust by deliberate overdesign than can a number of small vessels of the same design pressure. On the other hand, if the larger vessel has larger connecting lines, the relative risk may be greater if release rates through the larger lines increase the risk more than the inherently greater strength of the vessel reduces it. In transporting hazardous materials, maintaining tank car integrity in a derailment is often the most important line of defense in transportation of hazardous materials.

Safer Storage Conditions The hazards associated with storage facilities can often be reduced significantly by changing storage conditions. The primary objective is to reduce the driving force available to transport the hazardous material into the atmosphere in case of a leak (Hendershot, 1988). Some methods to accomplish this follow.

Dilution Dilution of a low-boiling hazardous material reduces the hazard in two ways:

1. The vapor pressure is reduced. This has a significant effect on the rate of release of material boiling at less than ambient temperature. It may be possible to store an aqueous solution at atmospheric pressure, such as aqueous ammonium hydroxide instead of anhydrous ammonia.
2. In the event of a spill, the atmospheric concentration of the hazardous material will be reduced, resulting in a smaller hazard downwind of the spill.

The reduction of vapor pressure by diluting ammonia, monomethylamine, and hydrochloric acid with water is shown in Table 26-9.

TABLE 26-9 Vapor Pressure of Aqueous Ammonia, Hydrochloric Acid, and Monomethylamine Solutions

Ammonia at 21°C		Monomethylamine at 20°C		Hydrochloric acid at 25°C	
Concentration wt.%	Vapor pressure, atm	Concentration wt.%	Vapor pressure, atm	Concentration wt.%	Vapor pressure, atm
100 (anhydrous)	8.8	100 (anhydrous)	2.8	100 (anhydrous)	46.1
48.6	3.0	50	0.62	41	1.0
33.7	1.1	40	0.37	38	0.36
28.8	0.75			32	0.055

SOURCE: Hendershot, 1988, by permission.

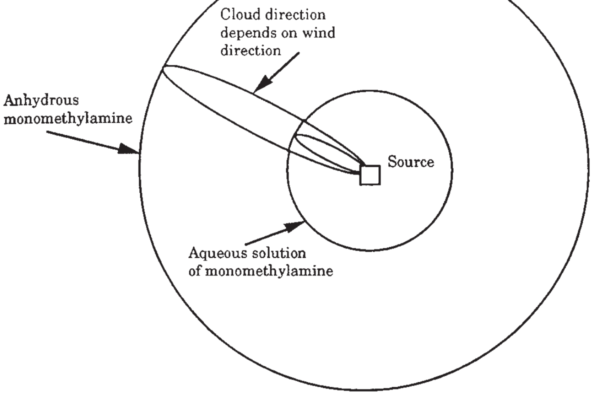


FIG. 26-28 Relative hazard zones for anhydrous and aqueous monomethylamine releases—relative distance within which there is a specified atmospheric concentration of monomethylamine and aqueous monomethylamine. (*Hendershot, 1988, by permission.*)

The relative size of hazard zones from possible loss of containment and releases to the atmosphere is much smaller for the cases in which the material is diluted, compared to the anhydrous materials. This is illustrated in Fig. 26-28 for monomethylamine.

The larger circle is the area that could be exposed to a specified atmospheric concentration of monomethylamine stored as an anhydrous liquid. The smaller circle is the area that could be exposed to a specified atmospheric concentration of monomethylamine stored as an aqueous solution. The elliptical figures represent a gas cloud caused by an east-southeast wind.

Refrigeration Loss of containment of a liquefied gas under pressure and at atmospheric temperature causes immediate flashing of a large proportion of the gas. This is followed by slower evaporation of the residue. The hazard from a gas under pressure is normally much less in terms of the amount of material stored, but the physical energy released if a confined explosion occurs at high pressure is large.

Refrigerated storage of hazardous materials that are stored at or below their atmospheric boiling points mitigates the consequences of containment loss in three ways:

1. The rate of release, in the event of loss of containment, will be reduced because of the lower vapor pressure in the event of a leak.
2. Material stored at a reduced temperature has little or no superheat and there will be little flash in case of a leak. Vaporization will be mainly determined by liquid evaporation from the surface of the spilled liquid, which depends on weather conditions.
3. The amount of material released to the atmosphere will be further reduced because liquid entrainment from the two-phase flashing jet resulting from a leak will be reduced or eliminated.

Refrigerated storage is most effective in mitigating storage facility risk if the material is refrigerated when received. Much of the benefit of refrigerated storage will be lost if the material is received at ambient temperature under its vapor pressure in a transport container. The quantity of material that could be released during unloading may be larger because unloading lines are normally sized to rapidly unload a truck or rail car and are often larger than the process feed lines. Thus, if the material is shipped at ambient temperature, the benefits of refrigeration will not be available during the operations with the highest release potential.

The economics of storage of liquefied gases are such that it is usually attractive to use pressure storage for small quantities, pressure or semirefrigerated storage for medium to large quantities, and fully refrigerated storage for very large quantities. Quantitative guidelines are available from Lees (1980, pp. 271–272).

It is generally considered that there is a greater hazard in storing large quantities of liquefied gas under pressure than at low temperatures and low pressures. The trend is toward replacing pressure storage by refrigerated low-pressure storage for large inventories. However, it is necessary to consider the risk of the entire system, including the refrigeration system, and not just the storage vessel. The consequences of failure of the refrigeration system must be considered. Each case should be carefully evaluated on its own merits. In most cases, refrigerated storage of hazardous materials is undoubtedly safer, such as in the storage of large quantities of liquefied chlorine.

Design of Liquid Storage So Leaks and Spills Do Not Accumulate Under Tanks or Equipment Around storage and process equipment, it is a good idea to design dikes that will not allow toxic and flammable materials to accumulate around the bottom of tanks or equipment in case of a spill. If liquid is spilled and ignites inside a dike where there are storage tanks or process equipment, the fire may be continuously supplied with fuel and the consequences can be severe. It is usually much better to direct possible spills and leaks to an area away from the tank or equipment and provide a fire wall to shield the equipment from most of the flames if a fire occurs. The discussion on BLEVEs later in this section shows a design for diking for directing leaks and spills to an area away from tanks and equipment.

The surface area of a spill should be minimized for materials that are highly toxic and have a significant vapor pressure at ambient conditions, such as acrylonitrile or chlorine. This will make it easier and more practical to collect vapor from a spill or to suppress vapor release with foam. This may require a deeper nondrained dike area than normal or some other design that will minimize surface area, in order to contain the required volume. It is usually not desirable to cover a diked area to restrict loss of vapor if the spill consists of a flammable or combustible material.

Minimal Use of Underground Tanks The U.S. Environmental Protection Agency's (USEPA) Office of Underground Storage Tanks defines underground tanks as those with 10 percent of more of their volume, including piping, underground. An aboveground tank that does not have more than 10 percent of its volume (including piping) underground is excluded from the underground tank regulations. Note, however, that a 5000-gal tank sitting wholly atop the ground but having 1400 ft of 3-in buried pipe or 350 ft of 6-in buried pipe is considered an underground storage tank.

At one time, burying tanks was recommended because it minimized the need for a fire protection system, dikes, and distance separation. At many companies this is no longer considered good practice. Mounding, or burying tanks above grade, has most of the same problems as burying tanks below ground and is usually not recommended.

Problems with buried tanks include:

- Difficulty in monitoring interior and exterior corrosion (shell thickness)
- Difficulty in detecting leaks
- Difficulty of repairing a tank if the surrounding earth is saturated with chemicals from a leak
- Potential contamination of groundwater due to leakage

Governmental regulations concerning buried tanks are becoming stricter. This is because of the large number of leaking tanks that have been identified as causing adverse environmental and human health problems.

Consequences of Leaking Underground Tanks The following is a real possibility (Russell and Hart, 1987). A site where an underground tank has been used is found to have leaked. If the leak is not cleaned up to "background" levels by the time an environmental regulatory agency is involved, the agency may decide that a portion of the plant must be designated as a waste disposal site. The plant could then be required to provide a waste site closure plan, hold public hearings, place deed restrictions on the plant property, and, finally, provide a bond that would cover the cost of closing the site and also analyzing and sampling groundwater for up to 30 years.

Product leaking from an underground storage tank will migrate downward until it encounters the water table, where it will then flow with the groundwater, leaving a long trail of contaminated soil. Above the water table, some product will be absorbed on the soil particles and in the pore space between the soil particles. If the soil is later saturated by water, product stored in the pore spaces may be released, causing a reappearance of the free product and movement of the material into previously unaffected soil.

The scope of the problem was revealed by the USEPA in 1983 when it reported that, in the United States, 11 million gallons of gasoline seep into the soil each year. Just one gallon of gasoline can make one million gallons of water unsafe to drink; one ounce would pollute an Olympic-size swimming pool full of drinking water. Most of the contaminated sites the USEPA has documented involve corroded single-wall steel tanks and piping that have been in the ground for at least 16 years (Semonelli, "Secondary Containment of Underground Storage Tanks," *Chem. Eng. Prog.*, June 1990). A number of states have enacted laws setting standards for underground storage tanks. The USEPA has issued regulations requiring notification to the appropriate regulatory agency about age, condition, and size for underground storage tanks containing commercial chemical products.

Secondary Containment for Underground Storage Acceptable secondary containment systems for underground storage are described as barriers either integral to the tank system design (such as double-walled tanks or double-walled pipes) or located within the underground storage tank system that present a barrier between all parts of the underground storage tank system and the environment. Double-walled tanks and piping should be considered for aboveground tanks and piping containing highly toxic liquids.

Concrete and fiberglass vaults are often used, although they can be subject to environmentally induced cracks. Soil and clay liners are not allowed. Flexible liner systems have been developed that may be a cost-effective and environmentally sound alternative. State-of-the-art liner technology has overcome many of the previous problems with seams, low mechanical strength, and chemical resistance.

Piping Systems for Underground Service An important consideration is the USEPA's concern over piping systems. For all underground storage tank systems, performance standards consistent with those for tanks were set for pipes and pipe systems. There is evidence that 84 percent of underground storage tank system test failures are due to loose tank fittings or faulty piping. Piping releases occur twice as often as tank releases. In particular, loose joints tend to occur. For hazardous substance underground storage tank systems, there are two options: trench liners and double-walled pipes. Double-walled pipes are difficult to assemble and are subject to failure caused by service conditions, such as frost heaves or pressure from above. Flexible trench liners (discussed previously) are becoming a popular solution to secondary containment of piping systems.

Detecting Leaks Small leaks are difficult to detect. The USEPA and American Petroleum Institute standard for nonleaking underground tanks is 0.05 gal/h (3.15 cm^3/min), above which a tank is considered to be leaking. Leak detection measurements can be influenced by many factors, making it difficult to detect small leaks.

Corrosion Problems Tanks subject to internal corrosion are not good choices for underground service because of the necessity of monitoring wall thickness. Underground tanks and piping of carbon steel should be considered for corrosion protection measures such as external tarlike coatings and magnesium anodes. Joints in underground piping should be minimized by welding. Pipes may use a combination of wrapping and sprayed-on coatings. When flanges are necessary, such as with valves, external coatings should be used.

Summary of Use of Underground Tanks Because of more stringent regulatory requirements, potential future liabilities, and the cost of building and operating underground storage tank systems, it may be inherently safer to use aboveground storage with suitable spacing, diking, and fire protection facilities. With modern technology, if it is necessary, it is possible to design underground storage systems with a high degree of integrity and which will make leaks to the environment highly unlikely, but the cost may be high.

Design of Tanks, Piping, and Pumps Six basic tank designs are used for the storage of organic liquids: (1) fixed roof, (2) external floating roof, (3) internal floating roof, (4) variable vapor space, (5) low-pressure tanks, and (6) high-pressure tanks. The first four tank designs listed are not generally considered suitable for highly toxic hazardous materials.

Low-Pressure Tanks (below 15 psig) Low-pressure storage tanks for highly hazardous toxic materials should meet, as a minimum, the American Petroleum Institute (API) 620 Standard, "Recommended Rules for the Design and Construction of Large Welded, Low-Pressure Storage Tanks" (*API Standards*). This standard covers tanks designed for all pressures under 15 psig. There are no specific requirements in API 620 for highly hazardous toxic materials.

API 650, "Welded Steel Tanks for Oil Storage" (*API Standards*) has limited applicability to storage of highly hazardous toxic materials because it prohibits refrigerated service and limits pressures to 2.5 psig and only if designed for certain conditions. Most API 650 tanks have a working pressure approaching atmospheric pressure and hence their pressure-relieving devices must vent directly to the atmosphere. Its safety factors and welding controls are less stringent than required by API 620. Another reference for the design of low-pressure storage tanks may be found in ANSI/API-620-1986.

Horizontal and vertical cylindrical tanks are used to store highly toxic liquids at atmospheric pressure. Horizontal, vertical, and spherical tanks are used for refrigerated liquefied gases that are stored at atmospheric pressure. The design pressure of tanks for atmospheric and low-pressure storage at ambient temperature should not be less than 100 percent of the vapor pressure of the material at the maximum design temperature. The maximum design metal temperature to be used takes into consideration the maximum temperature of material entering the tank and the maximum ambient temperature, including solar radiation effects.

Since discharges of vapors from highly hazardous toxic materials cannot simply be released to the atmosphere, the use of a weak seam roof is not normally acceptable. It is best that tanks be designed and stamped for 15 psig to provide maximum safety, and pressure relief systems must be provided to vent to equipment that can collect, contain, and treat the effluent.

The minimum design temperature should be the lowest temperature to which the tank will be subjected, taking into consideration the minimum temperature of material entering the tank, the minimum temperature to which the material may be autorefrigerated by rapid evaporation of low-boiling liquids or mechanically refrigerated, and the minimum ambient temperature of the area where the tank is located. API 620 provides for installations in areas where the lowest recorded one-day mean temperature is −50°F.

While either rupture disks or relief valves are allowed on storage tanks by Code, rupture disks by themselves should not be used on tanks for the storage of highly hazardous toxic materials since they do not close after opening and may lead to continuing release of toxic material to the atmosphere.

The API 620 Code requires a combined pneumatic hydrotest at 125 percent of design tank loading. In tanks designed for low-density liquid, the upper portion is not fully tested. For highly hazardous toxic materials, consideration should be given for hydrotesting at the maximum specified design liquid level. It may be required that the lower shell thickness be increased to withstand a full head of water and that the foundation be designed such that it can support a tank full of water or the density of the liquid if it is greater than water. Testing in this manner not only tests the containment capability of the tank, but it also provides an overload test for the tank and the foundation similar to the overload test for pressure vessels. API 620 also requires radiography.

Proper preparation of the subgrade and grade is extremely important for tanks that are to rest directly on grade. Precautions should be taken to prevent ground freezing under refrigerated tanks, as this can cause the ground to heave and damage the foundation or the tank. Designing for free air circulation under the tank is a method for passive protection from ground freezing.

Steels lose their ductility at low temperatures and can become subject to brittle failure. There are specific requirements for metals to be used for refrigerated storage tanks in API 620, Appendices Q and R.

Corrosive chemicals and external exposure can cause tank failure. Materials of construction should be chosen so that they are compatible with the chemicals and exposure involved. Welding reduces the corrosion resistance of many alloys, leading to localized attack at the heat-affected zones. This may be prevented by the use of the proper alloys and weld materials, in some cases combined with annealing heat treatment.

External corrosion can occur under insulation, especially if the weather barrier is not maintained or if the tank is operating at conditions at which condensation is likely. This form of attack is hidden and may be unnoticed for a long time. Inspection holes and plugs should be installed in the insulation to monitor possible corrosion under the insulation.

High-Pressure Tanks (above 15 psig) The design of vessels above 15 psig falls within the scope of the American Society of Mechanical Engineers (ASME) Boiler and Pressure Vessel Code, Section VIII "Pressure Vessels, Division I" and should be designated as lethal service if required. *Lethal service* means containing substances which are "poisonous gases or liquids of such a nature that a very small amount of the gas or vapor of the liquid mixed or unmixed with air is dangerous to life when inhaled. This class includes substances which are stored under pressure or may generate a pressure if stored in a closed vessel." This is similar to, but not exactly like, the same definition as that for "Category M" fluid service of the ASME Pressure Piping Code (see below). Pressure vessels for the storage of highly hazardous toxic materials should be designed in accordance with requirements of the ASME code even if they could be exempted because of high pressure or size. The code requires that the corrosion allowance be adequate to compensate for the more or less uniform corrosion expected to take place during the life of the vessel and not weaken the vessel below design strength.

Venting and Drainage In the installation of a storage tank, good engineering should go into the design of a drain and a vent. Low-pressure storage tanks are particularly susceptible to damage if good venting practices are not followed. A vent that does not function properly at all times may cause damage to the tank from pressure that is too high or too low. Vapors should go to a collection system, if necessary, to contain toxic and hazardous vents.

Piping Piping falls within Chapter VIII of the ASME Pressure Piping Code, "Piping for Category M Fluid Service." Category M Fluid Service is defined as "fluid service in which the potential for personnel exposure is judged to be significant and in which a single exposure to a small quantity of a toxic fluid, caused by leakage, can produce serious irreversible harm to persons on breathing or bodily contact, even when prompt restorative measures are taken."

Piping systems should meet the requirements for both Category M Fluid Service and for "severe cyclic conditions." Piping systems should be subjected to a flexibility analysis and, if found to be too rigid, flexibility should be added. Severe vibration pulsations should be eliminated. Expansion bellows, flexible connections, and glass equipment should be avoided. Pipelines should be designed with the minimum number of joints, fittings, and valves. Joints should be flanged or butt-welded. Threaded joints should not be used.

Instrumentation (Arthur D. Little, Inc., and Levine, 1986.) Instrument systems are an essential part of the safe design and operation of systems for storing and handling highly toxic hazardous materials. They are key elements of systems to eliminate the threat of conditions that could result in loss of containment. They are also used for early detection of releases so that mitigating action can be taken before these releases result in serious effects on people in the plant or in the public sector, or on the environment.

The basic approach is to direct the system to the safest operating level relative to people or the environment when any emergency condition is detected, including power loss. An important concept of process control safety is to have adequate redundancy to reduce unwanted shutdowns and maintain an adequate level of certainty that a safe state will result if a real emergency does occur. As far as possible, instruments should be of the fail-safe type.

Every effort should be made to eliminate direct (Bourdon-type) pressure gauges. Diaphragm pressure gauges constructed of appropriate corrosion-resistant materials are preferred. Flow limiters should be used to limit flow in case of loss of integrity.

An accurate indication of level is critical to the avoidance of overflow and other serious conditions in storage vessels. Level control is important to avoid overfilling to prevent a liquid release. A very low level can result in loss of pump suction and possible pump failure. Capacitance level sensors are often used because they require little maintenance and are highly reliable; since they give only point measurements, they are best used as backup for analogue devices such as differential pressure level gauges or strain gauges. Strain gauges (*load cells*) should be considered, as they are capable of high accuracy and do not require penetration of the containment vessel.

Flow measurements using nonintrusive or low mechanical action principles are desired, such as magnetic, vortex-shedding, or Coriolis-type flowmeters. Orifice plates are easy to use and reliable but have a limited range and may not be suitable for streams which are not totally clean. Rotameters with glass tubes should not be used.

Temperature measurements usually require intrusion into the fluid. Where thermowells are exposed to hazardous materials, they should comply with the same material requirements for vessels and pipes to reduce failure from erosion and corrosion. In storage tanks, tank temperature is often monitored but usually not controlled. Temperature indication is desirable to indicate that the tank contents are approaching a hazardous region and to indicate thermal stratification. For some materials, such as acrylic acid, temperature control is necessary during storage to prevent freezing if it gets too cold and prevent chemical reaction if it gets too warm.

Alarms should act as early warning devices to anticipate a potentially hazardous situation. Alarms that are essential to safety should be identified and classified separately from process alarms. Redundancy may be required.

Pumps and Gaskets Fugitive emissions often occur as a result of leakage of process materials through leak paths in rotating seals and susceptible gasketed joints such as are found in pipe flanges. When properly maintained, fugitive emissions from most conventional joints and sealing systems used in industry can be kept to a minimum. For volatile organic compounds (VOCs) this is usually significantly less than 500 ppm as measured at the leak path by a portable VOC analyzer specified in USEPA reference method 21 (40 CFR 60, Appendix A, Method 21). However, for some sealing systems such as packing glands on pump shafts in some services, the necessary maintenance frequency and potential risks of noncompliance have caused some companies to eliminate them from services where fugitive emissions are a concern and use tighter sealing systems such as mechanical seals instead. In services where entrained solids or fouling are not present to a significant extent and additional cost is justified, magnetic drive and canned-motor pumps, which have become more reliable and available in a wide variety of configurations and materials, are being used to virtually eliminate fugitive emissions from pumps. In services where fugitive emissions are a concern, valves such as quarter turn, diaphragm seal, or bellows seal valves, which are less susceptible to leakage, are sometimes being used in place of gate or globe valves with packed stem seals. However, under many service conditions, high-cost equipment options are not necessary to comply with the provisions of fugitive emission regulations. Properly maintained packing glands or single mechanical seals on valves and pumps can often meet all emissions requirements. An informed choice should be made when specifying new valves and pumps, considering factors such as the type of service, accessibility for maintenance, cost, and the degree of emission reductions which may be achieved.

The most common maintenance problem with centrifugal pumps is with the seals. Mechanical seal problems account for most of the pump repairs in a chemical plant, with bearing failures a distant second. The absence of an external motor (on canned pumps) and a seal is appealing to those experienced with mechanical seal pumps.

Sealless pumps are very popular and are widely used in the chemical industry. Sealless pumps are manufactured in two basic types: canned-motor and magnetic-drive. Magnetic-drive pumps have thicker "cans," which hold in the process fluid, and the clearances between the internal rotor and can are greater compared to canned-motor pumps. This permits more bearing wear before the rotor starts wearing through the can. Many magnetic-drive pump designs now have incorporated a safety clearance, which uses a rub ring or a wear ring to support the rotating member in the event of excessive bearing wear or failure. This design feature prevents the rotating member (outer magnet holder or internal rotating shaft assembly) from accidentally rupturing the can, as well as providing a temporary bearing surface until the problem bearings can be replaced. Because most magnetic-drive pumps use permanent magnets for both the internal and external rotors, there is less heat to the pumped fluid than with canned-motor pumps. Some canned-motor pumps have fully pressure-rated outer shells, which enclose the canned motor; others don't. With magnetic-drive pumps, containment of leakage through the can to the outer shell can be a problem. Even though the shell may be thick and capable of holding high pressures, there is often an elastomeric lip seal on the outer magnetic rotor shaft with little pressure containment capability.

Canned-motor pumps typically have a clearance between the rotor and the containment shell or can, which separates the fluid from the stator, of only 0.008 to 0.010 in (0.20 to 0.25 mm). The can has to be thin to allow magnetic flux to flow to the rotor. It is typically 0.010 to 0.015 in (0.25 to 0.38 mm) thick and made of Hastelloy. The rotor can wear through the can very rapidly if the rotor bearing wears enough to cause the rotor to move slightly and begin to rub against the can. The can may rupture, causing uncontrollable loss of the fluid being pumped.

It should not be assumed that just because there is no seal, sealless pumps are always safer than pumps with seals, even with the advanced technology now available in sealless pumps. Use sealless pumps with considerable caution when handling hazardous or flammable liquids.

Sealless pumps rely on the process fluid to lubricate the bearings. If the wear rate of the bearings in the fluid being handled is not known, the bearings can wear unexpectedly, causing rupture of the can.

Running a sealless pump dry can cause complete failure. If there is cavitation in the pump, hydraulic balancing in the pump no longer functions and excessive wear can occur, leading to failure of the can. *The most common problem with sealless pumps is bearing failure, which occurs either by flashing the fluid in the magnet area because of a drop in flow below minimum flow or by flashing in the impeller eye as it leaves the magnet area.* It is estimated that nine out of ten conventional canned-motor pump failures are the result of dry running. Canned pumps are available which, their manufacturer claims, can be operated dry for as long as 48 h.

It is especially important to avoid deadheading a sealless pump. Deadheaded sealless pumps can cause overheating. The bearings may be damaged and the pump may be overpressured. The pump and piping systems should be designed to avoid dead spots when pumping monomers. Monomers in dead spots may polymerize and plug the pump. There are minimum flow requirements for sealless pumps. It is recommended that a recirculation system be used to provide internal pump flow whenever the pump operates. Inlet line filters are recommended, but care must be taken not to cause excessive pressure drop on the suction side. Typical inlet filters use sieve openings of 0.0059 in (0.149 mm).

For many plants handling monomers and other hazardous materials, sealless pumps are the first choice. They can practically eliminate the pump problems that can occur due to seal leaks, which can include product loss, flammability, waste disposal, and exposure of personnel to hazardous vapors.

A number of liquids require special attention when applying canned-motor and magnetic-drive pumps. For example, a low-boiling liquid may flash and vapor-bind the pump. Solids in the liquid can also be bad for a sealless pump. Low-viscosity (in the range of 1 to 5 cP [1×10^{-3} to 5×10^{-3} Ns/m^2]) fluids are normally poor lubricators and one should be concerned about selecting the right bearings. For viscosities less than 1 cP, it is even more important to choose the right bearing material.

The Dow Chemical Company recommends canned-motor pumps or magnetic-drive pumps for phosgene service. Phosgene is an example of an extremely hazardous material. These pumps should have a secondary containment such that failure of the can does not create a phosgene release. The secondary containment should meet pipe specifications for pressure or relieve to the scrubber system in the plant. These pumps must have automated block valves on the suction and discharge. Operation of these valves should be managed such that the thermal expansion does not damage the pump.

A mistreated sealless pump can rupture with potentially serious results. The can can fail if valves on both sides of the pump are closed and the fluid in the pump expands either due to heating up from a cold condition or if the pump is started up. If the pump is run dry, the bearings can be ruined. The pump can heat up and be damaged if there is insufficient flow to take away heat from the windings. Sealless pumps, especially canned-motor pumps, produce a significant amount of heat, since nearly all the electrical energy lost in the system is absorbed by the fluid being pumped. *If this heat cannot be properly dissipated, the fluid will heat up with possibly severe consequences.* Considerable care must be used when installing a sealless pump to be sure that misoperations cannot occur.

The instrumentation recommended for sealless pumps may seem somewhat excessive. However, sealless pumps are expensive and they can be made to last for a long time, compared to conventional centrifugal pumps where seals may need to be changed frequently. Most failures of sealless pumps are caused by running them dry and damaging the bearings. Close monitoring of temperature is necessary in sealless pumps. Three temperature sensors (resistance temperature devices, or RTDs) are recommended: (1) in the internal fluid circulation loop, (2) in the magnet, or shroud, area, and (3) in the pump case area.

It is very important that sealless pumps be flooded with liquid before starting, to avoid damage to bearings from imbalance or overheating. Entrained gases in the suction can cause immediate imbalance problems and lead to internal bearing damage. Some type of liquid sensor is recommended. Sealless pumps must not be operated deadheaded (pump liquid full with inlet and/or outlet valves closed).

Properly installed and maintained, sealless pumps, both canned and magnetic-drive, offer an economical and safe way to minimize hazards and leaks of hazardous liquids.

Air Quality Regulatory Issues (Englund and Holden, 1995.) Environmental issues and regulations have developed from matters of secondary interest on the part of business to broad-ranging measures which affect the fundamental ways in which companies carry out the details of their business. The fast pace of development of environmental regulations and their changing, sometimes inconsistent requirements have made it difficult and expensive for companies to keep their facilities current. Many companies have adopted programs to keep them aware and abreast of continuing regulatory developments.

Although companies often fall under specific regulations pertaining only to their particular industry segments, a common thread running through a large number of manufacturing and commercial operations is the need to store materials considered to be toxic or hazardous. As a result, environmental regulations affecting the storage of toxic materials, either directly or indirectly, have had some of the most significant impacts on companies throughout the world in terms of both cost and operations. The Comprehensive Environmental Response, Compensation, and Liability Act of 1980, commonly known as Superfund, with its requirements to immediately report releases of reportable quantities of listed materials, has made the prevention of even minor spills, leaks, and releases from storage of toxic materials an important concern for owners. Also, storage and disposal of hazardous wastes are strictly and extensively regulated under the Resource Conservation and Recovery Act (RCRA) as amended in 1984.

In addition, restrictions on industrial air emissions under the Clean Air Act (CAA) as amended in 1977, the Clean Air Act Amendments (CAAA) of 1990, and other state and local statutes and regulations have universal impact on the storage of toxic materials, with direct and significant effects on the design and operation of toxic material storage facilities. Whereas the primary factors which once determined how air emissions from storage tanks were handled were fire protection and loss prevention, in recent years environmental protection concerns nearly always determine the extent and nature of the air emission controls required to be installed.

Permitting and Control Technology Requirements (*Air Quality Handbook,* 1988.) Almost any process equipment or facility that emits air pollutants will need to obtain an air emission permit from the appropriate local, state, or federal governmental authority before construction or modification begins. The application for the air emission permit generally must describe the pollutant-generating process to be installed or modified, along with any emission control equipment or techniques, state the emission rates of all pollutants emitted, support the statement of emissions with a technical analysis or study, and describe the way that the process and control equipment will be operated to comply with regulatory requirements.

In reviewing the permit application, the local, state, or federal permitting authority will normally evaluate the application for completeness, check the accuracy of calculations, analyze the stated emissions for compliance with applicable regulations and environmental acceptability, and review the previous compliance history of the source and source owner. The source must operate within the bounds of the permit conditions in order to be considered in compliance with the permit. The source must still comply with all other air pollution laws, regulations, and ordinances, even if the permit conditions do not directly address them.

The process of evaluating air emission permit applications for large sources which are subject to federal permitting requirements is called New Source Review (NSR) and can be quite complicated, taking from six months to four years to complete. An NSR application would be required for a new source which could emit 100 tons per year or more of any criteria pollutant, after accounting for any air pollution control equipment.

The specific requirements to complete the NSR process will vary depending on the source location and characteristics, the federal and state regulations which apply, the compliance status of the facility if it is existing, and the nature of other sources in the area. Atmospheric dispersion modeling is often necessary to determine the maximum offsite ambient air concentrations of the various pollutants that will be emitted by the proposed new source or modification. All of the information in a permit application will normally be open to public scrutiny, including the details of the engineering study, except for specific process details that can be shown by the applicant to be trade secrets or proprietary business information. Nothing pertaining to the quality or quantity of air pollutant emissions can be claimed as proprietary.

The permitting requirements and procedures for a proposed NSR source are quite different, if the source is to be located in a nonattainment area for any of its major emitted pollutants, than if it is to be located in an attainment area. This usually increases the complexity of the permit application for such a source.

Federal Permitting in Nonattainment Areas If the source subject to NSR is to be located in an area which is nonattainment for any of the major pollutants that the source will emit, it will need to follow the federally approved state permitting requirements for nonattainment areas of that pollutant. In most such cases, offsetting emission reductions at the same or other source locations in the area so as to be at least equivalent to the allowed emission, increases at the proposed source must be provided.

HAZARDOUS MATERIALS AND CONDITIONS

REACTIVE CHEMICALS

GENERAL REFERENCES: Bartknecht, *Dust Explosions,* Springer-Verlag, Berlin, 1989. Bartknecht, *Explosions Course Prevention, Protection,* Springer-Verlag, Berlin, 1981. Beever, “Hazards in Drying Thermally Unstable Powders,” *Inst. Chem. Engr., Hazards X,* Symp. Ser. 115, 1989. Beever, “Scaling Rules for Prediction of Thermal Runaway,” *Intl. Symp. on Runaway Reactions,* CCPS-AIChE. Cambridge, Mass., 1989. Beever and Thorne, “Isothermal Methods for Assessing Combustible Powders—Theoretical and Experimental Approach,” *Inst. Chem. Eng.,* Symp. Ser. 68, 1981. Bowes, “A General Approach to the Prediction and Control of Potential Runaway Reaction,” *Inst. Chem. Eng.,* Symp. Ser. 68, 1981. Bowes, *Self-heating: Evaluating and Controlling the Hazards,* Elsevier, 1984. *Bretherick's Reactive Chemical Hazards Database,* Version 2.0, Butterworth-Heinemann, Oxford, 1995. Brogli, Giger, Randegger, and Regenass, “Assessment of Reaction Hazards by Means of a Bench Scale Calorimeter,” *Inst. Chem. Eng.,* Symp. Ser. 68, 1981. Brogli, Gygax, and Myer, “Differential Scanning Calorimetry—A Powerful Screening Method for the Estimation of the Hazards Inherent in Industrial Chemical Reactions,” *Therm. Analy.,* 6th Symp., vol. 1, 549, 1980. Coates, “The ARC™ in Chemical Hazard Evaluation,” *Chem. Ind.* **6:** 212, 1984. Coates, “The ARC™ in Chemical Hazard Evaluation,” *Thermochim. Acta.* **85:** 369–372, 1984. Fenlon, “Calorimetric Methods Used in the Assessment of Thermally Unstable or Reactive Chemicals,” *International Symposium for the Prevention of Major Chemical Accidents,* AIChE, 1987. Frank-Kamenetskii, *Diffusion and Heat Transfer in Chemical Kinetics,* Plenum Press, 1969. Grewer, “Direct Assessment and Scaling of Runaway Reaction and Decomposition Behavior Using Oven and DEWAR Tests,” *Inst. Chem. Eng.,* Symp. Ser., 68, 1981. Grewer, “Use of DEWAR Calorimetry,” *Proc. Runaway Chem. Reac. Haz. Symp.,* IBC, Amsterdam, November 1986. Halk, “SEDEX Versatile Instrument for Investigating Thermal Stability,” *I. Chem. Eng.,* Symp. Ser. 68, 1981. Hub, “Adiabatic Calorimetry and SIKAREX Technique,” *Inst. Chem. Eng.,* Symp. Ser. 68, 1981. Hub, “Experiences with the TSC 500 and RADEX Calorimeter,” *Proc. Runaway Chem. Reac Haz Symp.,* IBC, Amsterdam, November 1986. Hub, “Heat Balance Calorimetry and Automation of Testing Procedures,” *Proc. Runaway Chem. Reac. Haz. Symp.,* IBC, Amsterdam, November 1986. *International Conference/Workshop on Modeling and Mitigating the Consequences of Accidental Releases of Hazardous Materials,* CCPS-AIChE, 1991. *International Conference on Hazard Identification and Risk Analysis, Human Factors and Human Reliability in Process Safety,* CCPS-AIChE, 1992. Kohlbrand, “Reactive Chemical Screening for Pilot Plant Safety,” *Chem. Eng. Prog.* **81**(4): 52, 1985. Kohlbrand, “The Relationship Between Theory and Testing in the Evaluation of Reactive Chemical Hazards,” *International Symposium for the Prevention of Major Chemical Accidents,* AIChE, 1987. Manufacturing Chemists Association, *Selected Case Histories,* Washington. D.C., 1951–1973. NFPA 491M, *Hazardous Chemical Reactions,* National Fire Protection Association, Quincy, Mass., 1991. Stull, “Fundamentals of Fire and Explosion,” AIChE, 1976. Stull, “Linking Thermodynamics and Kinetics to Predict Real Chemical Hazards,” *Loss Prevention,* AIChE, vol. 7, p. 67, 1976. Thomas, “Self Heating and Thermal Ignition—A Guide to Its Theory and Application,” ASTM STP 502, ASTM, pp. 56–82, 1972. Townsend, “Accelerating Rate Calorimetry,” *Inst. Chem. Eng.,* Symp. Ser. 68, 1981. Townsend and Kohlbrand, “Use of ARC™ to Study Thermally Unstable Chemicals and Runaway Reactions,” *Proc. Runaway Chem. Reac. Haz. Symp.,* IBC, Amsterdam, November 1986. Townsend and Tou, “Thermal Hazard Evaluation by an Accelerating Rate Calorimeter,” *Thermochem. Acta.* **73:** 1–30 and references therein, 1980. Urben, Peter, ed. (Courtaulds), *Bretherick's Handbook of Reactive Chemical Hazards,* 5th ed., Butterworth-Heinemann, Oxford, 1994.

Understanding the Reactive Chemicals and Reactive Chemicals Systems Involved The main business of most chemical companies is to manufacture products through the control of reactive chemicals. The reactivity that makes chemicals useful can also make them hazardous. Therefore, it is essential that people who design or operate chemical processes understand the nature of the reactive chemicals involved.

Usually reactions are carried out without mishaps, but sometimes chemical reactions get out of control because of problems such as using the wrong raw material, using raw materials containing trace impurities, changed operating conditions, unanticipated time delays, equipment failure, or wrong materials of construction.

Such mishaps can be worse if the chemistry is not fully understood. A chemical plant can be *inherently safer* if knowledge of the chemistry of the process and the reactive chemicals systems involved is used in its design.

Reactive Hazard Review Reactive hazards should be evaluated using reviews on all new processes and on all existing processes on a periodic basis. There is no substitute for experience, good judgment, and good data in evaluating potential hazards. Reviews should include:

1. Review of process chemistry, including reactions, side reactions, heat of reaction, potential pressure buildup, and characteristics of intermediate streams
2. Review of reactive chemicals test data for evidence of flammability characteristics, exotherms, shock sensitivity, and other evidence of instability
3. Review of planned operation of process, especially the possibility of upsets, modes of failure, unexpected delays, redundancy of equipment and instrumentation, critical instruments and controls, and worst-credible-case scenarios

Worst-Case Thinking At every point in the operation, the process designer should conceive of the *worst* possible combination of circumstances that could *realistically* exist, such as loss of cooling water, power failure, wrong combination or amount of reactants, wrong valve position, plugged lines, instrument failure, loss of compressed air, air leakage, loss of agitation, deadheaded pumps, and raw-material impurities.

An engineering evaluation should then be made of the worst-case consequences, with the goal that the plant will be safe even if the worst case occurs. A HAZOP study could be used to help accomplish worst-case thinking. When the process designers know what the worst-case conditions are, they should:

1. Try to avoid worst-case conditions.
2. Be sure adequate redundancy exists.
3. Identify and implement lines of defense.
    - *a.* Preventive measures
    - *b.* Corrective measures

Sometimes, as a last resort, it may be desirable to use a high degree of process containment or, possibly, abandon the process if the hazard is unacceptable.

It is important to note that the worst case should be something that is realistic, not something that is conceivable but extremely unlikely. The Dow Chemical Company has adopted the following philosophy for design scenarios in terms of independent causative effects:

1. All single events that can actually and reasonably occur are credible scenarios.
2. Scenarios that require the coincident occurrence of two or more totally independent events are not credible design scenarios.
3. Scenarios that require the occurrence of more than two events in sequence are not credible.
4. A failure that occurs while an independent device is awaiting repair represents but one failure during the time frame of the initiation of the emergency and is therefore credible. The lack of availability of the unrepaired device is a preexisting condition.

Reactive Chemicals Testing Much reactive chemical information involves thermal stability and the determination of (1) the temperature at which an exothermic reaction starts, (2) the rate of reaction as a function of temperature, and (3) heat generated per unit mass of material.

The evaluation of thermal stability requires the determination of the temperature at which an exothermic reaction occurs, the rate of such a reaction as a function of temperature, and the heat generated per unit mass of material by the reaction. In many cases, data on the increase of pressure during a reaction are also required, especially for vent sizing. The term *onset temperature* T_{onset} is used in two contexts:

1. In a testing context, it refers to the first detection of exothermic activity on the thermogram. The differential scanning calorimeter (DSC) has a scan rate of 10°C/min, whereas the accelerating rate calorimeter (ARC)[*] has a sensitivity of 0.02°C/min. Consequently, the temperature at which thermal activity is detected by the DSC can be as much as 50°C different from ARC data.
2. The second context is the process reactor. There is a potential for a runaway if the net heat gain of the system exceeds its total heat loss capability. A self-heating rate of 3°C/day is not unusual for a monomer storage tank in the early stages of a runaway. This corresponds to 0.00208°C/min, 10 percent of the ARC's detection limit. ARC data for the stored chemical would not show an exotherm until the self-heating rate was 0.02°C/min. Therefore, onset temperature information from ARC testing must be used with considerable caution.

Sources of Reactive Chemicals Data

Calculations Potential energy that can be released by a chemical system can often be predicted by thermodynamic calculations. If there is little energy, the reaction still may be hazardous if gaseous products are produced. Kinetic data is usually not available in this way. Thermodynamic calculations should be backed up by actual tests.

Differential Scanning Calorimetry (DSC) Sample and inert reference materials are heated in such a way that the temperatures are always equal. If an exothermic reaction occurs in the sample, the sample heater requires less energy than the reference heater to maintain equal temperatures. If an endothermic reaction occurs, the sample heater requires more energy input than the reference heater.

Onset-of-reaction temperatures reported by the DSC are higher than the true onset temperatures, so the test is mainly a screening test.

Differential Thermal Analysis (DTA) A sample and inert reference material are heated at a controlled rate in a single heating block. If an exothermic reaction occurs, the sample temperature will rise faster than the reference temperature. If the sample undergoes an endothermic reaction or a phase change, its temperature will lag behind the reference temperature.

This test is basically qualitative and can be used for identifying exothermic reactions. Like the DSC, it is also a screening test. Reported temperatures are not reliable enough to be able to make quantitative conclusions. If an exothermic reaction is observed, it is advisable to conduct tests in the ARC.

Mixing Cell Calorimetry (MCC) The MCC provides information regarding the instantaneous temperature rise resulting from the mixing of two compounds. Together, DSC and MCC provide a reliable overview of the thermal events that may occur in the process.

Accelerating Rate Calorimeter (ARC) The ARC can provide extremely useful and valuable data. This equipment determines the self-heating rate of a chemical under near-adiabatic conditions. It usually gives a conservative estimate of the conditions for and consequences of a runaway reaction. Pressure and rate data from the ARC may sometimes be used for pressure vessel emergency relief design. Activation energy, heat of reaction, and approximate reaction order can usually be determined. For multiphase reactions, agitation can be provided.

Nonstirred ARC runs may give answers that do not adequately duplicate plant results when there are reactants that may settle out or that require mixing for the reaction to be carried out (DeHaven and Dietsche, The Dow Chemical Company, Pittsburgh, Calif., "Catalyst Explosion: A Case History," *Plant Operations Progress*, April 1990).

An example of data from an ARC run is shown in Fig. 26-29.

Vent Sizing Package (VSP) The VSP is an extension of ARC technology. The VSP is a bench-scale apparatus for characterizing runaway chemical reactions. It makes possible the sizing of pressure relief systems with less engineering expertise than is required with the ARC or other methods.

Reactive System Screening Tool (RSST) The RSST is a calorimeter that quickly and safely determines reactive chemical hazards. It approaches the ease of use of the DSC with the accuracy of the VSP. The apparatus measures sample temperature and pressure within a sample containment vessel. The RSST determines the potential for runaway reactions and measures the rate of temperature and pressure rise (for gassy reactions) to allow determinations of the energy and gas release rates. This information can be combined with simplified methods to assess reactor safety system relief vent requirements. It is especially useful when there is a need to screen a large number of different chemicals and processes.

Shock Sensitivity Shock-sensitive materials react exothermically when subjected to a pressure pulse. Materials that do not show an exotherm on a DSC or DTA are presumed not to be shock sensitive. Testing methods include:

- *Drop weight test.* A weight is dropped on a sample in a metal cup. The test measures the susceptibility of a chemical to decompose explosively when subjected to impact. Weight and height can be varied to give semiquantitative results for impact energy. This test should be applied to any materials known or suspected to contain unstable atomic groupings.
- *Confinement cap test.* Detonatability of a material is determined using a blasting cap.
- *Adiabatic compression test.* High pressure is applied rapidly to a liquid in a U-shaped metal tube. Bubbles of hot compressed gas are

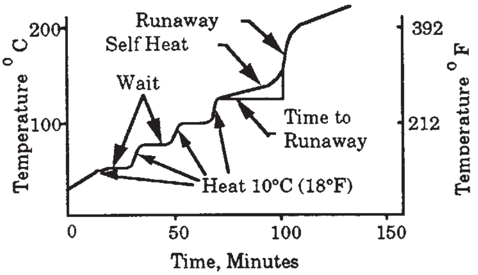


FIG. 26-29 Operation of the ARC.

---

[*] ARC is the trademark of Columbia Scientific Industries Corporation.

driven into the liquid and may cause explosive decomposition of the liquid. This test is intended to simulate water hammer and sloshing effects in transportation, such as humping of railway tank cars. It is very severe and gives worst-case results.

Flammability–Flash Point The closed-cup flash point determination produces the most important data to determine the potential for fire. The flash point is the lowest temperature at which the vapors can be ignited under conditions defined by the test apparatus and method.

Flammable Limits Flammable limits, or the flammable range, are the upper and lower concentrations (in volume percent) which can just be ignited by an ignition source. Above the upper limit and below the lower limit no ignition will occur. Data are normally reported at atmospheric pressure and at a specified temperature. Flammable limits may be reported for atmospheres other than air and at pressures other than atmospheric.

Autoignition Temperature The autoignition temperature of a substance, whether liquid, solid, or gaseous, is the minimum temperature required to initiate or cause self-sustained combustion in air, with no other source of ignition. Autoignition temperatures should be considered only as approximate. Test results tend to give temperatures that are higher than the actual autoignition temperature.

Dust Explosions Combustible, dusty materials, with particle sizes less than approximately 200 mesh, can explode if a sufficient concentration in air is present along with an ignition source. The standard test has been designed to determine rates of pressure rise during an explosion, the maximum pressure reached, and the minimum energy needed to ignite the material. These data are useful in the design of safe equipment to handle dusty combustible materials in a process. Combustible dusts need a minimum volume to develop their full reaction velocity. Bartknecht states that for determination of explosion data of combustible dusts, a minimum volume of 16 L (4.23 gal) would be required to ensure correlation with data from large test vessels (Bartknecht, 1981, p. 39). This has been confirmed by comprehensive testing with a 20-L (5.28-gal) sphere.

Unstable Compounds (Bretherick, L., British Petroleum Co. Ltd., *Handbook of Reactive Chemical Hazards,* 4th ed., Butterworths, London, pp. S1–S23, 1990, by permission of Butterworth-Heinemann and L. Bretherick; note that the 5th ed. is available in electronic format from *Bretherick's Reactive Chemical Hazards Database,* Version 2.0, Butterworth-Heinemann, Oxford, 1995.) Explosibility may be defined as the tendency of a chemical system (involving one or more compounds) to undergo violent or explosive decomposition under appropriate conditions of reaction or initiation. It is of great interest to be able to predict which compound or reaction systems are likely to exhibit explosability, and much work has been devoted to this end. The contributions of various structural factors (bond-groupings) have been evaluated in terms of heats of decomposition and oxygen balance of the compound or compounds involved in the system. Oxygen balance is the difference between the oxygen content of the chemical compound and that required to fully oxidize the carbon, hydrogen, and other oxidizable elements in the compound. Materials or systems approaching zero oxygen balance give the maximum heat release and are the most powerfully explosive.

Most chemical reactions are exothermic. In the few endothermic reactions that are known, heat is absorbed into the reaction product or products, which are known as endothermic or energy-rich compounds. Such compounds are thermodynamically unstable because heat would be released on decomposition of their elements. The majority of endothermic compounds possess a tendency toward instability and possibly explosive decomposition under various circumstances of initiation.

Following are the classes of compounds that have a tendency to undergo violent or explosive decomposition.

Acetylenic compounds
Acyl or alkyl nitrates
Alkyl hydroperoxides, peroxyacids
Alkyl perchlorates
Aminachromium peroxocomplexes
Aminemetal oxosalts
Ammonium perchlorates
Arenediazo aryl sulfides
Arenediazoates
Arenediazoniumolates
Azides (acyl, halogen, nonmetal, organic)
Azo compounds
Bis-arenediazo sulfides
Chlorite salts
Diazirines
Diazo compounds
Diazonium carboxylates or salts
Diazonium sulfides and derivatives, Xanthates
Difluoramino compounds
1,2-epoxides
Fluorodinitromethyl compounds
Halo-aryl metals
Haloacetylene derivatives
Haloarenemetal π-complexes
Halogen azides
Halogen oxides
High-nitrogen compounds
Hydrazinium salts
Hydroxylammonium salts
Hypohalites
Metal acetylides
Metal fulminates or *aci*-nitro salts oximates
N,N,N-trifluoroalkylamidines
N-azolium compounds
N-halogen compounds
N-haloimides
N-metal derivatives
N-nitro compounds
Nitroalkanes, *c*-nitro, and polynitroaryl compounds
Nitroso compounds
Oxosalts of nitrogeneous bases
Perchloric acid
Perchloryl compounds
Peroxides, (cyclic, diacyl, dialkyl), Peroxyesters
Poly(dimercuryimmonium salts)
Polynitroalkyl compounds
Tetrazoles
Triazenes
Trinitroethyl orthoesters

COMBUSTION AND FLAMMABILITY HAZARDS

General References: Bartknecht, *Explosions Course Prevention Protection,* Springer-Verlag, Berlin, 1981. Bartknecht, *Dust Explosions,* Springer-Verlag, Berlin, 1989. Beneditti, ed., *Flammable and Combustible Liquids Code Handbook,* 3d ed., based on NFPA 30, *Flammable and Combustible Liquids Code and Automotive and Marine Service Station Code,* National Fire Protection Association, Quincy, Mass., 1987. Bodurtha, Engineering Dept., Du Pont, *Industrial Explosion Prevention and Protection,* McGraw-Hill, 1980. Cawse, Pesetsky, and Vyn, *The Liquid Phase Decomposition of Ethylene Oxide,* Union Carbide Corporation, Technical Center, South Charleston, W.Va. *CPQRA (Guidelines for Chemical Process Quantitative Risk Analysis),* CCPS-AIChE, New York, 1989. Crowl and Louvar, *Chemical Process Safety: Fundamentals with Applications,* Prentice Hall, Englewood Cliffs, N.J., 1990. DiNenno, P. J. (ed.), *SPFE Handbook of Fire Protection Engineering,* 1st ed., National Fire Protection Association, Quincy, Mass., 1988. Drysdale, *An Introduction to Fire Dynamics,* Wiley, Suffolk, 1985. *Fire Safety Data,* Fire Protection Association, London 1980. *Guidelines for Engineering Design for Process Safety,* CCPS-AIChE, 1993. Lees, *Loss Prevention in the Process Industries,* Butterworths, London, 1980. Stull, *Fundamentals of Fire and Explosion,* New York, 1976.

Introduction The enchanting flame has held a special mystery and charm the world over for thousands of years. According to Greek myth, Prometheus the Titan stole fire from the heavens and gave it to mortals—an act for which he was swiftly punished. Early people made use of it anyway. Soon the ancients came to regard fire as one of the basic elements of the world. It has since become the familiar sign of the hearth and the mark of youth and blood—as well as the object of intense curiosity and scientific investigation.

Suitably restrained, fire is of great benefit; unchecked or uncontrolled, it can cause immense damage. We respond to it with a powerful fascination coupled with an inbred respect and fear. A good servant but a bad master is Thoreau's "most tolerable third party" (Cloud, "Fire, the Most Tolerable Third Party," *Michigan Natural Resources,* May-June 1990).

What Is Fire? (DiNenno, 1988.) Fire or combustion is normally the result of fuel and oxygen coming together in suitable proportions and with a source of heat. The consumption of a material by a fire is a chemical reaction in which the heated substance combines with oxygen. Heat, light, smoke, and products of combustion are generated. The net production of heat by a fire involves both heat-producing and heat-absorbing reactions, with more heat being produced than is absorbed.

A flame is a rapid self-sustaining chemical reaction that occurs in a distinct reaction zone. Two basic types of flame are (1) the diffusion flame, which occurs on ignition of a fuel jet issuing into air, and for which the limiting rate is controlled by diffusion, and (2) the aerated, or premixed, flame, which occurs when fuel and air are premixed before ignition, and for which the limiting rate is controlled by reaction kinetics. The main concern in fire applications is with diffusion flames, as contrasted to premixed flames where fires and oxidants are premixed or brought together to the combustion region. At high turbulence in diffusion flames, kinetics and diffusion may be of roughly equal importance. Combustion is self-propagating; burning materials produce heat, which causes more of the solid to produce flammable vapors until either the fuel or oxygen is exhausted, or until the fire is extinguished in some other way (*API Recommended Practices,* 3d ed., Practice 521, November 1990).

Energy in the form of heat is required:

1. To produce vapors and gases by vaporization or decomposition of solids and liquids. Actual combustion usually involves gases or vapors intimately mixed with oxygen molecules.
2. To energize the molecules of oxygen and flammable vapors into combining with one another and so initiating a chemical reaction.

The amount of energy needed to cause combustion varies greatly. Hydrogen and carbon disulfide can be ignited by tiny sparks or simply by static generated as the gases or vapors discharge from pipes into air. Other materials, such as methylene chloride, require such large amounts of energy to be ignited that they are sometimes considered nonflammable.

Fire can also result from the combining of such oxidizers as chlorine and various hydrocarbon vapors; oxygen is not required for a fire to take place.

Ordinarily, combustible solids do not combine directly with oxygen when they burn. They give off vapor and gaseous decomposition products when they are heated, and it is the vapors or gases which actually burn in the characteristic form of flames. Thus, before a solid can be ignited it must be heated sufficiently for it to give off flammable concentrations of vapors. There are exceptions to the general rule that a solid must vaporize or decompose to combine with oxygen; some finely divided materials such as aluminum powder and iron powder can burn and it is probable that they do not vaporize appreciably before burning. Some metallic dusts will explode in air by light radiation alone without conduction and convection (Bartknecht, 1989, p. 14).

Products of Combustion Heat, light, smoke, and asphyxiating and toxic gases are produced by fire. In a hot, well-ventilated fire, combustion is usually nearly complete. Nearly all the carbon is converted to carbon dioxide, all the hydrogen to steam, and oxides of various other elements such as sulfur and nitrogen are produced.

This is not the case in most fires where some of the intermediate products, formed when large, complex molecules are broken up, persist. Examples are hydrogen cyanide from wool and silk, acrolein from vegetable oils, acetic acid from timber or paper, and carbon or carbon monoxide from the incomplete combustion of carbonaceous materials. As the fire develops and becomes hotter, many of these intermediates, which are often toxic, are destroyed—for example, hydrogen cyanide is decomposed at about 538°C (1000°F).

Small airborne particles of partially burnt carbonaceous materials from smoke, which is often made more opaque by steam from combustion or from water added to the fire, may be formed when there is only partial combustion of fuel.

Many hydrocarbon flames are luminous because of the incandescent carbon particles formed in the flames. Under certain conditions, these particles are released from the luminous flames as smoke. Smoke from hydrocarbons is usually formed when the system is fuel rich, either overall or locally.

Common materials—such as textiles in the form of fibers or fabrics, foamed rubber, foamed plastics, thin sheets of plastic, paper, corrugated cardboard, combustible dusts, dry grass and twigs, and wood shavings—are all examples of materials with large surface areas in relation to their volumes. In a well-established fire, materials with relatively small surface areas, such as chunks of coal or logs, burn readily.

Combustible Dusts Dusts are particularly hazardous; they have a very high surface area–to–volume ratio. When finely divided as powders or dusts, solids burn quite differently from the original material in the bulk. Dust and fiber deposits can spread fire across a room or along a ledge or roof beam very quickly. On the other hand, accumulations of dust can smolder slowly for long periods, giving little indication that combustion has started until the fire suddenly flares up, possibly when no one suspects a problem.

Many combustible dusts produced by industrial processes are explosible when they are suspended as a cloud in air. A spark may be sufficient to ignite them. After ignition, flame spreads rapidly through the dust cloud as successive layers are heated to ignition temperature. The hot gases expand and produce pressure waves, which travel ahead of the flame. Any dust lying on surfaces in the path of the pressure waves will be thrown into the air and could cause a secondary explosion more violent and extensive than the first.

Liquids A vapor has to be produced at the surface of a liquid before it will burn. Many common liquids give off a flammable concentration of vapor in air without being heated, sometimes at well below room temperature. Gasoline, for example, gives off ignitable vapors above about −40°C (−40°F), depending on the blend. The vapors are easily ignited by a small spark or flame. The reason there are not many fires in automobile gasoline tanks is that the vapor space above the gasoline is almost always above the upper flammability limit. Other liquids, such as fuel oil and kerosene, need to be heated until sufficient vapor is produced to produce a flammable concentration.

For any flammable vapor there are maximum and minimum concentrations of vapor in air beyond which it cannot burn. When the concentration of vapor in air is too low, there is insufficient fuel for burning; when it is too high, there is insufficient oxygen for burning.

If the density of a vapor is greater than air, as is the case with most gases and vapors encountered in industry, flammable concentrations may collect at low levels, such as at floor level or in basements, and can travel considerable distances to a source of ignition and the flames will then flash back.

Gases Flammable gases are usually very easily ignited if mixed with air. Flammable gases are often stored under pressure, in some cases as a liquid. Even small leaks of a liquefied flammable gas can form relatively large quantities of gas, which is ready for combustion.

Transparent (Invisible) Flames Some materials have nearly nonluminous flames, which may not be visible, especially in the daytime. For example, hydrogen has a nearly nonvisible flame in the daytime. A person may walk unaware into a hydrogen leak flame. Some other materials, including some alcohols such as methanol, also have nearly nonluminous flames and may be unusually hazardous because the flames cannot be seen in the daytime.

The Fire Triangle The well-known *fire triangle* (see Fig. 26-33) is used to represent the three conditions necessary for a fire: (1) fuel, (2) oxygen or other oxidizer (a gaseous oxidizer such as chlorine, a liquid oxidizer such as bromine, or a solid oxidizer such as sodium bromate), and (3) heat (energy).

If one of the conditions in the fire triangle is missing, fire does not occur, and if one is removed, fire is extinguished. Usually a fire occurs when a source of heat contacts a combustible material in air, and then the heat is supplied by the combustion process itself.

The fire triangle indicates how fires may be fought or prevented:

1. Cut off or remove the fuel.
2. Remove the heat—usually done by putting water on the fire.
3. Remove the supply of oxygen—usually done by foam or inert gas.

Stoichiometric Concentration (Used by permission of Frank T. Bodurtha, Inc., New London, New Hampshire). In a combustion reaction in air, the stoichiometric concentration, C_{st}, of any reactant is the concentration theoretically required for complete conversion by reacting completely with oxygen. For example, for the combustion of propane in air:

$$C_3H_8 + \overbrace{5O_2 + 18.8N_2}^{\text{Air}} \rightarrow 3CO_2 + 4H_2O + 18.8N_2$$

$$C_{st} \text{ for propane} = \left(\frac{1}{1 + 5 + 18.8}\right)100 = 4.0\% \text{ (volume)}$$

Moles at start = 24.8; moles after combustion = 25.8.

The change in moles upon the combustion of propane and many other hydrocarbons is either zero or small. Usually, pressure rise in the combustion of a vapor or gas is due mainly to change in temperature, not change in moles.

The C_{st} for a flammable solid may also be calculated. For sugar, whose molecular weight is 342, C_{st} is calculated as follows:

$$\underbrace{\overbrace{C_{12}H_{22}O_{11}}^{\text{Sugar}} + \overbrace{12O_2 + 46.4N_2}^{\text{Air}}}_{\text{58.4 volumes}} \rightarrow \underbrace{12CO_2 + 11H_2O + 46.4N_2}_{\text{69.4 volumes}}$$

TABLE 26-10 Flammability Limits, Autoignition Temperature, and Flash Points of Selected Substances in Air at Atmospheric Pressure

Chemical compound	Flam. limits, lower, % v/v	Flam. limits, upper, % v/v	Autoignition temperature, °C	Flash point, closed cup, °C	Flash point, open cup, °C
Acetone	2.6	13	465	−18	−9
Acetylene	2.5	100	305	—	—
Ammonia	15	28	651[*]	—	—
Benzene	1.4[*]	8.0[*]	562[*]	−11	—
n-Butane	1.8	8.4	405	−60	—
Carbon disulfide	1.3	50	90	−30	—
Carbon monoxide	12.5	74	—	—	—
Cyclohexane	1.3	7.8	245	−20	—
Ethane	3.0	12.4	515	−135	—
Ethylene	2.7	36	490	−121	—
Ethylene dichloride	6.2[*]	15.9[*]	413[*]	13	18
Ethylene oxide	3[*]	100[*]	429[*]	—	−20
Hydrogen	4	75	400	—	—
Methane	5	15	540	—	—
Propane	2.1	9.5	450	<−104	—
Propylene	2.4	11	460	−108	—
Styrene	1.1[*]	6.1[*]	490[*]	32	38
Toluene	1.3[*]	7.0[*]	536[*]	4	7
Vinyl chloride	4[*]	22[*]	472[*]	—	−78

[*] Factory Mutual Engineering Corporation, 1967.

SOURCES: Lees, 1980.

Flammability limits and autoignition temperatures: Zabetakis, *Bureau of Mines Bulletin 627*, except where given in footnotes.

Flash points: Factory Mutual Engineering Corporation, 1967.

$$C_{st} = \frac{(342)(1000)}{(12 + 46.4)(22.4)(298/273)} = 239.5 \text{ mg/L air at } 25°\text{C}$$

Table 26-10 shows flammability limits, autoignition temperature, and flash points of selected substances in air at atmospheric pressure.

Burning in Pure Oxygen The flammability of a substance depends strongly on the partial pressure of oxygen in the atmosphere. Increasing oxygen content affects the lower flammability limit only slightly, but it has a large effect on the upper flammability limit. Increasing oxygen content has a marked effect on the ignition temperature (reduces it) and the burning velocity (increases it). Use of air enriched with oxygen, or pure oxygen, can greatly increase the hazards of combustion reactions.

Burning in Other Oxidizable Atmospheres Chemically, oxygen is not the only oxidizing agent, though it is the most widely recognized and has been studied the most. Halogens are examples of oxidants that can react exothermically with conventional fuels and show combustion behavior. The applicability of flammability limits applies to substances that burn in chlorine. Chlorination reactions have many similarities to oxidation reactions. They tend not to be limited to thermodynamic equilibrium and often go to complete chlorination. The reactions are often highly exothermic. Chlorine, like oxygen, forms flammable mixtures with organic compounds. Flames can also propagate in mixtures of oxides of nitrogen and other oxidizable substances.

Flame Quenching Flame propagation is suppressed if the flammable mixture is held in a narrow space. If the space is sufficiently narrow, flame propagation is suppressed completely. The largest diameter at which flame propagation is suppressed is known as the *quenching diameter.* For an aperture of slotlike cross section, there is a critical slot width. The term *quenching distance* is sometimes used as a general term covering both quenching diameter and critical slot width and sometimes meaning only the latter.

There is a maximum safe gap measured experimentally which will prevent the transmission of an explosion occurring within a container to a flammable mixture outside the container. Critical and maximum experimental safe gaps for a number of materials in air are listed in Lees (1980, pp. 491–492). These quenching effects are important in the design of flame arresters and flameproof equipment.

Heterogeneous Mixtures (Zabetakis, *Flammability Characteristics of Combustible Gases and Vapors,* Bulletin 627, Bureau of Mines, 1965.) Heterogeneous (poorly mixed) gas phase mixtures can lead to fires that normally would be totally unexpected. It is important to recognize that heterogeneous mixtures can ignite at concentrations that would normally be nonflammable if the mixture were homogeneous. For example, 1 L of methane can form a flammable mixture with air at the top of a 100-L container, although the mixture would contain only 1.0 percent methane by volume. This would be below the lower flammable limit if complete mixing occurred at room temperature and the mixture would not be flammable. This is an important concept since *layering* can occur with any combustible gas or vapor in both stationary and flowing mixtures.

Heterogeneous mixtures are formed, at least for a short time, when two gases or vapors are first brought together.

Explosions in the Absence of Air Some gases with positive heats of formation can be decomposed explosively in the absence of air. Ethylene reacts explosively at elevated pressure and acetylene at atmospheric pressure in large-diameter piping. Heats of formation of these materials are +52.3 and +227 kJ/mol (+22.5 and +97.6 × 10^3 Btu/lb mol), respectively.

Explosion prevention can be practiced by mixing decomposable gases with inert diluents. For example, acetylene can be made nonexplosive at a pressure of 100 atm (10.1 MPa) by including 14.5 percent water vapor and 8 percent butane (Bodurtha, 1980). One way to prevent the decomposition reaction of ethylene oxide vapor is to use methane gas to blanket the ethylene oxide liquid.

GAS EXPLOSIONS

GENERAL REFERENCES: Bartknecht, *Explosions,* Springer-Verlag, New York, 1981. Bodurtha, *Industrial Explosion Prevention and Protection,* McGraw-Hill, New York, 1980. Coward and Jones, "Limits of Flammability of Gases and Vapors," *U.S. Bur. Mines Bull. 503* (USNTIS AD-710 575), 1952. Lees, *Loss Prevention in the Process Industries,* vols. 1 and 2, Butterworths, London, 1980. National Fire Protection Association, *Explosion Prevention Systems,* NFPA 69, Quincy, Mass. National Fire Protection Association, *Venting of Deflagrations,* NFPA 68, Quincy, Mass. Zabetakis, "Flammability Characteristics of Combustible Gases and Vapors," *U.S. Bur. Mines Bull. 627* (USNTIS AD-710 576), 1965. NOTE: *NFPA reviews, and may change, its standards and guides periodically. Always check the latest edition.*

Fuel and Oxygen

Flash Point and Flammable Limits Flash points and flammable limits in percent by volume have been tabulated by the National Fire Protection Association (NFPA) (National Fire Protection Association, *Fire Hazard Properties of Flammable Liquids, Gases, and*

Volatile Solids, NFPA 325, Quincy, Mass.). Pressure particularly affects flash point and the *upper flammable limit* (UFL); see later section entitled "Effect of Temperature, Pressure, and Oxygen." Mists of high-flash-point liquids may be flammable; the *lower flammable limit* (LFL) of fine mists and accompanying vapor is about 48 g/m^3 of air, basis 0°C and 1 atm (0.048 oz/ft^3).

For practical purposes, LFL is the same as *lower explosive limit* (LEL). (Ignitability limits depend upon the strength of the ignition source; the ignitability range for relatively weak ignition sources is less than the flammable range.) LFLs in percent by volume generally decrease as molecular weight increases.

The equilibrium vapor pressure of a flammable liquid at its closed-cup flash point about equals its LFL in percent by volume. Thus, the vapor pressure of toluene at its closed-cup flash point (4.4°C or 40°F) of 1.2 percent (1.2 kPa) is close to its LFL of 1.1 percent. The composite LFL of a mixture may be estimated by Le Chatelier's Rule:

$$\text{Composite LFL (\% by vol.)} = \frac{100}{C_1/\text{LFL}_1 + C_2/\text{LFL}_2 + \cdots + C_n/\text{LFL}_n} \tag{26-43}$$

where the *C*s are percentages of volume of total fuel, i.e., without air or inert gas. As shown in Table 26-11, the indicated mixture is flammable even though each component is below its LFL. The composite LFL stays the same if the concentration of each component is multiplied by the same number. Composite upper flammable limits may be approximated similarly.

The concentration of fuel in air in a process should be maintained at or below 25 percent of the LFL, with automatic instrumentation and safety interlocks; however, up to 60 percent of LFL is permitted by the NFPA—except for ovens or furnaces. (Ovens and furnaces are covered in NFPA 86.)

Limiting Oxidant Concentration (LOC) It is often prudent to base explosion prevention on inerting. The LOC is the concentration of oxidant—normally oxygen—below which a fuel-oxidant explosion cannot occur. (The LOC is also called MOC, the minimum oxygen for combustion.) With adequate depletion of oxygen, an explosion cannot occur *whatever the concentration of fuel.* Nevertheless, in these circumstances a fuel–air–inert gas mixture may become flammable if sufficient air is added. Many LOCs are given in NFPA 69. In general, organic flammable gases or vapors will not propagate flame in mixtures of the organic, added nitrogen, and air below about 10.5 percent by volume O_2 at 1 atm and near normal room temperature. Hydrogen (LOC = 5 percent) and some other inorganic gases have lower LOCs.

For LOCs of 5 percent and greater, the O_2 concentration should not exceed 60 percent of the LOC, but with continuous monitoring the O_2 may be kept 2 percent below the LOC (NFPA 69, 1992). Neutronics, Inc., of Exton, Pennsylvania, supplies an inerting control system that has had wide application in many industries.

Explosion prevention by inerting has several advantages over explosion protection techniques, such as explosion venting. For example, with successful inerting, fires or business interruptions cannot occur. Nevertheless, beware of the potential of asphyxiation with inerting; proper vessel entry procedures must be implemented and occasionally it may be prudent to monitor for oxygen in workplaces.

Effect of Temperature, Pressure, and Oxygen LFLs and LOCs at 1 atm decrease about 8 percent of their values at near normal room temperature for each 100°C increase. Upper flammable limits increase approximately 8 percent for the same conditions.

TABLE 26-11 Le Chatelier's Rule

	Concentration, vol %	C, %	LFL, vol %
Hexane (1)	0.8	24.2	1.1
Methane (2)	2.0	60.6	5.0
Ethylene (3)	0.5	15.2	2.7
Total fuel	3.3		
Air	96.7		

$$\text{Composite LFL} = \frac{100}{24.2/1.1 + 60.6/5.0 + 15.2/2.7} = 2.5 \text{ vol \%}$$

Pressure affects flash point. A decrease in pressure lowers the flash point. With toluene, for example, at two-thirds of an atmosphere the vapor pressure must be only 0.74 kPa (5.6 mm Hg) to equal the LFL of 1.1 percent. (No significant difference in LFL will exist at two-thirds of an atmosphere compared to the published LFL of 1.1 percent at one atmosphere.) This vapor pressure occurs at −3°C, corresponding to a decrease in flash point of about 7.4°C from one atmosphere. Conversely, an increase in pressure raises the flash point.

Pressure also affects flammable limits. A decrease in pressure to about one-half atmosphere does not affect the flammable range significantly. At lower pressure the flammable range narrows and the flammable limits may disappear below about 6.7 kPa (50 mm Hg). An increase in pressure lowers LFLs and LOCs on a volume basis only slightly. But on a *weight basis,* LFLs are proportional to the absolute pressure. For example, the LFL of hexane is 43 g/m^3 (0.043 oz/ft^3) air at 1 atm, basis 0°C, but it is 86 g/m^3 air (0.086 oz/ft^3) at 2 atm. An increase in pressure increases UFLs greatly. The effect of elevated pressure on LFLs, LOCs, and UFLs for ethane is tabulated in Table 26-12. Based on tests by the U.S. Bureau of Mines, UFLs at high pressure and near normal room temperatures may be *estimated* by

$$\text{UFL}_p = \text{UFL} + 20.6\,(\log_{10} P + 1) \tag{26-44}$$

where UFL_p (percent by volume) is at the elevated absolute pressure, *P* is in megapascals absolute (MPa), and UFL (percent by volume) is at 1 atm. LFLs are about the same in oxygen as in air, since oxygen in air is in excess for combustion at LFL, but UFLs increase markedly in oxygen compared to air, as shown by the examples in Table 26-13. For organic substances, UFLs at 1 atm are about 48 percent higher in oxygen than in air. Moreover, the *minimum ignition energies* (MIE) in oxygen are about 1/100 of the MIEs in air, so vapors in oxygen are extraordinarily easy to ignite.

Ignition Sources Normally it is best practice not to base explosion safety solely on the presumed absence of an ignition source. Explosion control should be based on prevention or protection techniques, or both. Even so, all reasonable measures should be taken to eliminate ignition sources.

TABLE 26-12 Effect of Elevated Pressure on LFL, LOC, and UFL of Ethane*†

Pressure MPa gauge, psig	LFL, vol %	% decrease in LFL	LOC, vol %	% decrease in LOC	UFL, vol %	% increase in UFL
0 (0)	2.85	—	11.0	—	12.3	
0.69 (100)	2.80	1.75	—	—	30.0	144
1.72 (250)	2.70	5.20	9.3	15.5	40.0	225
3.45 (500)	2.55	10.5	8.9	19.1	47.0	282
5.17 (750)	2.40	15.8	—	—	50.0	306
6.20 (900)	—	—	8.8	20.0		
6.90 (1000)	2.20	22.8	—	—	51.5	319

*Nitrogen as inert gas. Near normal room temperature. % decrease and increase is from 0 MPa gauge.

†After Kennedy, Spolan, Mock, and Scott, "Effect of High Pressures on the Explosibility of Mixtures of Ethane, Air and Carbon Dioxide, and of Ethane, Air and Nitrogen," *U.S. Bureau of Mines Report Invest.,* 4751, 1950.

TABLE 26-13 Flammability Limits in Air and Oxygen at Ordinary Temperatures and 1 atm*

	LFL in air, vol %	LFL in O_2, vol %	UFL in air, vol %	UFL in O_2, vol %	Δ UFL, vol %
Butane	1.9	1.8	8.5	49	40.5
1-Butene	1.6	1.8	9.3	58	48.7
Ethane	3.0	3.0	12.5	66	53.5
Ethylene	3.1	3.0	32	80	48
Isopropyl ether	—	—	21	69	48
Methane	5.3	5.1	14	61	47
Propane	2.2	2.3	9.5	55	45.5
Vinyl chloride	4.0	4.0	22	70	48

*Based on Coward and Jones, "Limits of Flammability of Gases and Vapors," *U.S. Bureau of Mines Bulletin 503* (USNTIS AD-701575), 1952.

Autoignition The minimum autoignition temperature (AIT) of a substance is the minimum temperature at which vapors ignite spontaneously from the heat of the environment. (Flash points are lower than minimum autoignition temperatures; in flash-point tests an open flame is used as an igniter.) The ignition temperature found in NFPA 325 is the same as minimum autoignition temperature. A method for determination of autoignition temperatures is given in E659, *Standard Test Method for Autoignition Temperatures of Liquid Chemicals,* of the American Society for Testing and Materials (ASTM). Autoignition depends on many factors—namely, ignition delay, concentration of vapors, environmental effects (volume, pressure, and oxygen content), catalytic material, and flow conditions. Based on a development by A. Beerbower, Exxon Research and Engineering, for the effect of volume on AIT (see Coffee, "Cool Flames and Autoignitions: Two Oxidation Processes," *Chem. Eng. Prog. 13th Loss Prev. Symp.,* Houston, 1979, pp. 79–82):

$$t_a = \frac{(t_d - 75)(15 - \log_{10} V_a)}{(15 - \log_{10} V_d)} + 75 \qquad (26\text{-}45)$$

where t_a (°C) = minimum AIT for volume V_a (mL)
t_d (°C) = minimum AIT as measured in volume V_d (mL)

For a plant vessel of 3.785×10^6 mL (1000 U.S. liquid gallons) and $t_d = 330$°C in a 500-mL test vessel (ASTM E659), $t_a = 249$°C, i.e., 81°C less than measured in the 500-mL flask.

As a guide, because of convection that occurs from hot surfaces, ignition by a hot surface in open air should not be assumed unless the surface temperature is at least 200°C above the published minimum autoignition temperature (American Petroleum Institute, *Ignition Risk of Hot Surfaces,* API PSD 2216, Washington, 1980).

Autooxidation Autooxidation—spontaneous ignition—is the phenomenon of self-heating by slow oxidation with accompanying evolution of heat, leading to ignition when the heat of oxidation cannot be dissipated adequately. Thermal insulation or rags wet with oils or other organic liquids susceptible to oxidation have caused serious fires. A fire may occur even if the hot surface is below the minimum AIT. Relatively high flash-point materials are most susceptible to autooxidation; low-flash-point materials may evaporate without ignition. Leaks that may contaminate insulation should be eliminated or diverted away from insulation to the extent feasible. Thermal insulation known to be wetted with oil or other high-boiling organic fluids should be removed promptly and replaced.

Compression Adiabatic compression results in high temperatures determined by the compression and specific heat ratios, as shown in Eq. (26-46):

$$\frac{T_2}{T_1} = \left(\frac{P_2}{P_1}\right)^{(k-1)/k} \qquad (26\text{-}46)$$

where the subscript 2 refers to the final state, T is the absolute temperature, P is the absolute pressure, and k is the ratio of specific heats.

Various types of rapid, adiabatic compressions have caused explosions. With propane at an initial temperature of 25°C, T_2 = 432°K (159°C) for compression and specific heat ratios of 25 and 1.13, respectively. Assume that now air enters a compressor to bring propane into the flammable range at 5 percent by volume. The mixture then will be mostly air with $k = 1.47$. The same compression ratio of 25 will elevate the final temperature T_2 to 834°K (561°C), i.e., above the published autoignition temperature of 450°C for propane and perhaps high enough to cause an explosion.

Other Ignition Sources Hazardous classification of locations for electrical installations is covered in Articles 500–504 of the *National Electrical Code* (NEC) (NFPA 70). Proper hazardous classification is essential for safety and for prevention of explosion and fire losses. Class 1 in the NEC is for vapors and gases; in the United States, in brief, Division 1 of Class 1 includes those locations where flammable concentrations exist continuously or frequently. Division 2 includes locations where flammable concentrations may exist only in case of accidental escape of vapors or gases, or in case of abnormal operation of equipment. Static electricity, which causes fires and explosions with flammable vapors and gases, is covered later in Sec. 26. Other ignition sources include friction and impact plus rubbing; with rubbing beware of metal-to-metal contact where heat cannot be conducted away. Even with grounded equipment, *hydrogen may ignite spontaneously,* often, for instance, when it exits a stack or leaks out of a pipe. (The minimum ignition energy of hydrogen is about 0.02 mJ, approximately 1/10 of the MIEs for paraffin hydrocarbons.)

Explosion Pressure An *explosion* is the action of "going off" with a loud noise under the influence of suddenly developed internal energy. Thus, an explosion is a result, not a cause. Deflagrations and detonations cause chemical explosions. A *deflagration* is a reaction that propagates to the unreacted material at a speed less than the speed of sound in the unreacted material. A *detonation* is a reaction that propagates to the unreacted material at a speed greater than the speed of sound in the unreacted material; it is accompanied by a shock wave and inordinately high pressure.

Deflagration Pressure The increase in pressure in a vessel from a deflagration results from an increase in temperature; the actual maximum flame temperature for propane, for example, is 1925°C (3497°F). No significant increase in moles of gas to cause pressure buildup results from combustion of propane in air.

Peak deflagration pressure in closed equipment is approximately eight times the initial absolute pressure, whether atmospheric, subatmospheric, or elevated. This maximum pressure occurs at a concentration just slightly richer in fuel than the stoichiometric concentration for combustion in air (C_{st}), as shown in Table 26-14 for propane and methane:

Some flammable liquids generate a vapor pressure close to the C_{st} near normal room temperature, as shown in Table 26-15.

Toluene is a notoriously poor electrical conductor; even in grounded equipment it has caused several fires and explosions from static electricity. Near normal room temperature it has a concentration that is one of the easiest to ignite and, as previously discussed, that generates maximum explosion effects when ignited (Bodurtha, 1980, p. 39). Methyl alcohol has similar characteristics, but it is less prone to ignition by static electricity because it is a good conductor. Acetone is also a good conductor, but it has an equilibrium vapor pressure near normal room temperature, well above UFL. Thus, acetone is not flammable in these circumstances.

Several environmental factors affect maximum deflagration pressure and pressure rise, as highlighted in Table 26-16.

TABLE 26-14 Optimum Concentrations for Maximum Deflagration Pressure

	Stoichiometric concentration, vol %	Maximum deflagration pressure, vol %
Propane	4.0	5.0
Methane	9.5	10.3

TABLE 26-15 Liquids Having Equilibrium Vapor Pressure near the C_{st}

	Equilibrium vapor pressure at 20°C, vol %	C_{st}, vol %
Toluene	2.9	2.3
Methyl alcohol	12.6	12.2
Acetone (UFL = 12.8)	24.6	5.0

TABLE 26-16 Effect of Environmental Factors on Deflagration Pressure and Pressure Rise*

	Pressure	Temperature	Vessel volume	Turbulence	Strength of ignition
Maximum deflagration pressure	+	−	Minor	Minor	Minor
Maximum rate, deflagration pressure rise	+	+	−	+	+

*Unvented vessel: + = an increase in indicated factor increases pressure or pressure rise.
− = an increase in indicated factor decreases pressure or pressure rise.

Vessel volume has a large effect on the maximum rate of deflagration pressure rise; the cubic law states, all else being equal

$$(r_m)(V^{1/3}) = \text{constant } (K_G) \qquad (26\text{-}47)$$

where r_m = maximum rate of deflagration pressure rise, bar/s
V = volume, m^3
K_G = deflagration index for gases, bar·m/s

In compartmented equipment, higher deflagration pressure than noted in the preceding discussion can occur from pressure piling. After ignition in the first compartment, some of the gas mixture ahead of the flame front is pushed through a connection between the two compartments. Pressure of the original flammable mixture in the second compartment increases, and the resulting now-compressed mixture is ignited by the flame from the first compartment; abnormally high deflagration pressure may occur in this second compartment. This pressure piling effect is an important one and may pose difficult safety problems in design, if flammable mixtures cannot be prevented. As a rough guide, the ratio of compartment volumes of at least 5 to 1 apparently is required for pressure piling; generally, initial ignition must be in the larger compartment (Fitt, "Pressure Piling: A Problem for the Process Engineer," *Chem. Eng.* [Rugby, England], no. 368, pp. 237–239, May 1981.)

Detonation A deflagration can develop into a gaseous detonation in vessels and piping under certain conditions with enhanced explosion effects. Many factors affect detonation formation and effects. Briefly, upon ignition, pressure waves in a closed tube move through unburned gas. Subsequent waves move faster through the unburned gas, because of heating from previous pressure waves. Adiabatic compression results in high enough temperature to ignite gas ahead of the original flame and a detonation develops. (This ignition by compression to form a detonation is sometimes also called *pressure piling.*) The peak pressure in a stable detonation is on the order of 30 times the initial absolute pressure, disregarding the usually nondamaging spike of still higher pressure; reflected pressure is much higher than this 30 multiplier. (Special review is necessary for overpressure developed in an unstable [overdriven] detonation.) Nevertheless, in usual plant vessels without large length/diameter ratios, detonation is unlikely at 1 atm and near normal room temperature. Strong equipment may be subject to damage in a detonation, and rupture disks alone cannot control a detonation. Flame arresters are now commonly used to help protect against detonations; see the article on flame arresters in this section. But the best procedure to guard against the destructive effects of detonations is to prevent the formation of flammable mixtures.

Explosion Protection Where prevention of flammable mixtures may not be feasible, protection facilities must be installed; sometimes, too, backup explosion protection facilities are used in conjunction with inerting systems. Containment, suppression, or venting are used for protection against internal deflagrations in fuel-air mixtures. Although these methods may protect against deformation or rupture of a vessel, damage to internal appurtenances may still occur. Containment and suppression prevent the discharge of environmentally unacceptable materials to the atmosphere.

Containment The design pressure (maximum allowable working pressure) to prevent rupture of equipment for most gas-air mixtures initially at 1 atm should be 304 kPa gauge (44.1 psig), and to prevent permanent deformation, 608 kPa gauge (88.2 psig) (National Fire Protection Association, *Explosion Prevention Systems,* NFPA 69, Quincy, Mass., 1992, p. 11). NFPA 69 provides important additional design information on deflagration pressure containment.

Explosion Suppression With explosion suppression, an incipient explosion is detected and—within a few milliseconds—a suppressant is discharged into the exploding medium to stop combustion. Pressure and optical detection systems are used; suppressors are pressurized and release the suppressants when actuated by an electroexplosive device.

Deflagration pressure can be reduced substantially by suppression. Figure 26-30 shows the pressures measured in an ethylene-air explosion and a sodium bicarbonate-suppressed ethylene-air explosion. Fike Corporation, Blue Springs Missouri, and Fenwal Safety Systems, Marlborough, Mass., supply explosion suppression systems.

To reduce the chance of false activation of the suppression system by vibration, a flexible pressure detector standoff is often used. Also, two detectors in series may be employed to reduce further the possibility of false activation.

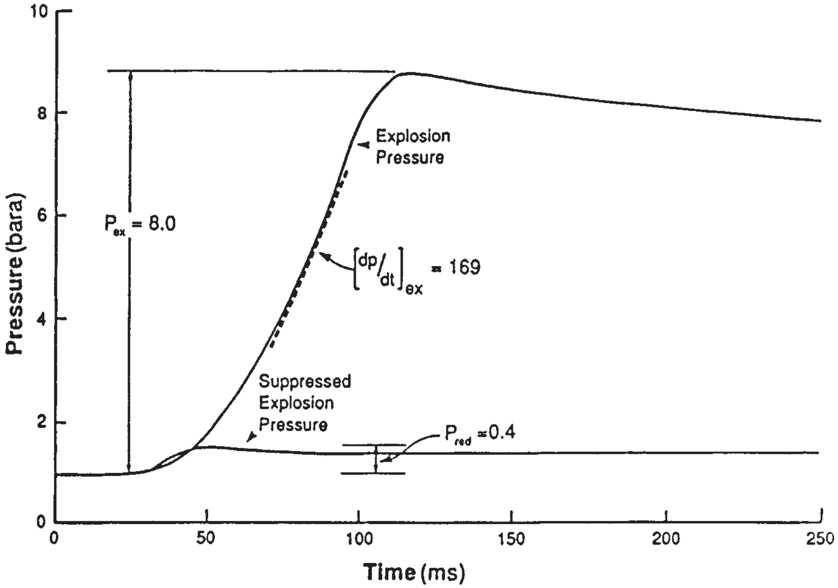


FIG. 26-30 Suppression of explosions. Pressures in an ethylene explosion and a sodium bicarbonate suppressed ethylene explosion. Tests conducted by Fike Corp. in a 1-m^3 vessel. Ethylene concentration = 1.2 times stoichiometric concentration for combustion. $(dp/dt)_{ex}$ = 169 bar/s (2451 psi/s). P_{red} = reduced explosion pressure = 0.4 bar gauge (5.8 psig). (*From Chatrathi, "Explosion Testing,"* Safety and Technology News, *vol. 3, issue 1, Fike Corp., 1989, by permission.*)

Explosion Venting The technology of explosion venting has advanced in recent years but is still not exact; thus, considerable care in sizing explosion vents is essential. The NFPA standard, *Guide for Venting of Deflagrations,* NFPA 68, provides excellent guidance on the practice of explosion venting.

Venting requirements in NFPA 68 are based on the cubic law in Eq. (26-47). The deflagration venting nomographs of the NFPA are subject to several caveats clearly specified in NFPA 68. Particularly, the nomographs do not apply with high initial turbulence. Moreover, the NFPA 68 nomographs must not be used for venting detonations, runaway reactions, or gas mixtures containing elevated oxygen compared to air.

Equations have been developed by L. L. Simpson for the Bartknecht nomographs for gases in NFPA 68 (Bartknecht, *Explosions,* Springer-Verlag, New York, 1981; Simpson, "Equations for the VDI and Bartknecht Nomograms," *Plant/Oper. Prog.*, vol. 5, no. 1, January 1986, pp. 49–51). Those equations are shown in Table 26-17 for quiescent methane, propane, and hydrogen. NFPA 68 explains how to determine vent areas for other gases and vapors. That determination is based on fundamental burning velocities. As an approximation without serious error, the equation for quiescent propane may be used, for example, for vent areas for the quiescent gases in Table 26-18.

The following precautions must be considered in application of the NFPA 68 nomographs or Simpson's equations:

1. Do not use relief valves as explosion vents.
2. Do not use rupture disks in series, unless the space between them is vented to air or a telltale is installed to warn of pressure buildup in that space.
3. Set the release pressure of a rupture disk or other vent closure as close to the operating pressure as practical. Note that the maximum overpressure in a vented explosion will exceed the opening pressure of the vent closure.
4. Locate explosion vents as close as possible to the most likely ignition sources.
5. Locate deflagration vents so discharge from them will not endanger personnel or damage equipment.
6. Install equipment to be vented outdoors, weather and other factors permitting.
7. Place equipment to be vented close to an exterior wall, if it must be placed indoors; the vent ducts should be free of bends and no longer than 3 m (10 ft).
8. *Do not discharge explosion vents within buildings;* serious fires and explosions have occurred by such venting.
9. Consider reaction forces on vented equipment from the discharge of explosion products from the vent.
10. Design the vents to prevent the development of damaging negative pressure from cooling of hot products of combustion.
11. Consider the safety of personnel in rooms or buildings if those spaces are to be vented, e.g., by vent panels.

TABLE 26-17 Explosion Venting Equation for Quiescent Gases

$$A_v = d \cdot V^f \cdot \exp(gP_{\text{stat}}) \cdot P_{\text{red}}^h$$

Gas	d	f	g	h
Methane	0.105	0.770	1.23	−0.823
Propane	0.148	0.703	0.942	−0.671
Hydrogen	0.279	0.608	0.755	−0.393

where d, f, g, h = constants as tabulated above
A_v = vent area, m^2
P_{red} = maximum explosion pressure during venting, bar g
P_{stat} = vent closure release pressure, bar g
V = vessel volume, m^3

TABLE 26-18 Vent Areas Calculated for Propane May Be Used for the Following Quiescent Gases

Acetone
Acrylonitrile
Benzene
n-Butane
Butanone
1-Butene
Carbon disulfide
Cyclohexane
Cyclopropane
Diethyl ether
Dimethyl ether
Ethane
Ethyl acetate
n-Heptane
n-Hexane
Isopropyl alcohol
n-Pentane
1-Pentene
Propylene
Toluene

UNCONFINED VAPOR CLOUD EXPLOSIONS (UVCEs) AND BOILING LIQUID EXPANDING VAPOR EXPLOSIONS (BLEVEs)

GENERAL REFERENCES: AIChE/CCPS, *Guidelines for Chemical Process Quantitative Risk Analysis,* New York, 1989. AIChE/CCPS, *Guidelines for Evaluating the Characteristics of Vapor Cloud Explosions, Flash Fires and BLEVEs,* New York, 1994. Bodurtha, *Industrial Explosion Prevention and Protection,* McGraw-Hill, New York, 1980. Brasie and Simpson, "Guidelines for Estimating Damage Explosion," *Chem. Eng., Prog. Second Loss Prev. Symp.*, St. Louis, 1968, pp. 91–102. Crowl and Louvar, *Chemical Process Safety: Fundamentals with Applications,* Prentice Hall, Englewood Cliffs, N.J., 1990. Johansson, "The Disaster at San Juanico," *Fire J.*, vol. 80, no. 1, January 1986, pp. 32–37, 93–95. Kletz, "Protect Pressure Vessels from Fire," *Hydrocarbon Processing,* August 1977, pp. 98–102. Lees, *Loss Prevention in the Process Industries,* 2 vols., Butterworths, London, 1980. Martinsen, Johnson, and Terrell, "BLEVEs: Their causes, effects, and prevention," *Hydrocarbon Process.*, vol. 65, no. 11, November 1986, pp. 141, 142, 146, 148. Pietersen, "Analysis of the LPG Disaster in Mexico City," presented at the *Societe de Chemie Industrielle 5th Int. Symp. on Loss Prev. and Safety Promotion in the Process Ind.*, Cannes, 1986, vol. 1, preprints, pp. (21) 1–15. Pikaar, "Unconfined Vapour Cloud Dispersion and Combustion: An Overview of Theory and Experiments," *Chem. Eng. Res. Des.*, vol. 63, no. 2, March 1985, pp. 75–81. Prugh and Johnson, *Guidelines for Vapor Release Mitigation,* AIChE/CCPS, New York, 1988. Prugh, "Quantify BLEVE Hazards," *Chem. Eng. Prog.*, vol. 87, no. 2, February 1991, pp. 66–72. Prugh, "Quantitative Evaluation of Fireball Hazards," *Process Safety Prog.*, vol. 13, no. 2, April 1994, pp. 83–91. TNO, *Methods for the Calculation of the Physical Effects of the Escape of Dangerous Materials: Liquids and Gases ("The Yellow Book"),* Apeldoorn, The Netherlands, 1979. Walls, "Just What Is a BLEVE?," *Fire J.*, vol. 72, no. 6, November 1978, pp. 46–47.

See also General References in "Gas Dispersion" in this section.

Unconfined Vapor Cloud Explosions (UVCEs)

Background Unconfined vapor cloud explosions (also known as vapor cloud explosions) in open air often result when accidental releases of vapors or gases to the atmosphere are ignited. Astonishingly high pressure can result from an unconfined vapor cloud explosion; 70 kPa (10 psi) or so may occur at the outer edge of the exploding cloud, with still higher pressures near the center of the blast. Numerous severe explosions of this nature have occurred in past years (Lenoir and Davenport, "A Survey of Vapor Cloud Explosions: Second Update," *Process Safety Prog.*, vol. 12, no. 1, January 1993, pp. 12–33). In a survey of property damage losses in 100 large losses in the hydrocarbon-chemical industries, M & M Protection Consultants of Marsh & McLennan found that a vapor cloud was the initiating mechanism in 43 percent of the cases. Releases of liquefied dense gases have caused many of the reported UVCEs. Such heavy gases tend to hug the ground with limited dispersion in ambient air; this condition results in accumulation of these gases where they can cause maximum casualties to people and damage to property, if ignited. Notwithstanding, releases of mammoth amounts of *compressed* natural gas from ruptured pipelines have caused vapor cloud explosions. As an example, in 1969 a 356-mm (14-in) pipeline carrying natural gas at more than 5378 kPa gauge (780 psig) ruptured; about 8 to 10 min later the escaping gas exploded violently (National Transportation Safety Board, *Pipeline Accident Report Mobil Oil Corporation, High-Pressure Natural Gas Pipeline Accident, Houston, Texas, September 9, 1969,* NTBS-Par-71-1, Washington, D.C., 1971).

Elevated emergency unflared releases with vents of sufficient height normally do not cause damaging overpressure at the ground, if accidentally ignited (Bodurtha, "Vent Heights for Emergency Releases of Heavy Gases," *Plant/Operations Prog.*, vol. 7, no. 2, April 1988, pp. 122–126).

Numerous tests on dispersion of heavy gases and on causes of UVCEs have been performed in recent years. Dispersion tests and computer models based on them may not be representative of all conditions at a plant, however, because of equipment plus heat sources that cause better spreading of a plume than is modeled in tests.

Moreover, vapors flashed from release of a liquefied gas will be cold; such vapors flowing over warmer ground may promote atmospheric instability with accompanying turbulence and, thereby, cause more mixing with ambient air than in some tests. In addition, some tests have been so-called meteorological area sources, while the dispersion equations are generally meteorological point sources. (Only concentrations relatively close to the location of discharge of the vapors will be affected by this difference in sources.) Also, the *momentary* concentration of a combustible gas or flammable vapor is the important duration of a concentration for UVCEs; not all dispersion models specify their averaging time of concentrations. Thus, *predictions of concentrations must be treated as estimates.*

Dispersion One way to determine concentrations is with a modified gaussian dispersion equation (Bodurtha, 1980). (See "Gas Dispersion" in this section for discussion of and references to other methods plus definition of atmospheric stabilities.) In that equation, *E* atmospheric stability is used for dense gases for all light to moderate wind speeds, whatever the actual atmospheric stability may be. The equation in Bodurtha (1980) overpredicts concentrations close to an emission source for a dense gas where the major effects of a UVCE are experienced, and, therefore, where uncertainty exists, is on the safe side. On the other hand, the modified gaussian equation underpredicts concentrations for dense gases at relatively large distances, and it should not be used for such gases beyond about 1000 m. Concentrations determined from the equation in Bodurtha (1980) are compared in Table 26-19 with concentrations of ammonia (which was dense by virtue of coldness) in Desert Tortoise Series Test #4 (Goldwire, "Large-Scale Ammonia Spill Tests," *Chem. Eng. Prog.*, vol. 82, no. 4, April 1986, pp. 35–41); wind speed is 4.5 m/s (10 mi/h); and vapor release rate for calculated values in the table is 108.8 m^3/s. (Calculated momentary concentrations include a *virtual source*, i.e., a fictitious upwind source so that concentrations equal 100 percent—and no more—at the release point.)

In assessing the hazard of a UVCE or in investigating a UVCE it is often necessary to (1) estimate the maximum distance to the lower flammable limit (LFL) and (2) determine the amount of gas in a vapor cloud above the LFL. Figure 26-31 shows the maximum distance to the lower flammable limit, i.e., in the centerline of the cloud, based on the previous method from Bodurtha (1980) for wind speeds of 1 m/s (2.2 mi/h) and 5 m/s (11 mi/h). Maximum concentrations probably occur near 1 m/s. The volume of fuel from the LFL up to 100 percent may be estimated by

$$V_f = 0.64 \cdot Q \cdot x_L/u \qquad (26\text{-}48)$$

where V_f = volume of fuel (no air) from the LFL up to 100%, m^3 at 25°C
Q = continuous dense vapor emission rate, m^3/s at 25°C
x_L = distance to momentary LFL in centerline of cloud, m
u = wind speed, m/s

For application of Eq. (26-48), x_L should not exceed 300 m (984 ft). The reason for selecting 100 percent, instead of the upper flammable limit (UFL), in the equation for V_f is that in an incipient explosion vapor above the UFL may be mixed with additional air and, thereby, contribute to explosion pressure.

TABLE 26-19 Comparison of Measured and Calculated Ammonia Concentrations in Ammonia Spill Tests

Distance from release, m	Measured concentrations by Goldwire, vol %	Calculated momentary concentrations,* vol %
200	4.9	11.6
300	4.0	7.2
500	3.0	3.6
800	2.1	1.8
1000	1.7	1.3

*From equation in Bodurtha, 1980.

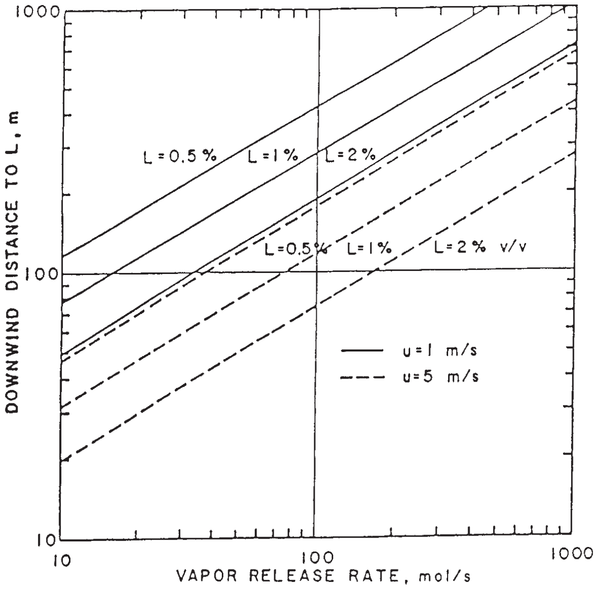


FIG. 26-31 Estimated maximum downwind distance to lower flammable limit *L*, percent by volume at ground level in centerline of vapor cloud, vs. continuous dense vapor release rate at ground level. *E* atmospheric stability. Level terrain. Momentary concentrations for *L*. Moles are gram moles; *u* is wind speed. (*From Bodurtha, 1980, p. 105, by permission.*)

Pressure Development Overpressure in a UVCE results from turbulence that promotes a sudden release of energy. Tests in the open without obstacles or confining structures do not produce damaging overpressure. Nevertheless, combustion in a vapor cloud within a partially confined space or around turbulence-producing obstacles may generate damaging overpressure. Also, turbulence in a jet release, such as may occur with compressed natural gas discharged from a ruptured pipeline, may result in blast pressure.

Example The combustion process in large vapor clouds is not known completely and studies are in progress to improve understanding of this important subject. Special study is usually needed to assess the hazard of a large vapor release or to investigate a UVCE. The TNT equivalent method is used in this example; other methods have been proposed. Whatever the method used for dispersion and pressure development, a check should be made to determine if any governmental unit requires a specific type of analysis.

Assume a continuous release of pressurized, liquefied cyclohexane with a vapor emission rate of 130 g mol/s, 3.18 m^3/s at 25°C (86,644 lb/h). (See "Discharge Rates from Punctured Lines and Vessels" in this section for release rates of vapor.) The LFL of cyclohexane is 1.3 percent by vol., and so the maximum distance to the LFL for a wind speed of 1 m/s (2.2 mi/h) is 260 m (853 ft), from Fig. 26-31. Thus, from Eq. (26-48), $V_f \approx 529$ m^3 ≈ 1817 kg. The volume of fuel from the LFL up to 100 percent at the moment of ignition for a continuous emission is *not* equal to the total quantity of vapor released; that V_f *volume stays the same even if the emission lasts for an extended period* with the same values of meteorological variables, e.g., wind speed. For instance, in this case 9825 kg (21,661 lb) will have been emitted during a 15-min period, which is considerably more than the 1817 kg (4005 lb) of cyclohexane in the vapor cloud above LFL. (A different approach is required for an instantaneous release, i.e., when a vapor cloud is explosively dispersed.) The equivalent weight of TNT may be estimated by

$$W_{\mathrm{TNT}} = \frac{0.01 \cdot \alpha \cdot H_c \cdot W_c}{4.52} \qquad (26\text{-}49)$$

where W_{TNT} = equivalent weight of TNT, kg
α = explosion efficiency of UVCE, %

H_c = lower heat of combustion of flammable vapor, MJ/kg
W_c = weight of flammable vapor between LFL and 100% for continuous release, kg

and energy of detonation of TNT = 4.52 in MJ/kg.

The explosion efficiency α is difficult to assess; it appears that the maximum efficiency for vapor between the LFL and 100 percent, as in this example, is 10 to 20 percent. So, for this case with α = 10 percent, H_c for cyclohexane = 43.84 MJ/kg, and W_c = 1817 kg, the W_{TNT} = 1762 kg. Thus, 1 kg of cyclohexane, or generally any hydrocarbon at 10 percent explosion efficiency, equals 1 kg TNT. Overpressure may be estimated from "Guidelines for Estimating Damage" in this section. (See "Guidelines for Estimating Damage Explosion" by Brasie and Simpson and "Guidelines for Evaluating the Characteristics of Vapor Cloud Explosions, Flash Fires and BLEVEs," New York, 1994, in General References for other procedures.)

Prevention and Protection It is difficult to cope with a potential UVCE once an accidental release has occurred. Consequently, *the best procedure to guard against a UVCE is to prevent the release in the first place.* Safe piping is essential to protect against UVCEs. Forty percent of all major plant losses are due to piping failures, and corrosion is one of the largest single causes of plant and equipment breakdown (Hancock, "Safer Piping: Awareness Training for the Process Industries," *Plant/Oper. Prog.*, vol. 9, no. 2, April 1990, pp. 114–116). Moreover, mistakenly open valves that caused mammoth emissions of hydrocarbons have resulted in two major UVCEs with a total of 29 deaths in those two instances. Thus, close scrutiny regarding piping and valves is mandatory to help prevent UVCEs. Some other protection methods are summarized as follows.

Remotely Operated Shutoff Valves These should be considered for supply lines and other vulnerable pipelines. Excess flow valves that close when flow exceeds a set amount are possible substitutes, but they are not acceptable to some operators.

Flammable Vapor Detectors These should be installed to warn of leaks, although such devices do not effectively control UVCEs with sudden, massive releases.

Elevated or Remote Air Intakes Elevated or remote air intakes for control rooms will help in reducing ingress of dense, flammable vapors into those rooms. Ordinarily, elevating the tip of the air intake duct 9 m (30 ft) above the ground is sufficient. Installing flammable vapor detectors in the air intake ducts provides additional protection. Controls that automatically stop air to control rooms if vapor concentrations reach 25 percent of their LFL should also be considered.

Intentional Ignition Intentional ignition to ignite a vapor cloud early before it spreads out to a large volume has been used or considered only rarely. Such ignition should not be employed for control of UVCEs solely without thorough study of the ramifications of its use. (In some infrequent cases when the gas is both flammable and particularly toxic, intentional ignition may be warranted.)

Large Fans These could be used to dilute a vapor cloud below its LFL with ambient air (see, for example, Whiting and Shaffer, "Feasibility Study of Hazardous Vapor Amelioration Techniques," *Proc. 1978 Nat. Conf. on Control of Hazardous Material Spills,* USEPA, Miami Beach, April 1978). But caution must be exercised because the turbulence produced by fans will likely promote rapid combustion and a resulting UVCE unless vapors are diluted below the LFL. Nevertheless, in new plants, strategic placement of air coolers may provide enough air flow to reduce the risk of a UVCE.

Water Sprays and Steam Curtains These have been used and/or advocated to help protect against a UVCE. Such devices entrain air to dilute a vapor cloud. Also, some claim that water curtains form a physical barrier to stop the flow of the vapor cloud. As with large fans, vapors need to be reduced below LFLs to decrease the possibility of UVCEs from enhanced turbulence by the sprays or curtains. Moodie studied water spray barriers using carbon dioxide to approximate a heavy, flammable vapor cloud (Moodie, "The Use of Water Spray Barriers to Disperse Spills of Heavy Gases," *Plant/Oper. Prog.*, vol. 4, no. 4, October 1985, pp. 234–241). He used CO_2 rates of 2 and 4.2 kg/s (15,859 and 33,304 lb/h). (Propane would give the same vapor rates as these CO_2 weight rates.) There may be an upper practical limit for the emission rate of heavy gases that can be effectively dispersed by water sprays or steam curtains (Seifert, Maurer, and Giesbrecht, "Steam Curtains—Effectiveness and Electrostatic Hazards," presented at the *Institution of Chemical Engineers 4th Int. Symp. on Loss Prevention and Safety Promotion in the Process Ind.*, Harrogate, England, 1983, vol. 1, preprints, pp. F1–F12). In any event, this equipment could be useful near known ignition sources, such as furnaces, to guard against a UVCE. Steam will be electrically charged with steam curtains. Care must be taken to assure that nearby electrical conductors are grounded. If not, the conductor could obtain an electrostatic charge from the steam and cause an incendiary spark for ignition of the vapor cloud.

Release of a pressurized, liquefied gas to the atmosphere will cause the gas to cool and condense water vapor in ambient air, forming a visible vapor cloud. Firefighters and operators who attempt to move such a cloud away from furnaces and the like with fire hoses and water jet guns are at risk, because of the possibility of a UVCE near them. Plants and governmental agencies who recommend such practices need to reexamine their policies.

Structures Structures that include partially confined spaces and turbulence-producing obstacles such as pipe bridges plus closely packed equipment, promote UVCEs. This undesirable architecture—relative to UVCEs—is often a product of congestion on a plant. Congestion is an enemy of safety. Thus, the probability of a UVCE, plus property losses and casualties, will likely be greater at a congested plant than at an uncongested site.

Vapor cloud explosions also occur indoors when large amounts of flammable vapors are discharged accidentally into buildings. Turbulence from the myriad of equipment and piping in an operating building likely cause a sudden release of energy for the room-air explosion. As one of several examples, seven were killed when vinyl chloride exploded in a building after failure of a sight glass (Walls, "Vinyl Chloride Explosion," *Natl. Fire Prot. Assoc. Q.*, vol. 57, no. 4, April 1964, pp. 352–362).

Strong Buildings Strong buildings may be prudent where people congregate, such as control rooms. For new plants, serious consideration must be given to stronger design of buildings that are vulnerable to a UVCE, compared to past designs.

BLEVEs can occur when a vessel containing a liquid above its atmospheric boiling point ruptures. The resulting ultrarapid vaporization of much of the liquid results in fire, if the liquid is flammable, plus overpressure. (Initial catastrophic failure of the vessel must occur for a BLEVE; the opening of a relief valve does not cause a BLEVE, nor does it necessarily protect against one.) BLEVE overpressure has occurred with pressurized *nonflammable* liquids, such as chlorine and carbon dioxide (Clayton and Griffin, "Catastrophic Failure of a Liquid Carbon Dioxide Storage Vessel," *Process Safety Prog.*, vol. 13, no. 4, October 1994, pp. 202–209).

Cause As discussed by Prugh (1991) and others, BLEVES can occur from:

1. Mechanical damage caused, for example, by corrosion or collision
2. Overfilling and no relief valve
3. Runaway reaction or polymerization—e.g., vinyl chloride monomer (Kim-E and Reid, "The Rapid Depressurization of Hot, High Pressure Liquids or Supercritical Fluids," chap. 3, in M. E. Paulaitis et al., eds., *Chemical Engineering at Supercritical Fluid Conditions,* Ann Arbor Science, 1983, pp. 81–100)
4. Overheating with an inoperative relief valve
5. Vapor-space explosion
6. Mechanical failure
7. Exposure to fire

A common cause of a BLEVE in plants of the hydrocarbon-chemical industry is exposure to fire. With an external fire below the liquid level in a vessel, the heat of vaporization provides a heat sink, as with a teakettle; evolved vapors exit through the relief valve. But if the flame impinges on the vessel above the liquid level, the metal will weaken and may cause the vessel to rupture suddenly, even with the relief valve open. The explosive energy for a BLEVE comes from superheat. This energy is at a maximum at the superheat limit temperature. (SLT is the maximum temperature to which a liquid can be heated before homogeneous nucleation occurs with explosive vaporization of the liquid and accompanying overpressure.) The SLT depends on the final pressure attained, and with letdown to 1 atm, it may be estimated by the simple relationship (Porteous and Reid, "Light Hydrocarbon Vapor Explosions," *Chem. Eng. Prog.*, vol. 72, May 1976, pp. 83–89):

$$\text{SLT} = 0.89\ T_c \tag{26-50}$$

where T_c is the critical absolute temperature. With propane, for example, SLT from Eq. (26-50) = 57°C, only a degree or so higher than the measured value (Reid, in *Advances in Chemical Engineering*, vol. 12, Academic Press, New York, 1983).

Fireballs Giant hazardous fireballs result from large BLEVEs. Several formulas for BLEVE physical parameters and thermal radiation hazards have been summarized by the Center for Chemical Process Safety (CCPS) of the American Institute of Chemical Engineers and by Prugh. (See AIChE/CCPS, 1989; Prugh, 1994.) For the maximum fireball diameter, $D_{\max}$ in meters, CCPS has selected

$$D_{\max} = 6.48\ M^{0.325} \tag{26-51}$$

where M is the initial weight of the flammable liquid, in kilograms. Thus, the maximum diameter of a propane fireball from an initial propane weight of 150 metric tons (150,000 kg = 330,690 lb) is 312 m (1024 ft).

Overpressure Significant blast overpressures result from BLEVEs. In addition, portions of ruptured tanks may rocket large distances with clear danger to firefighters and innocent onlookers. In one test it was reported that the BLEVE blast overpressure before ignition about 10 m (33 ft) away from an exploding tank initially containing 450 kg (992 lb) propylene was 75 kPa gauge (10.9 psi). Assuming that pressure to be incident (side-on) blast pressure, it can be determined from Fig. 26-9 that $W_{\text{TNT}} = 23.3$ kg (51.4 lb), i.e., about 5 percent of the initial weight of propylene.

Prevention and Protection Several methods may be used to protect against the causes of BLEVEs itemized earlier in this part of Section 26. They include thermal insulation, water cooling, depressuring facilities, corrosion control, and ground sloping (see Kletz, 1977; Martinsen et al., 1986; Prugh, 1991). A desirable diking method with ground sloping to minimize impingement of flame on a tank is shown in Fig. 26-32.

Fauske has suggested two passive designs for prevention of BLEVEs (Fauske, "Preventing Explosions During Chemicals and Materials Storage," *Plant/Oper. Prog.* vol. 8, no. 4, October 1989, pp. 181–184). One method keeps a normally unwetted internal surface of a tank wet; the second surrounds the high-pressure storage tank with an open atmospheric tank filled with water. Additional BLEVE prevention and protection methods follow.

1. *Minimize inventory* to the extent feasible. Expected benefits from minimum inventory may be offset by hazards resulting from more frequent and smaller shipments. The relative hazards should be reviewed (Englund, "Design and Operate Plants for Inherent Safety—Part 1," *Chem. Eng. Prog.*, vol. 87, no. 2, March 1991, pp. 85–91).
2. *Consider refrigerated storage* at atmospheric pressure. A BLEVE cannot occur with the liquid at its atmospheric boiling point (no superheat), although a fire hazard may still exist. The Dow Chemical Company in Texas stores chlorine as a liquid at atmospheric pressure at about −34°C (Englund, ibid. 1991).
3. *Set the safety relief valve* to open as far below the pressure corresponding to the SLT at 1 atm as is feasible (Reid, "Possible Mechanism for Pressurized-Liquid Tank Explosions or BLEVE's," *Science,* vol. 23, March 23, 1979, pp. 1263–1265). The pressure at propane's SLT of 57°C is 2000 kPa abs. (290 psia = 275 psig).
4. *Eliminate turned-down vents* from safety relief valves, i.e., upside down U. Possible accidental ignition of releases from such vents will likely result in flame impingement on the top external surface of the tank, above the internal wetted surface. BLEVE! Some means to handle rainwater from a desirable upward vertical vent have been listed by Bodurtha (ibid., April 1988). Moreover, a safety relief valve must function properly when required and must be sized properly to help prevent an explosion.

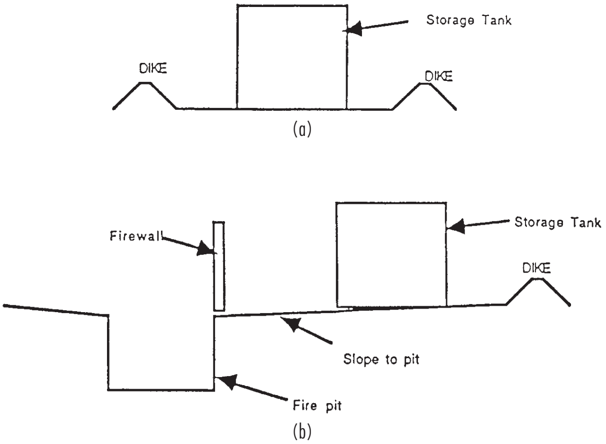


FIG. 26-32 Methods of diking for flammable liquids: (*a*) traditional diking method allows leaks to accumulate around the tank. In case of fire, the tank will be exposed to flames that can be supplied by fuel from the tank and will be hard to control. (*b*) In the more desirable method, leaks are directed away from the tank. In case of fire, the tank will be shielded from most flames and fire will be easier to fight. (*From Englund, in* Advances in Chemical Engineering, *vol. 15, Academic Press, San Diego, 1990, pp. 73–135, by permission.*)

DUST EXPLOSIONS

GENERAL REFERENCES: Bartknecht, *Dust Explosions,* Springer, New York, 1989. Bartknecht, *Explosionsschutz* (Explosion Protection), Springer, Berlin, 1993. Crowl/Louvar, *Chemical Process Safety,* Prentice Hall, New Jersey, 1990. "Dust Explosions," *28th Annual Loss Prevention Symposium,* Atlanta, Georgia, 1994. Eckhoff, *Dust Explosions in the Process Industries,* Butterworth-Heinemann, London 1991. *Health, Safety and Loss Prevention in the Oil, Chemical and Process Industries,* Butterworth-Heinemann, Singapore, 1993. NFPA 69, *Standard on Explosion Prevention Systems,* 1992. VDI-Report 975, *Safe Handling of Combustible Dust,* VDI-Verlag GmbH, Düsseldorf, 1992. VDI-Guideline 2263, *Dust Fires and Dust Explosions,* Beuth Verlag, Berlin, 1992.

Definition of Dust Explosion A dust explosion is the rapid combustion of a dust cloud. In a confined or nearly confined space, the explosion is characterized by relatively rapid development of pressure with a flame propagation and the evolution of large quantities of heat and reaction products. The required oxygen for this combustion is mostly supplied by the combustion air. The condition necessary for a dust explosion is a simultaneous presence of a dust cloud of proper concentration in air that will support combustion and a suitable ignition source.

Explosions are either deflagrations or detonations. The difference depends on the speed of the shock wave emanating from the explosion. If the pressure wave moves at a speed less than or equal to the speed of sound in the unreacted medium, it is a *deflagration;* if it moves faster than the speed of sound, the explosion is a *detonation.*

The term *dust* is used if the maximum particle size of the solids mixture is below 500 µm.

In the following, only dusts are called combustible in the airborne state if they require oxygen from the air for exothermic reaction.

Glossary

activation overpressure, P_a That pressure threshold, above the pressure at ignition of the reactants, at which a firing signal is applied to the suppressor(s).

cubic low The correlation of the vessel volume with the maximum rate of pressure rise. $V^{1/3} \cdot (dP/dt)_{\max} = \text{constant} = K_{\max}$

dust Solid mixture with a maximum particle size of 500 µm.

dust explosion class, St Dusts are classified in accordance with the $K_{\max}$ values.

equivalent ignition energy (EIE) The amount of energy which, when transformed into an electrical spark discharge, has the same incendivity as the ignition source under characterization.

explosion Propagation of a flame in a premixture of combustible gases, suspended dust(s), combustible vapor(s), mist(s), or mixtures thereof, in a gaseous oxidant such as air, in a closed, or substantially closed, vessel.

explosion pressure resistant (EPR) Design of a construction following the calculation and construction directions for pressure vessels.

explosion pressure-shock resistant (EPSR) Design of a construction allowing greater utilization of the material strength than the EPR design.

limiting oxygen concentration (LOC) Maximum oxygen concentration in a mixture of a combustible and air and inert gas, in which an explosion will not occur.

maximum explosion overpressure, $\mathbf{P}_{max}$ The maximum pressure reached during an explosion in a closed vessel through systematically changing the concentration of dust-air mixture.

maximum reduced explosion overpressure, $\mathbf{P}_{red,max}$ The maximum pressure generated by an explosion of a dust-air mixture in a vented or suppressed vessel under systematically varied dust concentrations.

maximum explosion constant, $\mathbf{K}_{max}$ Dust and test-specific characteristic calculated from the cubic law. It is equivalent to the maximum rate of pressure rise in a 1-m^3 vessel.

maximum rate of pressure rise, $(\mathbf{dP/dt})_{max}$ The maximum rate of pressure rise obtained in a closed vessel through systematically changing the concentrations of a dust-air mixture.

minimum ignition energy (MIE) Lowest electrical energy stored in a capacitor which, upon discharge, is just sufficient to effect ignition of the most ignitable atmosphere under specified test conditions.

minimum ignition temperature (MIT) The lowest temperature of a hot surface on which the most ignitable mixture of the dust with air is ignited under specified test conditions.

static activation overpressure, $\mathbf{P}_{stat}$ Pressure which activates a rupture disk or an explosion door.

***vent area,* A** Area of an opening for explosion venting.

venting capability, EF Measure to evaluate the efficiency of the pressure relief device in comparison with a rupture disk with the same vent area.

Prevention and Protection Concept against Dust Explosions Explosion protection encompasses the measures implemented against explosion hazards in the handling of combustible substances and the assessment of the effectiveness of protective measures for the avoidance or dependable reduction of these hazards. The explosion protection concept is valid for all mixtures of combustible substances and distinguishes between:

1. Measures which prevent or restrict formation of a hazardous, explosible atmosphere
2. Measures which prevent the ignition of a hazardous, explosible atmosphere
3. Constructional measures which limit the effects of an explosion to a harmless level

From a safety standpoint, priority must be given to the measures in item 1. Group 2 cannot be used as a sole protective measure for flammable gas or solvent vapors in industrial practice with sufficient reliability, but can be applied as the sole protective measure when only combustible dusts are present if the minimum ignition energy of the dusts is high (>10 mJ) and the operating areas concerned can easily be monitored.

If the measures under (1) and (2), which are also known as *preventive measures,* cannot be used with sufficient reliability, the *constructional measures* (3) must be applied.

Preventive Explosion Protection The principle of preventive explosion protection comprises the reliable exclusion of one of the requirements necessary for the development of an explosion. In pictorial terms, therefore, at least one of the sides of the hazard triangle shown in Figure 26-33 will be broken open.

An explosion can thus be excluded with certainty by:

- Avoiding the development of explosible mixtures
- Replacing the atmospheric oxygen by *inert gas,* working in a vacuum, or using *inert dust*
- Preventing the occurrence of effective ignition sources

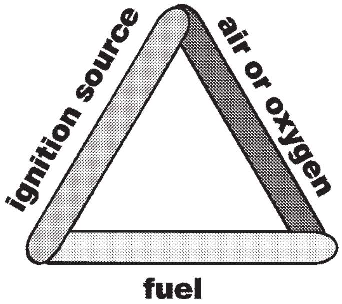


FIG. 26-33 Hazard triangle: principle of preventive explosion protection.

Avoidance of Explosible Combustible Substance-Air Mixtures For combustible dusts, the explosibility limits do not have the same meaning as with flammable gases and flammable vapors, owing to the interaction between dust layers and suspended dust. This protective measure can, for example, be used when dust deposits are avoided in operating areas or in the air stream of clean air lines after filter installations where in normal operation the lower explosibility limit is not reached. However, dust deposits must be anticipated with time. When these dust deposits are whirled up in the air, an explosion hazard can arise. Such a hazard can be avoided by regular cleaning. The dust can be extracted directly at its point of origin by suitable ventilation measures.

Avoidance of Explosions through Inerting The introduction of inert gas in the area to be protected against explosions lowers the oxygen volume content below the limiting oxygen concentration (LOC) so that ignition of the mixture can no longer take place. This process is called *inerting.*

One has to be aware of the danger of asphyxiation from gases in inerted equipment. This is also important for surrounding areas in case of major leaks.

Inerting is *not* a protective measure to avoid exothermic decompositions. For the avoidance of (smoldering) fires, oxygen concentrations lower than the LOC must usually be adhered to and must be determined from case to case. In addition to the nitrogen normally used, all nonflammable gases which do not support combustion or react with the combustible dust can be considered for use as the inert gas. The inerting effect generally decreases in the following order: carbon dioxide → water vapor → flue gas → nitrogen → noble gases. In special gases, liquid nitrogen or dry ice is used.

The LOC depends upon the combustible material and the type of inert gas used. It decreases with increased temperature and pressure. A distinction has to be made between the determined LOC value and the concentration which results by subtracting a safety margin.

The maximum allowable oxygen concentration (MAOC), which is, in general, 2 vol % below the LOC, has to include the following considerations: fluctuation in oxygen concentrations due to process and breakdown conditions per time and location, as well as the requirement for protective measures or emergency measures to become effective. In addition, a concentration level for an alarm has to be set below the MAOC.

For example, in rotary vacuum dryers it is possible to prevent the formation of explosible dust-air mixtures by setting and monitoring a certain partial vacuum (negative pressure). This pressure value must be determined by experiment for each type of dust. With pressures of less than 0.1 bar, in general, hazardous effects of dust explosions need not be anticipated. If the vacuum system malfunctions, the partial vacuum must be released by inert gas and the installation shut down.

Explosible dusts can also be changed into mixtures which are no longer explosible by the addition of inert dusts (e.g., rock salt, sodium sulfate). In general, inert dust additions of more than 50 wt % are necessary here. It is also possible to replace flammable solvents and cleaning agents by nonflammable halogenated hydrocarbons or water, or flammable pressure transmission fluids by halocarbon oils.

Avoidance of Effective Ignition Sources Explosions can be prevented if ignition sources capable of igniting combustible material-air mixtures can successfully be avoided. A distinction is made between *trivial ignition sources* (e.g., welding, smoking, cutting) and *ignition sources expected if operational malfunctions occur* (e.g., mechanically generated sparks, mechanically generated hot surfaces, lumps of smoldering material, static electricity). Trivial ignition sources can also reliably be excluded by organizational measures such as the systematic employment of permits.

For every installation, a check has to be made to determine which ignition source may become effective and whether it can be prevented with a sufficient degree of safety. With more sensitive products and complex installations, it becomes more and more difficult to exclude ignition sources with ample safety (Siwek et al., "Ignition Behavior of Dusts," *Proc. Loss Prevention Symposium,* Atlanta, April 12–19, 1994).

Mechanically generated sparks and *resultant hot surfaces* together are regarded as one of the more important causes of ignition in industrial practice. With mechanically generated sparks, a distinction is made between grinding, impact, and friction sparks which are formed by brief contact (<5 s) between materials. Mechanically generated hot surfaces, on the other hand, are formed by relatively long rubbing (>>5 s) against steel. The hot surfaces show considerably better incendivity in comparison with the short-lived mechanically generated sparks. Neither ignition source appears in industrial practice from the normal metallic materials of construction rubbing against each other or against stone if the relative circumferential speeds v_c are less than or equal to 1 m·s^{-1} (see Table 26-20). This is not valid for cerium-iron, titanium, and zirconium.

TABLE 26-20 Influence of Relative Circumferential Speeds v_c on Danger of Ignition for Combustible Dusts

$v_c \leq 1$ m·s^{-1}	There is no danger for ignition.
$v_c > 1$ .. 10 m·s^{-1}	Every case has to be judged separately, considering the product and material-specific characteristics.
$v_c > 10$ m·s^{-1}	In every case there is danger for ignition.

The ignition behavior of mechanically generated sparks in dust-air mixtures depends on the *minimum ignition energy* (MIE) and the *minimum ignition temperature* (MIT) of the dust in question. The ignition effectiveness of mechanically generated sparks decreases from *steel-friction sparks* to *steel-grinding sparks* to *aluminum/rust-impact sparks.* According to Fig. 26-34, it can be stated that the type of spark-producing material, together with the MIT and the MIE requirement, determines whether an ignition of dust-air mixture has to be anticipated from friction, grinding, or impact sparks. The mechanically generated sparks can thus be assigned different equivalent ignition energies toward dust-air mixtures with an MIT of less than or equal to 500°C. For example, if the MIT of a dust is 300°C, steel-friction sparks can ignite this dust only with an MIE (equivalent energy) up to 3000 mJ. The equivalent energy, also known as the *equivalent ignition energy* (EIE), is the amount of energy which, when transformed into an electrical spark discharge, has the same incendivity as the sparks shown in Fig. 26-34.

Mechanically generated hot surfaces represent an ignition hazard if, irrespective of the MIT and the MIE, the *surface temperature* is 1100°C or higher and the *hot surface area* by itself is large enough (see Fig. 26-35). Higher surface temperatures and larger surfaces have a better incendivity; lower temperatures and smaller surfaces have a poorer incendivity.

Lumps of smoldering material always represent a hazard when the dust can be classed as capable of forming such lumps; i.e., its burning behavior class at 100°C is greater than 3. A smoldering lump surface of a cube, $A_o = 9600$ mm^2, and a surface temperature, $T_o = 900$°C, is sufficient to ignite the mixtures of dusts with an MIT of less than 600°C (see Fig. 26-35). Higher surface temperatures and larger surfaces have a better incendivity; lower temperatures and smaller surfaces, a poorer incendivity.

An *electrostatic ignition source* (see also material on static electricity) which follows an electrostatic discharge can be incendive when the energy released is equal to or greater than the minimum ignition energy of a mixture. The energy released depends, among other things, on the type of discharge. This in turn depends on the geometry and material of the participating surfaces as well as on certain other conditions. The following overview summarizes the ignition behavior of several types of electrostatic discharges (see Table 26-21).

The experimental investigations of numerous dusts with different ignition sources have shown that the incendivity of an ignition source is not only influenced by its energy content, but the nature of the source also plays a role (Glor et al., "Recent Developments in the Assessment of Electrostatic Hazards Associated with Powder Handling," *Proc. 8th Int. Symposium Loss Prevention and Safety Promotion in the Process Industries,* Antwerp, Elsevier, Amsterdam, 1995). The minimum ignition energy determined by the standard procedure can also be used for the assessment of the incendivity of such ignition sources.

Brush Discharge With dusts with MIE values of less than 3 mJ determined with purely capacitive spark discharges (without induc-

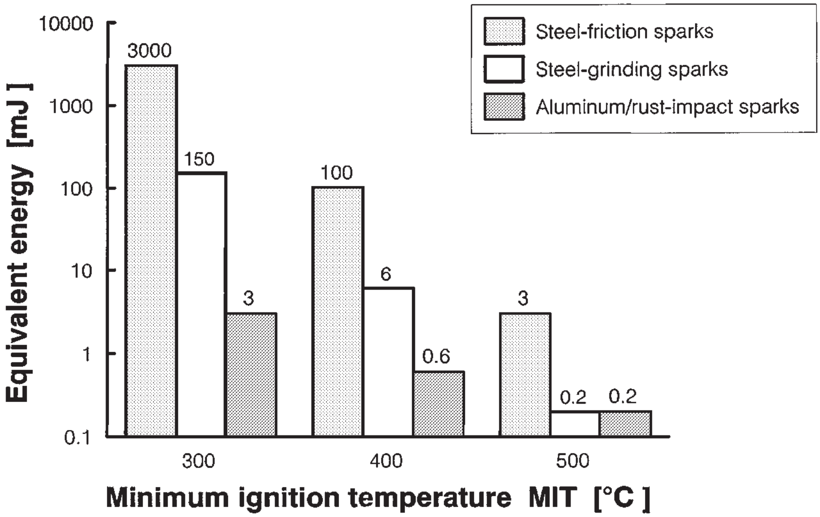


FIG. 26-34 Equivalent energies of mechanically generated sparks.

TABLE 26-21 Examples of Different Types of Electrostatic Discharges

Ignition sources	Requirement for formation	Incendivity for
Brush discharge	A nonuniform electric field between a charged dielectric and a conductor that has a moderate radius of curvature	MIE < 3 mJ
Bulk surface discharge	In rapid heaping of highly insulated bulk material, particularly when coarse material (diameter ≥ 1 mm) is present	MIE < 1 J (silo diameter 3 m)
Spark discharge	Ungrounded, conductive object	MIE < 1 J
Propagating brush discharge	Very high charging of nonconductive material, preferably in contact with a conductive surface	MIE < 10 J

tance), an ignition by brush discharges cannot be excluded with certainty. With such *extremely easily ignitable* dusts, the use of the protective measure, "avoidance of effective ignition sources," by itself is generally not sufficient. In this case, the brush discharge must also be considered as an ignition source, although it is normally important only for gases and vapors. For such dusts, the protective measure, "inerting" or "constructional explosion protection," must be used during large-scale handling operations. Toward dust-air mixtures, the brush discharges are assigned an equivalent ignition energy EIE ≤ 3 mJ for safety considerations.

Bulk Surfaces Discharge (Conical Pile Discharge) These discharges may also be generated with fine powder and not just with granules, as was previously assumed. These discharges from fine powder have, however, a much less equivalent ignition energy EIE compared to those associated with granules. The energy of conical pile discharges increases with increasing silo diameter. The probability of their occurrence increases with increasing charge-to-mass ratio in the powder and increasing mass filling rate. Findings to date show that the EIE of conical pile discharges using highly insulating granules for generating the discharges toward dust-air mixtures is about 1 J if the silo diameter is restricted to 3 m. Because of the large diameters, the granules generating the discharges are unlikely to give dust explosions; therefore, a possible explosion hazard must be associated with the simultaneous presence of an explosible cloud of an additional, fine dust fraction. This may be the explanation for why the frequency of the occurrence of an explosion in silos initiated by bulk surfaces discharges is relatively low.

Sparks Discharge Spark discharges can ignite dust-air mixtures up to an MIE of 1 J. If an uncertainty area is taken into account, this corresponds to an EIE of 1 to 10 J.

Propagating Brush Discharge The incendivity of the propagating brush discharge is so large that an ignition of dust-air mixtures with an MIE up to around 100 J must be anticipated. For dust-air mixtures, this corresponds to an EIE range of 10 to 100 J.

For industrial practice, the following principles have resulted for the protective measures to be implemented. Their application is selective and depends on the prevailing circumstances.

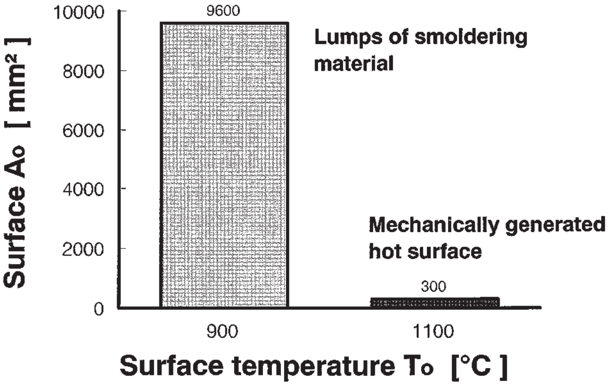


FIG. 26-35 Equivalent energies of mechanically generated hot surfaces and lumps of smoldering material.

- Ground all conductors.
- Ground people.
- Prevent and reduce charging by use of conductive materials.
- Keep conveying speeds low.

If difficulties arise in the avoidance of electrostatic ignition sources, the advice of experts must be sought.

Explosion Protection through Design Measures In applying design measures, the possibility of an explosion is not prevented. Therefore, all exposed equipment has to be built to be explosion pressure resistant, in order to withstand the anticipated explosion pressure. The anticipated explosion pressure may be the maximum explosion overpressure or the maximum reduced explosion overpressure. In addition, any propagation of an explosion to other parts or process areas has to be prevented. Depending on the anticipated explosion pressure, a distinction is made between the following explosion-pressure-resistant designs:

- Capable of withstanding the *maximum* explosion overpressure
- Capable of withstanding an explosion overpressure *reduced* by explosion suppression or explosion venting

The strength of the protected vessels or apparatus may be either explosion pressure resistant or explosion pressure shock resistant.

Constructional measures which restrict the effects of an explosion to a safe level are always necessary when the goal of avoiding explosions cannot be achieved—or at least not with sufficient reliability—through the use of preventive explosion protection. This ensures that people are not injured and further that the protected equipment is usually ready for operation a short time after an explosion. All endangered equipment parts must thus have an *explosion-resistant* construction and withstand the overpressure expected if an explosion occurs. A distinction is made between the *explosion-pressure-resistant* (EPR) and *explosion-pressure-shock-resistant* (EPSR) construction of vessels and silos. Design of the EPR construction is implemented following the calculation and construction directions for pressure vessels, e.g., the ASME pressure vessel code. The EPSR construction allows greater utilization of the material strength (see Figs. 26-36 and 26-37).

For the EPR design, the ASME pressure vessel code requires design to be done at two-thirds of the alloy's yield strength (see Fig.

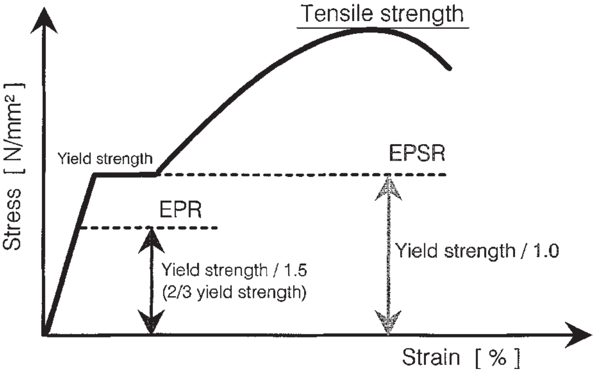


FIG. 26-36 Schematic drawing of stress-strain curve for plate steel.

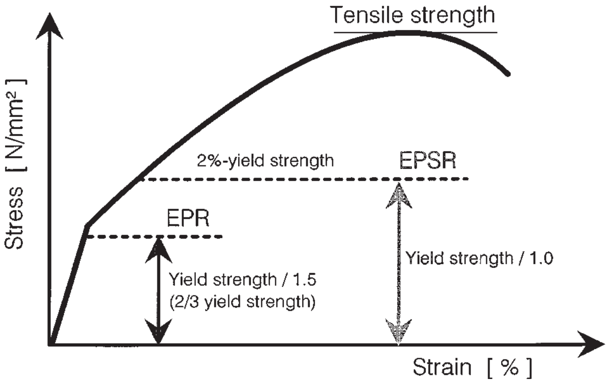


FIG. 26-37 Schematic drawing of stress-strain curve for austenitic stainless steels.

26-36). At such low stresses, there would be no permanent deformation of an ASME code vessel subjected to an explosion overpressure.

For EPSR design, the stress level to contain an explosion is set at the yield strength, a design factor of 1. Thus, for an alloy, the design stress level would be about 1.5 times the ASME code design stress. So a pressure vessel rated at 6 bar for the ASME code (EPR) would have an EPSR rating of 9 bar.

For stainless steel, the stress-strain curve (see Fig. 26-37) has no sharp yield point at the upper stress limit of elastic deformation. Yield strength is generally defined as the stress at 2 percent elongation.

There is still a substantial safety margin up to the ultimate tensile strength, which amounts to 60 to 90 percent, depending on the steel (Kirby, Siwek, "Preventing Failures of Equipment Subject to Explosions," *Chemical Engineering*, June 23, 1986).

Despite the use of explosion-pressure-resistant equipment for the full explosion pressure or other design measures outlined later, everything possible must be done to prevent effective ignition sources, because loss of product and interruption of production are equally undesirable.

Containment (Explosion-Pressure-Resistant Design for Maximum Explosion Overpressure) An explosion-resistant construction is understood to mean the possibility of designing vessels and equipment for the *full maximum explosion overpressure*, which is generally of the order $P_{\max} = 9$ bar. The explosion-resistant vessel can then be designed as explosion pressure resistant or explosion pressure shock resistant. This protective measure is generally employed when small vessel volumes need to be protected, such as small filter units, fluidized-bed dryers, cyclones, rotary valves, or mill housings.

One has to consider that all connected devices must also withstand the maximum explosion overpressure.

Explosion Venting (Explosion-Pressure-Resistant Design for Maximum Reduced Explosion Overpressure with Explosion Venting) The concept of explosion venting encompasses all measures used to open the originally closed vessels and equipment either briefly or permanently in a nonhazardous direction following an explosion. *Explosion venting is inadmissible when the escape of toxic or corrosive, irritating, carcinogenic, harmful-to-fruit, or genetically damaging substances is anticipated.* In contrast to the closed vessel, explosions in a vented vessel are characterized by the maximum reduced explosion overpressure $P_{\text{red,max}}$ instead of the maximum explosion overpressure $P_{\max}$ (see Fig. 26-38) and by the maximum reduced rate of pressure rise $(dP/dt)_{\text{red,max}}$ instead of the maximum rate of pressure rise $(dP/dt)_{\max}$.

By this method, in general, the expected inherent maximum explosion overpressure of the order $P_{\max} = 7$ to 10 bar will be reduced to a value of $P_{\text{red,max}} < 2$ bar. In this case, the static activation overpressure of the venting device is $P_{\text{stat}} \leq 0.1$ bar. The resulting $P_{\text{red,max}}$ may not exceed the design pressure of the equipment. The explosion as such is not prevented; only the dangerous consequences are limited. However, subsequent fires must be expected.

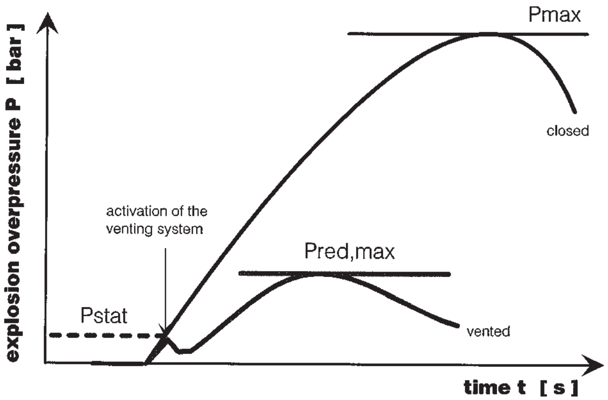


FIG. 26-38 Pressure behavior vs. time for a normal and a vented explosion.

Rupture disks or explosion doors may be used as venting devices. Safety valves are not suitable for this purpose. Obviously, the static activation overpressures P_{stat} of the venting devices have to be equal to or smaller than the strength of the equipment to be protected (corresponding to the $P_{\text{red,max}}$).

Rupture disks—for example, plastic foil or aluminum foil—have a low mass and will respond almost without inertia once the activation pressure is exceeded. They can be installed independently of the location and guarantee a dust-tight closure. In case of an explosion they will free the whole area after their destruction. Common materials of construction for rupture disks are metal or alloys. Rupture disks may be combined with signaling devices—for example, ripping wires—which will trigger a shutdown or a controlling mode. Only these rupture disks are to be used that are restrained through design measures.

Explosion doors open in case of an explosion, thereby releasing the vent area. Depending on the application, explosion doors may be selected which remain open or close automatically after releasing the explosion.

The inertia, the opening behavior of the movable cover of the explosion door, and its arrangement (horizontal, vertical) can affect the venting efficiency EF. This results in a higher maximum explosion overpressure $P_{\text{red,max}}$ in the protected vessel (see Fig. 26-39).

The venting capability EF and therefore the effective vent area A_w of the explosion door is normally smaller than the capability of a plastic or aluminum foil rupture disk with the same area. Therefore, such devices need testing to determine the mechanical strength before actual use, and the venting capability or the pressure rise, respectively,

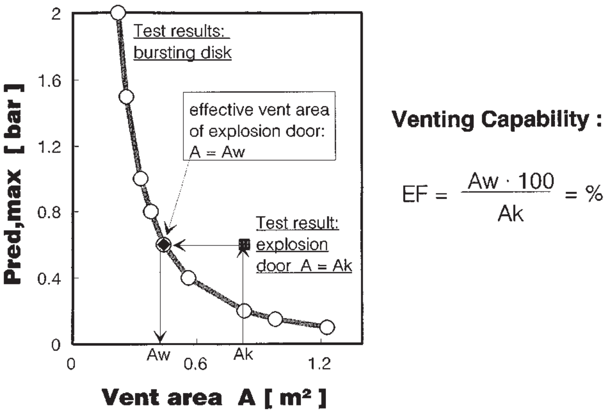


FIG. 26-39 Definition of the venting capability EF of an explosion door in comparison with a plastic foil rupture disk.

have to be chosen relative to the $P_{\text{red,max}}$ of the rupture disk of the same area.

When using explosion doors that close the vent area after the explosion, the cooling of the hot gases of combustion may create a vacuum in the vessel, resulting in its deformation. In order to prevent this from happening, vacuum breakers have to be provided.

The vented material discharged from an enclosure during an explosion should be directed to a safe location to avoid injury to personnel and to minimize property damage. If it is necessary to locate equipment that requires explosion venting inside buildings, the vents must not discharge within the building. Flames and pressure waves discharging from the enclosure during venting represent a threat to personnel and could damage other equipment. Therefore, vent ducts should be used to direct vented material from the equipment to the outdoors. If vented equipment is located within buildings, it should be placed close to the exterior walls so that the vent duct will be as short as possible. Vent ducts will significantly increase the pressure development in the equipment during venting. They require at least the same cross section as the vent area and the same design pressure as the protected vessel.

During pressure venting, a recoil is generated by the unburned mixtures and products of combustion flowing through the vent opening. The force bearing on the protected equipment depends on the explosion reduced overpressure and vent area. Not only the recoil force which can be calculated, but also its variation over time, are decisive for the practical design of the structure which supports the explosion-vented vessel. If the influence of the recoil forces is compensated for by arranging vent areas of equal size opposite each other, it is possible for one vent to open before another. Such imbalance should be considered when designing enclosure restraints for resisting thrust force.

For calculation of the venting area, empirical numerical value equations or nomograms can be used (Guideline VDI-3673, *Dust Explosion Venting,* VDI-Verlag, Düsseldorf, 1995; NFPA 68, *Guide for Venting of Deflagrations,* 1994). The calculation methods are not only dependent on the dust explosion constant $K_{\max}$, on the maximum reduced explosion overpressure $P_{\text{red,max}}$, on the static activation overpressure P_{stat} of the venting device and on the vessel volume V, but also on the maximum explosion overpressure $P_{\max}$. The vent calculation procedure also makes a distinction between homogeneous dust dispersion (dust-air mixtures generated using the ISO procedure) (ISO Standard 6184/1, *Explosion Protection Systems, Part 1: Determination of Explosion Indices of Combustible Dusts in Air,* Geneva, 1985) and inhomogeneous dust dispersion (dust-air mixtures generated by pneumatic transport) (Siwek, "Dust Explosion Venting for Dusts Pneumatically Conveyed into Vessels," *Plant/Operations Progress,* vol. 8, no. 3, July 1989). When applying the equations between numerical values, it is necessary to decide whether the apparatus being protected is a *cubic* (height-to-diameter ratio less than 2) or an *elongated* vessel (height-to-diameter ratio equal or above 2).

Explosion venting is always accompanied by flame propagation plus pressure consequences in the surrounding areas. The flame length will be larger with a lesser static activation pressure and smaller vent area. Depending on the volume of the protected equipment, it can reach up to 50 m. The pressure effect in the vicinity of the vent area is influenced by the maximum reduced explosion pressure, the vent area, and the vessel volume. A maximum peak overpressure exists at a certain distance from the vent area, which can be calculated. As expected, the distance at which the peak pressure appears increases with increasing vessel volume. For larger distance, this peak pressure decreases.

Based on the hazards due to flame and pressure, personnel should not be endangered by the venting process. Also, the operation of any equipment which is important with regard to safety should not be restricted. This must be considered when designing the plant and may be accomplished by releasing the pressure upward. If this is not feasible, then the vent openings should be placed as high as possible at the side of the vessel. Due to the danger of dust ejection, one has to consider the location of the surface of the dust pile in the vessel. It should never reach the lower edge of the vent opening at maximum operation filling of the vessel.

Among other things, one prerequisite necessary to calculate the pressure relief openings needed on the apparatus is knowledge about the explosion threat definition and venting system hardware definition. The various influences are summarized in Table 26-22.

Explosion Suppression

Explosion-Pressure-Resistant Design for Reduced Maximum Explosion Overpressure with Explosion Suppression Explosion suppression systems provide one means to prevent the buildup of an inadmissibly high pressure, which is the consequence of explosions of combustible material in vessels. They operate by effectively extinguishing explosion flames in the initial stage of the explosion. An explosion of combustible material can generally be regarded as successfully suppressed when the maximum explosion overpressure can be lowered to a reduced explosion overpressure of not more than 1 bar (see Fig. 26-40).

Depending upon the design criteria of the installed suppression system, an unsuppressed explosion overpressure of around 7 to 10 bar is reduced to a suppressed reduced explosion overpressure which lies in the range of $P_{\text{red,max}} = 0.2$ to 1 bar. Thus, vessels need to be explosion resistant for an overpressure of maximum 1 bar (ISO Standard 6184/4, *Explosion Protection Systems Part 4: Determination of Efficacy of Explosion Suppression Systems,* Geneva, 1985).

The best advantages of explosion suppression systems is that they can also be used for explosions of combustible materials with toxic properties and that there is no penetration on the location of the process equipment for safe application.

Today, the technology of industrial explosion suppression has evolved to the extent that this technique can and does provide effective industrial safety for almost all industrial processing procedures and for most explosible materials. Developments in explosion suppression hardware—detectors, suppressors, and control equipment, together with new or improved suppressants—provide a versatility of capability which covers all dust explosion classes and process equipment volumes ranging from 0.2 to greater than 1000 m^3. Most significant, the theoretical understanding of explosion propagation and suppression has led to computer-aided design guidance, which has simplified system design.

Explosion suppression systems comprise explosion detectors, pres-

TABLE 26-22 Explosion Venting System Design Parameters

Explosion hazard definition	Venting system definition
Volume of vessel (free volume)	Type of venting device
Shape of vessel (cubic or elongated vessel)	Detection method for triggering a shutdown
Length-to-diameter ratio of vessel	Static activation overpressure P_{stat} of venting device
Strength of vessel	Venting capability of venting device
Type of dust cloud distribution (ISO method/pneumatic-loading method)	Location of venting device on the vessel
	Position of equipment to be protected in the building
Dust explosibility characteristics:	Length and shape of relief pipe if existent
maximum explosion overpressure $P_{\max}$	Recoil force during venting
maximum explosion constant $K_{\max}$	Duration of recoil force
toxicity of the product	Total transferred impulse
Maximum flame length	
Pressure outside the vent areas	

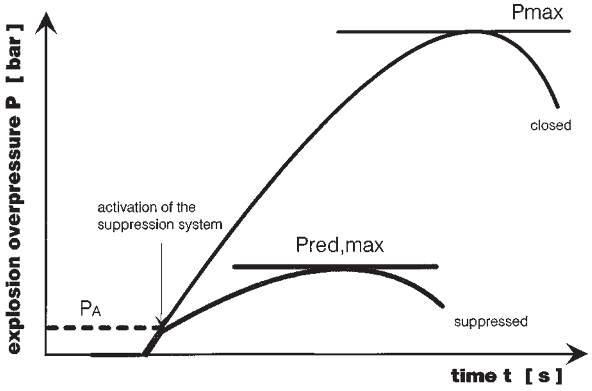


FIG. 26-40 Pressure behavior vs. time for a normal and a suppressed explosion.

surized HRD suppressors (high rate discharge) and a control and monitoring center.

Since the explosion pressure of an incipient explosion in a closed or essentially closed vessel propagates from the explosion epicenter at the speed of sound, pressure detection is an effective means of early explosion detection. Threshold pressure detection using a large area membrane explosion detector provides an electrical contact within milliseconds if the preset overpressure—the system activation pressure, P_a—is exceeded. Such a detector, which responds only to a pressure threshold, is called a *static pressure detector.* It is normal practice to mount two such devices mutually perpendicular and to trigger the explosion suppressors only when both detectors give coincident contact. This obviates the risk of spurious activation as a consequence of incident shock on the detector. Static pressure detectors have been extensively used in industrial applications and have a proven track record. The use of a large-area membrane for such devices ensures that their response is not influenced by the buildup of product or any crusting of product across the sensor surface of the detector. Dependent on selected membrane stiffness, such detectors can be set to operate at pressure thresholds of between 0.05 and 0.7 bar gauge. Static pressure detectors have only limited applicability for process equipment that operates at elevated pressures or that is subjected to significant extraneous pressure excursions.

For such applications, the more sophisticated rate-of-rise membrane pressure detectors must be used. In practice, these *dynamic explosion detectors* have a wide range of applicability. They have both rate-of-rise and pressure threshold trigger points that can be configured specific to the requirement. A timid explosion event may not attain the rate-of-rise criterion, a fact that necessitates a limit pressure threshold to trigger the explosion suppressors. Dynamic explosion detectors provide a means of achieving earlier detection than can be realized with static pressure detectors—and, thus, more effective suppression. Pressure fluctuations as a consequence of normal or abnormal process conditions, such as blocked filters, can be actively discriminated against, thus preventing spurious activation of the suppression system. In larger volumes, since the pressure rises only slowly, care must be taken to set up such detectors to meet appropriate detection response criteria. Dynamic explosion detectors can be used either as static or dynamic explosion detectors or in combination. The two parameters of pressure and time are programmed on-site specific to the installation. The dynamic detector control equipment facilitates event memory, enabling postevent analysis of the pressure domain causing the activation.

Dynamic explosion detectors use a piezoresistive pressure sensor installed behind the large-area, gas-tight, welded membrane. To ensure optimum pressure transference from the membrane to the active sensor element, the space between the membrane and the sensor is filled with a special, highly elastic oil. The construction is such that the dynamic explosion detector can withstand overpressures of 10 bar without any damage or effect on its setup characteristic. The operational range is adjustable between 0 and 5 bar abs. Dynamic explosion detectors are insensitive to shocks and vibration. For many applications, it is thus sufficient to install just one dynamic explosion detector to trigger the explosion suppressors. Since the commercial availability of this new detection method some two years ago, it has a proven performance capability and is being increasingly selected for use in explosion suppression systems.

High rate discharge (HRD) suppressors are available in a range of sizes. Dry powder suppressant is stored in a container, which is pressurized with dry nitrogen to an overpressure of, typically, P_s = 60 to 120 bar. An explosively actuated valve, such as a large-diameter membrane cut by a shaped charge, provides almost instantaneous unimpeded access for the suppressant, which is then expelled by the nitrogen gas and discharged through an appropriate nozzle into the process equipment.

Suppression efficiency is very dependent on the suppressant mass M_s discharge characteristic. This suppressant mass discharge rate is affected by outlet orifice area and propelling agent pressure. HRD suppressors that utilize a large-diameter outlet have superior suppression capability over those that rely on high propelling-agent pressure alone to expel the suppressant charge. The effectiveness of the HRD suppressors against a range of explosion hazards has been fully substantiated. The range of HRD suppressors available provides a wide range of suppression capability. The use of an explosive actuator provides the most effective means of rapid suppressant discharge—typically, less than 2 ms from activation to the start of suppressant release—and ensures the earliest suppression of any explosion event.

In some circumstances, the need to use an explosive actuator to effect suppressant release can be restrictive. HRD suppressors that are actuated by activating an electric initiator, which fractures fast-reacting rupture membrane, have been developed. Thus, within a few milliseconds of activation, an unimpeded opening is provided for the propelling agent to expel the suppressant. Upon fracture of the rupture membrane, the suppressant flows from the pressurized HRD suppressor through the outlet into a specifically engineered suppressant distribution piping system. These new types of HRD suppressors have, in order of magnitude, the same valve opening time and the same outlet orifice and provide an alternative means of suppressant deployment where explosive actuators are not admissible.

The HRD suppressor discharge elbow and the discharge nozzle have an important influence on suppression effectiveness. A nozzle that achieves a wide angular dispersion of suppressant is most effective for explosion suppression in smaller volumes, but the limited suppressant throw that results reduces its effectiveness for larger-volume explosion suppression. Irrespective of nozzle type, the suppressed explosion with an elbow (the HRD suppressor is mounted on the side of a vessel) is higher, demonstrating the effect of an elbow in slowing suppressant delivery into the vessel. On the other hand, if the HRD suppressor is mounted on the top (without an elbow) of the same vessel, a clearly more effective suppression is achieved, because no elbow is slowing the delivery of the suppressant. A normal arrangement of the nozzle for the distribution of the suppressant is protruding into the protected equipment. In practice, this is very often undesirable, especially if the enclosure handles dust with frequent production changes. To avoid disturbance of the production process (cleaning, product deposits, hygiene) by projection of the suppressant dispersion system into the protected vessel, movable, so-called telescopic nozzles (see Fig. 26-41) must be installed. Initially, the nozzle arrangement is located outside the vessel to be protected, separated from the latter by a membrane. This membrane does not reduce the HRD effectiveness. In applications where a true hygienic seal is required or where high-pressure excursions are to be expected, frangible metal or carbon discs are used. Such hermetic seals do slow, to a degree, the suppressant discharge from an HRD suppressor and this must be allowed for in the design. In the event of an explosion, once the HRD suppressor is activated, the nozzle is propelled forward by the suppressor pressure, rupturing the membrane and locating in its operating position to ensure effective suppressant deployment.

The most widely deployed industrial explosion suppressant is monoammonium phosphate powder (MAP). This suppressant has a wide range of effectiveness. However, it can prove to be a contaminant, necessitating stringent clean-down procedures after a suppressed explosion incident. This limitation is overcome by selecting a sodium

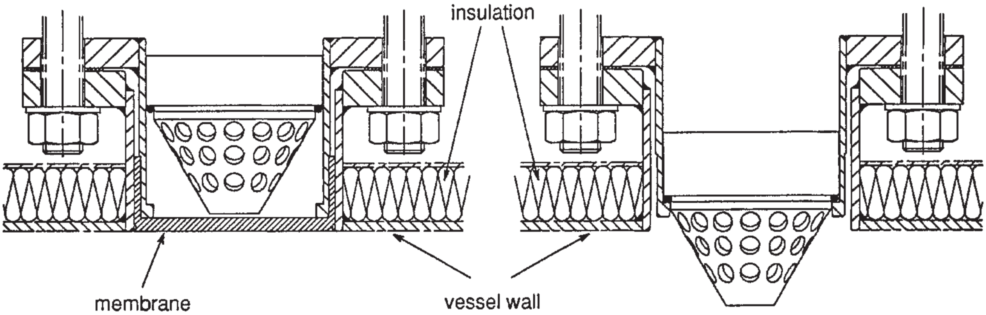


FIG. 26-41 Example for a telescopic nozzle arrangement.

bicarbonate (NaBi)–based dry powder suppressant. Food-grade compatible and readily water-soluble proprietary sodium bicarbonate suppressants are increasingly being used to protect industrial processes for manufacturing foodstuffs and pharmaceuticals. All types of suppressant have a fine particle size distribution—high specific surface—and flow additives to minimize particle agglomeration.

The sodium bicarbonate suppressant attains almost equivalence in performance with the monoammonium phosphate powder. Water has proven to be a very effective suppressant of dust, especially grain and fodder dusts. A suppressant is regarded as being very effective when an increase of the activation pressure P_a of the explosion system leads to an increase as small as possible in the maximum reduced explosion overpressure $P_{\text{red,max}}$ (see Fig. 26-42).

A recent development postulates that superheated water is a more effective suppressant than water alone because, on discharge, release of the superheated water charge results in partial flash vaporization of the water droplets to steam with a consequential fragmentation of the droplets, thus achieving a higher specific surface for effective suppression. At high temperature, effective suppression is achieved—but the effectiveness is very dependent on the control of temperature. The complication of maintaining the water suppressant charge at a fixed and controlled elevated temperature negates this option for most practical purposes.

Explosion suppression control equipment has traditionally been simple in operation, maintaining the highest level of reliability. In some applications, advantage can be achieved by introducing a level of intelligence and interpretation into the control equipment signal processing. New control and annunciation central control systems employ state-of-the-art electronics. Often called an *alarm center,* such a watchdog or operational center of any explosion suppression system is modular in construction. Individual modular "cards" can be plugged in, to accommodate the requirements of the full explosion protection system. Alarm centers are futureproof—they can be added to as the system expands. An alarm center records and monitors the signals transmitted by explosion pressure detectors, spark and flame detectors, temperature, and other safety sensors. Dependent on configuration, by interrogation and interpretation of the detector/sensor data, the alarm center selectively controls the actuation of explosion suppressors, extinguishing barriers, fast-shutting isolation valves, process equipment shutdown, water spray or extinguishant release, and all audible and visual alarms. System internal monitoring gives fault indication in the event of device or field wiring defect, and alarm and fault relay contacts can be connected as appropriate. Standby power is facilitated from an independent, monitored battery such that full explosion protection is assured during any power failure. System isolation to facilitate safe working on or in a protected vessel is standard, and remote actuation of key functions and system status record, via an on-line printer, are facilitated as options. Zoning of HRD suppressors enables the control system to ensure that suppressors deployed to inject extinguishant that is to act as an extinguishing barrier, and thus prevent flame propagation down a duct, are used to maximum effect.

A suitable locking mechanism must ensure that the production plant can be started up again only if the explosion suppression system is fully operational. The alarm center must be designed so that, if work is performed within the protected vessel, the detectors can be made inoperable and secured against inadvertent triggering.

Design of explosion suppression systems is clearly complex, since the effectiveness of an explosion suppression system is dependent on a large number of parameters. One hypothesis of suppression system design identifies a limiting combustion wave adiabatic flame temperature, below which combustion reactions are not sustained. Suppression is thus attained, provided that sufficient thermal quenching results in depression of the combustion wave temperature below this critical value. This hypothesis identifies the need to deliver greater than a critical mass of suppressant into the enveloping fireball to effect suppression (see Fig. 26-43).

If the suppression criterion is not met, the consequence is a failed

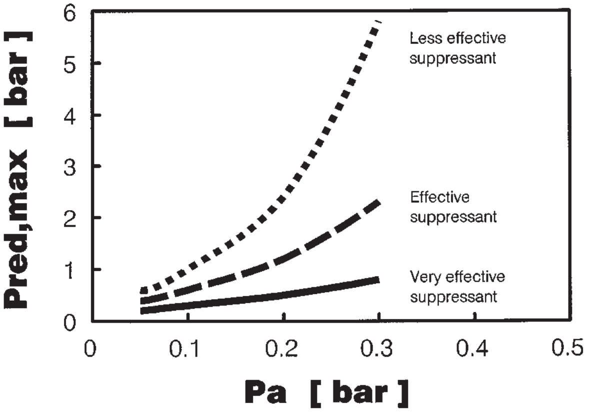


FIG. 26-42 Influence of the activation overpressure P_a and suppressant upon the effectiveness of a suppression system (constant test condition).

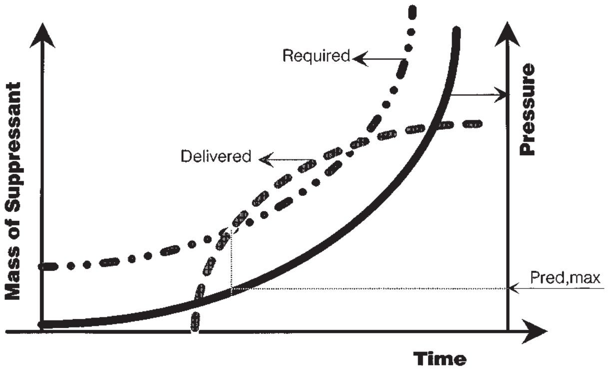


FIG. 26-43 Design basis for explosion suppression.

TABLE 26-23 Suppression System Design Parameters

Explosion hazard definition	Suppression system hardware definition
Volume of vessel (free volume V)	Type of explosion suppressant and its suppression efficiency
Shape of vessel (area and aspect ratio)	Type of HRD suppressors: number and free volume of HRD suppressors and the outlet diameter and valve opening time
Type of dust cloud distribution (ISO method/pneumatic-loading method)	Suppressant charge and propelling agent pressure
Dust explosibility characteristics:	Fittings: elbow and/or stub pipe and type of nozzle
Maximum explosion overpressure $P_{\max}$	Type of explosion detector(s): dynamic or threshold pressure, UV or IR radiation, effective system activation overpressure P_a
Maximum explosion constant $K_{\max}$	
Minimum ignition temperature MIT	Hardware deployment: location of HRD suppressor(s) on vessel

suppression, in which combustion is not arrested and high explosion pressures must be anticipated.

For any proposed suppression system design, it is necessary to ascribe with confidence an effective worst-case suppressed maximum explosion overpressure $P_{\text{red,max}}$. Provided that the suppressed explosion overpressure is less than the process equipment pressure shock resistance and provided further that this projected suppression is achieved with a sufficient margin of safety, explosion protection security is assured. These two criteria are mutually independent, but *both* must be satisfied if a suppression system is to be deployed to provide industrial explosion protection.

Suppression system design parameters fall into the two categories of explosion threat definition and suppression system hardware definition. The various influences are summarized in Table 26-23.

The type of HRD suppressors and their number and, hence, the extinguishing agent requirement can be determined with the aid of nomograms or simple numerical value equations developed from numerous experiments and model calculations (Siwek, Moore, "Extended Design Practice for Explosion Suppression Systems," *Proc. 8th Int. Symposium Loss Prevention and Safety Promotion in the Process Industries,* Antwerp, Elsevier, Amsterdam, 1995). As dry powder extinguishing agents are predominately used in industrial practice, the calculation fundamentals for the extinguishing agent requirement are limited to these extinguishing powders.

To achieve an effective and practical application, HRD suppressors of different sizes must be used for the different sizes and geometry of the protected vessels.

Of practical benefit to the processing industry is the combination technology of explosion venting and explosion suppression. It is evident that the deployment of a small explosion vent results in a useful further reduction in the resultant suppressed explosion pressure. Tests have shown that, provided the HRD suppressor is located such that the suppressant is deployed across the vent aperture, no flame ejection results. It is often the case in practical situations, where neither venting nor suppression alone can provide an appropriate safety solution, that, by combining the technologies, safety is assured. Where the primary protection means is explosion suppression, the addition of vents results in a lowering of the achievable reduced explosion pressure. Where the primary protection means is explosion venting, the addition of HRD suppressors reduces the vented explosion pressure. Results have shown that with high-$K_{\max}$ aluminum dust explosions, the reduced (vented) explosion pressure can be further reduced by more than 50 percent by the addition of HRD suppressors, although flame extinction is not achieved against the explosion threat. Tests on silos confirm that the deployment of an extinguishing barrier across the top of a silo fitted with explosion vents can prevent a secondary dust explosion in the room above the silo. This strategic use of extinguishing barriers ensures that flame ejection from a vented explosion incident is minimized. Similarly, extinguishing barriers in the vent pipes of relief venting systems minimize any flame ejection.

The combination of explosion safety technologies can provide more effective safety than is possible by deploying just one safety measure. In this respect, the improved capabilities of explosion suppression further enhance overall explosion protection capability.

Comparison of Explosion Protection Design Measures In Table 26-24, comparison is made of the explosion protection design measures of containment, explosion venting, and explosion suppression. Regarding the effectiveness of the different explosion design measures, all three techniques are equal if the design of these measures is performed properly.

Explosion Isolation For all equipment systems protected by design safety measures it is also necessary to prevent the propagation of an explosion from these protected vessels into operating areas or equipment connected via interconnecting pipeline. Such an approach is referred to as *explosion isolation.*

To prevent an explosion occurring in, for example, a constructional protected installation from spreading through a pipeline ($l > 6$ m) to part of the installation fitted with preventive explosion protection, explosion isolation measures (see Fig. 26-44) must be implemented. As explosions are generally propagated by *flames* and not by the pressure waves, it is especially important to detect, extinguish, or block this flame front at an early stage, i.e., to isolate or disengage the explosion. If there is no explosion isolation, the flame issuing from the equipment—for example, from the equipment protected through design (equipment part 1)—through the connecting pipeline comes into contact with a highly turbulent precompressed mixture in the equipment with preventive protection (equipment part 2). The mixture will ignite in an instant and explode; a large increase in the rate of

TABLE 26-24 Comparison of Explosion Protection Design Measures

	Containment	Explosion venting	Explosion suppression
Pressure resistance P	7–10 bar	Without relief pipe, up to 2 bar With relief pipe, up to 4 bar	St 1 up to 0.5 bar St 2+3 up to 1.0 bar
Location	Independent	Dependent	Independent
Limits of application	Products which decompose spontaneously	Toxic products and products which decompose spontaneously	Products which decompose spontaneously, metal dust hazard
Environmentally friendly	Yes	No (flame, pressure, and product)	Yes
Loss of material*	+++++	+++++	++
Maintenance requirements†	++++	++++	+++++

*The loss of material by using containment and explosion venting is always much greater than that by using explosion suppression.

†To ensure the reliability of explosion protection devices, regular servicing and maintenance are required. The nature and time intervals of these activities depend on technical specifications and on the plant situation. Normally, after commissioning of the plant, inspections are carried out in comparatively short intervals, e.g., every month. Positive experience may subsequently provide for longer service intervals (every three months). It is recommended to contract service and maintenance to reliable, specialized companies.

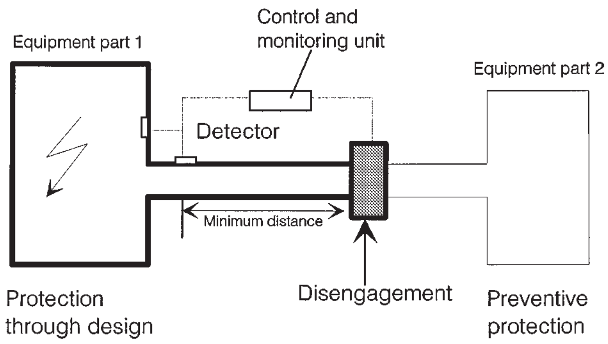


FIG. 26-44 Principle of the constructional measure explosion isolation.

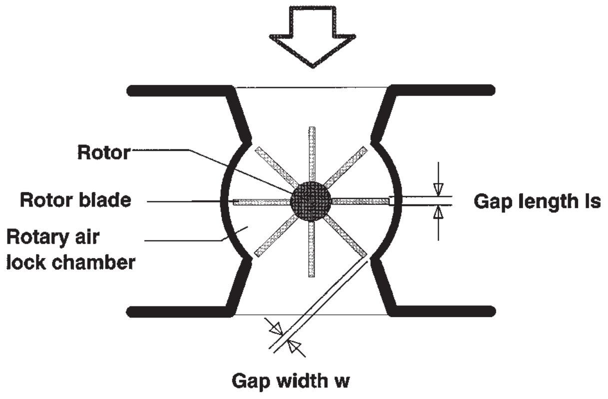


FIG. 26-45 Design features of a rotary valve.

combustion reaction and, naturally, in the reduced explosion overpressure is the result. The equipment in question may be destroyed.

The mechanical flame barriers, which are used for explosion isolation of flammable gas and solvent vapor explosions, are very susceptible to the action of dirt and, with one exception, are thus *not suitable for dust-carrying* pipelines. The exception involves the *rotary valve* (see Fig. 26-45), which is based on the flame-quenching effect through narrow gaps and is mainly used at product charging and discharging points.

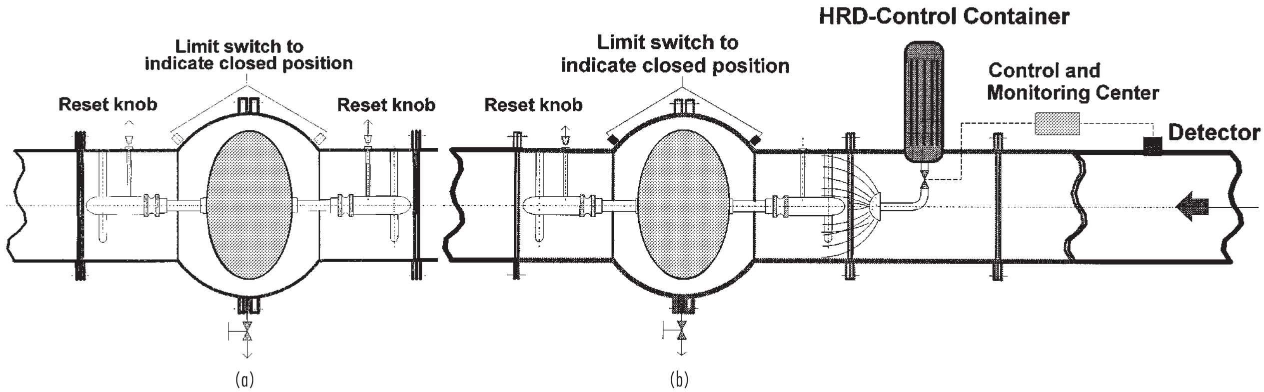
The size of the gap between the rotor blades and the housing depends on the construction and is important for the ignition breakthrough protection of the rotary valve. The maximum gap width of combustible dusts, like that of flammable gases, lies in the millimeter range. With knowledge of the ignitability of a dust, the gap length, and the number of constantly diametrically opposed rotor blades, a nomogram can be used to determine the maximum admissible gap between the blades and the inner wall of the rotary valve. In the event of an explosion, the valve must be automatically stopped to prevent any subsequent upstream fire or explosion due to passage of smoldering material or burning product through the valve. As a rule of thumb, it was found for normal organic dusts that the ignition cutout of rotary air locks is effective when three rotor blades on each side are diametrically opposed, provided that the blades are made of metal and the gap between the tip of the rotor blade and the housing is ≤0.2 mm (Siwek, "New Knowledge About Rotary Air Locks in Preventing Dust Ignition Breakthrough," *Plant/Operating Progress* vol. 8, no. 3, July 1989).

An *extinguishing barrier* comprises an optical flame sensor and an HRD suppressor located downstream of the detected flame front. The effectiveness of an extinguishing barrier is based on its ability to detect an explosion in a pipeline by means of an optical flame detector whose tripping signal is amplified and then very quickly actuates the detonator-actuated valves of the pressurized HRD suppressors. The extinguishing agent—preferably extinguishing powder—is discharged into the pipeline and forms a thick blanket, which extinguishes the incipient flame. There is a definite distance between the installation sites of the optical detector and the extinguishing barrier to ensure that the extinguishing agent acts directly on the flame. The amount of extinguishing agent required depends on the nature of the combustible dusts, the nominal diameter of the protected pipeline, the explosion velocity, and the maximum reduced explosion overpressure in the vessel. This type of barrier does not impede product throughput down the pipeline.

The alternative to the extinguishing barrier is the *rapid-action explosion isolation gate valve.* These valves must be tested for ignition breakthrough protection and pressure rating in dust explosions. They can meet these requirements for dust explosions and are effective against dust explosions at shorter distances than for gas explosions. When rapid-action gate valves are used, a dust explosion approaching the installation site in the pipeline is detected by an optical sensor and the closing process is initiated by a triggering mechanism. The closing time depends on the nominal width of the rapid-action devices and is generally less than 50 ms.

Explosion isolation can also be effected by *rapid action barrier valves.* At present, they can be arranged only in horizontal pipelines and are suitable, in general, only for streams with a small amount of dust. Such valves are thus frequently used to protect ventilation lines. As a certain explosion overpressure is necessary to close such valves, a distinction is made between *self-actuated* and *externally actuated* barrier valves (Fig. 26-46).

The interior of the barrier valve contains a valve cone mounted in



(a) (b)

FIG. 26-46 Rapid-action barrier valves: (*a*) self-actuated; (*b*) externally actuated.

spherical sockets, which can be moved axially in both directions; it is held in its middle position by springs. The spring tension is set for a maximum flow velocity of 25 $\mathrm{m \cdot s^{-1}}$, based on the pipeline cross section. If an explosion occurs, the valve closes automatically, owing to the kinetic energy of the pressure wave preceding the flame front. Here, either the explosion velocity must be greater than 25 $\mathrm{m \cdot s^{-1}}$ or the pressure difference in front of and behind the valve greater than 0.1 bar. The valve cone is pressed onto a rubberized valve seat on closing and held in place by a retaining device. It is released from outside. The self-actuating barrier valve (Fig. 26-46*a*) functions in both directions. Barrier valves can also be operated by a sensor-controlled auxiliary gas flow (jets of nitrogen from control containers onto the valve cone) in the direction of the pipe axis via a hemispherical nozzle (Fig. 26-46*b*). These are installed when low explosion overpressures are expected and, consequently, ignition breakthrough of an explosion through the installation site can occur with a self-actuated valve. The externally actuated barrier valve functions in one direction only.

Particularly reasonably priced explosion isolation of systems involves the use of a *relief pipe* with which the flow direction can be diverted by 180°. It prevents flame jet ignition with precompression in constructionally protected equipment. If suction is present, explosion propagation can occur. To prevent this, the use of an additional extinguishing barrier or a rapid-action gate valve is necessary. If a diverter is installed where positive pressure feed is given, then the diverter is, in general, safe against an explosion propagation.

Product removal mechanisms from apparatuses that are explosion resistant can be protected with a *double-slide* system. Here, the slides must be at least as resistant as the apparatuses. By means of proper control, it must be assured that a slide is always closed.

Finally, it must be pointed out that all devices suitable for use in explosion isolation—or, quite generally, all explosion protection devices used in practice—may be used only when their *pressure rating, ignition breakthrough protection,* and *reliability* have been proven in suitable investigations by competent bodies.

STATIC ELECTRICITY

Nomenclature

C	Capacitance, farads
C/kg	Charge density, coulombs/kg
C/$\mathrm{m^2}$	Surface charge density, coulombs/$\mathrm{m^2}$
F	Farads
J	Energy, joules
K_e	Relative dielectric constant, dimensionless
kV/m	Electric field intensity, kilovolts/meter
m	Meters
MIE	Minimum ignition energy, mJ
mJ	Millijoules
Ω^2	Resistivity value, ohms per square, usually used for fabrics and films
pS	Conductivity, picosiemens
pS/m	Electrical conductivity of liquid
RH	Relative humidity, %
S	Siemens (formerly mho)
T	Time, s
V	Electrical potential, volts
V/m	Electric field intensity, volts/meter

GENERAL REFERENCES: Bailey, "Charging of Solids and Powders," *J. Electrostatics* **30,** pp. 167–180, 1993. Blythe and Reddish, "Charges on Powders and Bulking Effects," *Electrostatics 1979,* Inst. Phys. Conf. Ser. No. 48, London, pp. 107–114, 1979. Finke, "Electrostatic Effects of Charged Steam Jets," *J. Electrostatics* **23,** pp. 69–78, 1989. *Generation and Control of Static Electricity,* Scientific Circular No. 803, National Paint and Coatings Association, Washington, D.C., 1988. Gibson and Lloyd, "Incendivity of Discharges from Electrostatically Charged Plastics," *Brit. J. Appl. Phys.* **16,** pp. 1619–1631, 1965. Owens, "Ignition Hazards of Charged Dielectrics in Flammable Environments," *IEEE Trans. Ind. Applic., IA-20,* no. 6, Nov./Dec. 1984. *Plant/Operations Progress* **7,** no. 1, Jan. 1988. Entire issue devoted to papers on static electricity, presented at AIChE meeting, Minneapolis, Minn., August 1987. Post, Glor et al., "The Avoidance of Ignition Hazards Due to Electrostatic Charges Arising During the Spraying of Liquids under High Pressure," *J. Electrostatics* **23,** pp. 99–110, 1989. *Protection Against Ignitions Arising Out of Static, Lightning and Stray Currents,* American Petroleum Institute Recommended Practice 2003, 1991.

Introduction Spark-ignition hazards must be considered whenever static charges may accumulate in an environment that contains a flammable gas, liquid, or dust. The need for electrical bonding and grounding of conductive process equipment in hazardous (classified) locations is widely recognized. Less well understood are the ignition hazards associated with static charges on poorly conductive, flammable liquids, solids, and powders. Static charges, generated on these materials by normal handling and processing, cannot be conducted to ground quickly and may cause hazardous charge accumulations. The electric fields associated with these charges may stress the surrounding air sufficiently to cause breakdown by some type of electrical discharge.

Electrical discharges from poorly conductive materials take several forms, each differing in its ability to ignite flammable mixtures. It is not possible to calculate the incendivity of these discharges, because of their varying time and spatial distributions. Several engineering rules of thumb for estimating the relative hazard of these discharges are discussed in the following.

Any analysis of static-ignition hazard should start with data on the ignition sensitivity of the particular flammable material at its most flammable concentration in air, i.e., its *minimum ignition energy* (MIE). This is especially important for dusts. It is prudent to determine this value on fines of the specific dust of interest, rather than to rely on published data. Hybrid mixtures (i.e., mixtures of dust and flammable vapor for which vapor concentrations may be below the lower explosive limit) can be ignited by smaller discharge energies than might be expected.

The key to safe operation is to provide an adequate means of charge dissipation from charged materials to ground. This requires mobility of charges in or on the charged material *plus* electrical continuity from the material to ground.

Definitions

antistatic material One with an electrical resistivity that is low enough to make it incapable of accumulating hazardous concentrations of static charges when grounded.

bonding A method of providing electrical continuity between two or more conductive objects to prevent electrical sparking between them.

charge relaxation time The time required for the charge in a liquid or on a solid material to dissipate to 36.8 percent of its initial value when the material is grounded.

electrical discharge A current flow, which occurs when the electrical field strength exceeds the breakdown value in a medium such as air.

flammable mixture A mixture of a gas, mist, or dust in air, which is within its flammable range.

grounding A special form of bonding, in which a conductive object is electrically connected to (earth) ground.

incendive discharge Any discharge that has sufficient energy to ignite a specified flammable mixture.

minimum ignition energy The smallest amount of spark energy that has been found capable of igniting a specified flammable mixture in a standard test (Calcote, Gregory et al., "Spark Ignition; Effect of Molecular Structure," *Industrial and Engineering Chemistry* **44,** no. 11, 1952).

Electrostatic Charging

Types The primary cause of electrostatic charging is *contact electrification,* which takes place when two different materials are brought into contact and separated. Other causes include induction charging, the formation of sprays, and impingement of charged mist on an ungrounded conductor.

Contact Electrification This form of charging involves the contact and separation of solid-solid, solid-liquid, or liquid-liquid surfaces. Pure gases do *not* cause charging unless they carry droplets or dust particles.

Efforts to quantify the magnitude and polarity of contact charging have had limited success, because minute variations in the types and concentrations of contaminants exert a large influence on charge separation. Even like solid-solid surfaces can produce significant charge separation. The charge density on separated solid-solid surfaces is, usually, very nonuniform. Each surface may contain both + and − polarity charges, with more of one polarity than the other. After separation, the charges will dissipate slowly or rapidly, depending upon the electrical resistivity of the material and the presence of a path to ground.

Contact electrification at liquid-liquid and liquid-solid interfaces is attributed to the absorption of ions of one polarity by one surface. Ions of opposite polarity form a diffuse layer near the interface. If the diffuse layer is carried along by moving liquid, as in a pipeline, the flowing charges (called a *streaming current*) may create a sparking hazard downstream. One protective measure is to keep the charged liquid in a closed, grounded system (a *relaxation chamber*) long enough to allow safe dissipation of the charges.

The magnitude of the streaming current in any given situation is not readily calculated. Equations, derived experimentally for some liquids (Bustin and Dukek, *Electrostatic Hazards in the Petroleum Industry,* Research Studies Press, Letchworth, England, 1983) show that flow velocity has the greatest influence on pipeline charging. Streaming currents can be limited to safe levels by limiting velocities to less than 1 m/s.

Charge Induction This charging takes place when a conducting object is exposed to electric fields from other charged objects. Examples include the induction charging of a human body by clothing, the charging of a conductive liquid in a charged, plastic container, or the charging of the conductive coating on one-side-metallized film by static charges on the uncoated surface.

Although charge induction can take place whether or not the conductive object is grounded, a sparking hazard is present only if the conductor is not grounded. This phenomenon can convert a relatively innocuous charge buildup on a nonconductor into a serious sparking hazard by raising the potential of the conductor above ground (Owens, "Spark Ignition Hazards Caused by Charge Induction," *Plant/Operations Progress* **7,** no. 1, pp. 37–39, 1988).

Spraying Droplets, formed by spray nozzles, tend to be highly charged even if the conductivity of the liquid is high. Because there is no path to ground from the droplets, their charges can accumulate on an ungrounded conductor to cause sparking. If flammable vapor is present, as in some tank-cleaning operations, it is essential that the spray nozzle and tank be bonded or separately grounded. It is safer to use a nonflammable cleaning solvent or one that has a conductivity greater than 1000 pS/m.

Mists Although charged mists are unable to cause ignition of flammable vapor by self-generated sparking, it is important that the mist not impinge upon an ungrounded conductor.

Charge Dissipation

General It is an experimental fact that charged objects exert a force on other charged objects. This behavior is explained by the presence of an *electric field,* i.e., electric lines of force, each of which emanates from a + charge and terminates on a − charge. The *magnitude* of the field is defined as the force on a unit test charge placed at the point of interest. The *direction* of the field is the direction of the force on a + test charge placed at the point.

Static charge generation causes an ignition hazard only if the accumulated charges create an electric field sufficient to produce an electrical discharge in a flammable atmosphere. In most processes, this means that the electric field intensity at some location must reach the breakdown strength of air (nominally 3×10^6 V/m). The objective of static-control measures is to ensure that electric field intensities cannot reach this value.

Conductors Bonding and grounding are the primary means of dissipating charges from conductive objects. Bonding clamps should be of the single-point type, which bites through oxide or enamel coatings to make contact with the bare metal. Owing to the sturdy construction of bonding clamps and cables, their initial resistance is less than 1 Ω.

It is good practice to visually inspect the condition of bonding cables during each use and to measure the resistance of temporary bonding cables, at least annually, to confirm that it is less than, say, 25 Ω.

Antistatic Materials These materials allow static charges to dissipate without causing hazardous accumulations. Charge dissipation normally takes place by conduction along the material to ground. The antistatic behavior of such materials is measured, at a controlled temperature and relative humidity, in terms of Ω^2 (ohms per square) of *electrical surface resistivity.* Resistivity values needed for safety depend upon the rate of charge generation, but are typically in the range of 10^8 to 10^{11} Ω^2 (ohms per square) for fabrics and films (ASTM Standard Test Method D-257-78, *DC Resistance or Conductance of Insulating Materials*).

An alternate test for antistatic performance is the *charge-decay* test, in which the time of charge-decay is measured after 5 kV have been applied to the specimen (Federal Test Method 101C, Method 4046.1). For many purposes, a charge-decay time of 0.5 s to 500 V, measured at the RH in end use, indicates good antistatic performance.

The electrical surface resistivity and charge-decay time of most materials vary substantially with the relative humidity. It is important that materials be tested at the lowest RH expected in use. Items that are antistatic at 50 percent RH may *not* be antistatic at 20 percent RH.

Some fabrics contain a small percentage of conductive fibers or staple, which limit charge accumulation by *air ionization.* These fabrics do not depend upon conduction of static charges and may not appear conductive in the electrical resistivity or the charge-decay test. Antistatic performance is not humidity-dependent. Work is under way to develop a standard test for these fabrics (Nelson, Rogers, and Gilmartin, "Antistatic Mechanisms Associated with FIBC Fabrics Containing Conductive Fibers," *J. Electrostatics* **30,** pp. 135–148, 1993).

Liquids The rate of dissipation of charges in a liquid, assuming that its conductivity and dielectric permittivity are constant, can be expressed as:

$$T = 8.85 \frac{K_e}{C} \tag{26-52}$$

where T = time required for the charge density to dissipate to 36.8% of its initial value, s

K_e = relative dielectric constant of the liquid, dimensionless

C = electrical conductivity of the liquid, pS/m

Flammable liquids are considered particularly static-prone if their electrical conductivity is within the range of 0.1 to 10 pS/m. If no particulates or immiscible liquid are present, these products are considered safe when their conductivity has been raised to 50 pS/m or higher. Blending operations or other two-phase mixing may cause such a high rate of charging that a conductivity of at least 1000 pS/m is needed for safe charge dissipation (British Standard 5958, part 1, *Control of Undesirable Static Electricity,* para. 8, 1991).

Electrostatic Discharges An electrostatic discharge takes place when a gas or vapor-air mixture is stressed, electrically, to its breakdown value. Depending upon the specific circumstances, the breakdown appears as one of four types of discharges, which vary greatly in origin, appearance, duration, and incendivity.

Sparks Spark discharges are most common between solid conductors, although one electrode may be a conductive liquid. They appear as a narrow, luminous channel, and carry a large peak current for a few microseconds or less. Sparks are the only form of discharge for which a maximum spark energy can be calculated, using the expression:

$$J = 0.5\, C \cdot V^2 \tag{26-53}$$

where J = total stored energy dissipated, J

C = capacitance of charged system, F

V = initial potential difference between electrodes

Incident investigations often require that an estimate be made of the possible spark energy from an ungrounded conductor. If the discharge path contains significant resistance, some of the stored energy is dissipated in the resistance, thereby lowering the energy in the spark gap.

Corona A corona is generated when a highly nonuniform electric field of sufficient strength terminates on a conductor that has a small radius of curvature (i.e., a point, wire, or knife-edge). The luminous (breakdown) region is confined to a small volume near the corona electrode. Because of their small peak currents and long duration, corona discharges do not have sufficient energy to ignite most flammable materials found in industry (i.e., materials having a minimum ignition energy above 0.2 mJ). For this reason, they can be used safely as static neutralizers in most hazardous (classified) locations. Corona discharges *can* ignite hydrogen-air and oxygen-enriched, gas mixtures.

Brush Discharges These discharges take place between conductors and charged nonconductors, where the radius of curvature of the conductor is too large for corona generation. The name refers to the brushlike appearance of the discharge, which spreads from the conductor to discrete areas on the nonconductor. The brush discharge may have a hot "stem" near the conductor which, though short-lived, may cause ignition by raising the temperature of the flammable mixture to its autoignition value (Norberg, "Modeling Current Pulse Shape and Energy in Surface Discharges," *IEEE Trans. Ind. Applic.* **28,** no. 3, pp. 498–503, May/June 1992).

Brush discharges from – charged nonconductors have been found more incendive than those from + charged nonconductors. Spark energies from brush discharges are limited to less than 4 mJ, because charges from a small area on the nonconductor are able to participate in the spark. Most dust-air mixtures cannot be ignited by brush discharges because their MIE exceeds 4 mJ (Gibson, "Electrostatic Hazards—A Review of Modern Trends," *Electrostatics 1983,* Inst. Phys. Conf. Ser. No. 66, London, pp. 1–11, 1983).

Surface charge densities cannot exceed the theoretical value of 2.7×10^{-5} C/m^2 (set by air breakdown) and will normally be less than 1.5×10^{-5} C/m^2.

Propagating Brush Discharges These discharges are much less common than brush discharges. They sometimes occur when a nonconductive film or plastic layer acquires a double layer of charges, i.e., + polarity charges on one surface and – polarity charges on the opposite surface. Surface charge densities can be very large, because they are not limited by the breakdown of air.

The double layer can be formed by contact (*triboelectric*) charging of one surface of the nonconductor, while the opposite surface is in contact with a conductor, e.g., a nonconductive coating on a metal chute or a plastic-lined, metal pipe for powders. A less frequent cause is contact-charging of one surface, while air ions are supplied to the opposite surface.

Investigations by Glor ("Discharges and Hazards Associated with the Handling of Powders," *Electrostatics 1987,* Inst. Phys. Conf. Ser. No. 85, pp. 207–216, 1987) and others conclude that propagating brush discharges require surface charge densities above 2.7×10^{-4} C/m^2. In addition, the breakdown voltage of the insulating layer must be greater than 4 kV for a thickness of 10 μm, or 8 kV for a thickness of 200 μm.

If a conductor approaches the charged surface, the electric field will produce air ionization at the surface, which creates a semiconductive layer, thereby allowing charges from a large area to participate in a single discharge. Because these discharges can have energies of 1 J or more, they are very hazardous in a flammable environment. They may also cause severe shocks to operators who reach into a nonconductive container that is receiving charged powder, pellets, or fibers.

Causes of Hazardous Discharges with Liquids

Self-Generated Discharges Vapor-air mixtures can be ignited by sparks from highly charged liquids. It is said that such liquids "carry their own match." Typical causes of such charging for poorly conductive (<50 pS/m) liquids include:

1. High-velocity flow
2. Free-fall/splashing
3. Filtering
4. Spraying
5. Agitation with air
6. Blending with powder
7. Settling of an immiscible liquid (e.g., water in gasoline)
8. Liquid sampling from pressurized lines, using ungrounded or nonconductive containers

Conductive liquids in nonconductive containers may cause sparking if the outside of the container is charged by rubbing.

External Causes of Incendive Static Discharges

1. Sparks from ungrounded persons
2. Brush discharges from flexible, intermediate, bulk containers (FIBCs), plastic bags, stretch wrap, or other plastic film
3. Propagating brush discharges from metal-backed plastic film or linings

Powders Contact charging of powders occurs whenever particles move, relative to one another or to a third surface. Significant charging can be generated by operations such as grinding, mixing, sieving, pouring, and pneumatic transfer. Maximum charge densities (C/kg) on airborne powder increase as particle size decreases, because of larger surface/mass ratios. Dry fines can be expected to charge more highly than those containing moisture. While suspended in air, charged powder poses an ignition risk only if nonconductive piping is used in the conveying lines or if conductive piping is not properly bonded.

The *collected* powder may accumulate so much charge per unit volume that the associated electric field strength causes breakdown of the surrounding air in the form of corona or a brush discharge. For receiving containers larger than about 1 m^3, so-called bulking discharges may be present, with energies of up to 10 mJ. The ignition hazard from bulking discharges can be minimized by, for example, using a rotary valve to prebulk small volumes of charged powder prior to its collection in a large receiver (Britton, "Static Hazards Using Flexible Intermediate Bulk Containers for Powder Handling," *Process Safety Progress* **12,** no. 4, pp. 240–250, October 1993).

Personnel and Clothing Sparks from ungrounded persons pose a serious ignition hazard in flammable gas-air, vapor-air, and some dust-air mixtures, because the body is a conductor and can store energies on the order of 40 mJ. Induction of charges on a person's ungrounded body by charged clothing is a common cause of personnel electrification. Even at the *threshold of shock sensation,* the stored energy is about 1 mJ.

It is essential that persons be grounded in hazardous (classified) locations. For most chemical operations, the resistance to ground from the body should not exceed 100 megohms. A lower allowable resistance may be specified for locations where the presence of primary explosives, hydrogen-air mixtures, oxygen-enriched mixtures, or certain solid-state devices requires faster charge dissipation.

The combination of conductive flooring *and* conductive footwear is the preferred method of grounding. Untreated concrete flooring with conductive footwear is usually adequate, but its conductivity should be measured (Fowler and Klein, "Static Phenomena and Test Methods for Static Controlled Floors," *EOS/ESD Symposium Proceedings,* pp. 27–38, 1992). Where this method is impractical, personnel grounding devices are available.

In most chemical areas, grounded persons can wear any type of clothing safely. For the unusually sensitive environments listed above, antistatic or conductive clothing should be worn, and persons must be grounded. Removal of outer garments in a flammable location can cause hazardous discharges and should be avoided (NFPA 77, *Static Electricity,* para. 2-2, 1993).

Noncontacting Electrostatic Measurements These measurements are made by instruments that respond to the electric fields at their sensing electrodes. Considerable care must be taken in the interpretation of the measurements. The three general types of devices are described as follows.

Static Locator These meters are the least expensive type. They usually indicate in volts, but should not be used for quantitative evaluations.

Static Voltmeter These instruments are calibrated to indicate the potential (V) on an ungrounded conductor and usually have more than one calibrated meter/surface spacing. They can be used, for example, to indicate the potential on ungrounded persons or equipment. A meter that indicates in volts or kilovolts is *not* an electric field meter.

Electric Field Meter These meters are calibrated to indicate the polarity and magnitude of the electric field (V/m) at the sensor. They should have only *one* calibrated meter/surface spacing and should be designed to establish a reasonably uniform electric field between the charged surface and the meter. This is needed to ensure that the measured field is approximately equal to the field at the charged surface.

To determine the level of electrification on an *insulating* surface, an electric field meter should always be used. There is a direct relationship between the charge density on the surface of an insulator and the electric field intensity at the surface. Measurements should be made at locations where the insulating surface is several inches away from other insulating or conductive surfaces. The area of the measured surface should be large, compared to the field of view of the meter. In locations where a flammable vapor-air mixture has an MIE greater than 0.2 mJ, field intensities of 500 kV/m or more should be considered unsafe.

HAZARDS OF VACUUM

Nomenclature

F_1	Friction loss in equivalent length, ft
g	Acceleration of gravity, ft/s^2
g_c	Conversion factor, ft·lb$_m$/ft·lb$_f$ s^2
H	Total tank vertical height, ft
h_o	Initial fluid height, ft
h_i	Height between tank base and centerline of pump suction, ft
h_f	Final height of liquid above tank base, ft
NPSH	Net positive suction head, ft
P	Final tank vacuum, in Hg
P_o	Atmospheric pressure, lb$_f$/in^2
ρ	Liquid density, lb$_m$/ft^3
R	Tank radius, ft
V_o	Initial airspace volume, ft^3
V_p	Vapor pressure of tank fluid equivalent, ft
γ	Ratio of molar specific heats, C_p/C_v (about 1.4 for diatomic gases)

Introduction Ask any chemical engineer who has had some plant experience what he or she knows about vacuum and the engineer will probably smile and tell some tale about some piece of equipment that tried to turn itself inside out. Usually no one was hurt, and often there was no massive leakage—but not always!

Causes of Vacuum Hazards The design for the internal pressure condition of vessels is usually straightforward and well understood. The design for external pressures is more difficult. The devious ways in which external pressure can be applied can often be overlooked.

Following are some obvious causes of vacuum collapse:

- Liquid withdrawal by pump or gravity draining
- Removal of gas or vapor by withdrawing with a blower, fan, or jet
- Siphoning of liquids

Less obvious causes include:

- Condensation of vapor
- Cooling of hot gas
- Combination of cooling and condensation of a mixture of gas and condensable vapor

Sometimes obscure causes of vacuum collapse include:

- Absorption of a gas in a liquid, for example, ammonia in water or carbon dioxide in water.
- Reaction of two or more gases to make a liquid or solid, for example, ammonia plus hydrogen bromide to form ammonium bromide.
- Reaction of a gas and a solid to form a solid, for example, corrosion in a tank. Air plus Fe or FeO may give Fe_2O_3 in the presence of water.
- Reaction of a gas and a liquid to give a liquid, for example, chlorination, hydrogenation, or ethylation.
- Sudden dropping of finely divided solids in a silo, creating a momentary vacuum that can suck in the sides of the silo.
- Plugging of flame arresters, for example:

In styrene service, vapor may condense in flame arresters, and the liquid formed is low in inhibitor. Liquid may polymerize and plug off the arrester. Possible solutions include cleaning the arrester frequently or using a PVRV (pressure-vacuum relief valve).

In liquid service in cold weather, vapor may condense in a flame arrester and the liquid formed may freeze and plug the arrester. A possible solution is to heat and insulate the arrester to prevent condensation.

- Maintenance and testing. It is not a good idea to apply vacuum on a vessel during maintenance or testing without full knowledge of the external pressure rating, unless a suitable vacuum relief device is in place and operable.

Location of Vacuum Relief Device (Carl Schiappa, Michigan Engineering, The Dow Chemical Company, Midland, Mich., personal communication, March 20, 1992.) If a vacuum relief device is used, locate the device at the highest point on the top of the tank. If the vacuum relief device is not installed in this location and the tank is overfilled with liquid, the relief device will be sealed in liquid and will be ineffective in protecting the tank. This is especially true for the part of the tank above the vacuum relief device if it is sealed in liquid, the liquid level is lowered, and the tank goes into a partial vacuum.

Protective Measures for Equipment There have been many incidents where vessels were designed for internal pressures of 25 psig or higher and the tank collapsed under vacuum. The internal pressure rating is not a good indication of the vacuum rating. If equipment may be subject to vacuum, consideration should be given to designing the equipment for full vacuum. This may eliminate the need for complicated devices such as relief valves and instruments; if they are used but fail or plug, designing the equipment for full vacuum will prevent collapse of the vessel. For vessels where steam is used in the tank, such as steam-sterilized sanitary-service tanks, a full vacuum rating is advisable under any circumstances.

A disadvantage of this approach is that it may appear at first to be more expensive to design equipment for full vacuum. The cost differential of adding vacuum rating is usually modest compared to the tank's value. It can be less than 10 percent for 15 psig tanks of up to 3000-gal nominal capacity (Wintner, "Check the Vacuum Rating of Your Tanks," *Chem. Eng.*, February 1991, pp. 157–159). When the total cost of a suitably instrumented vessel not designed for vacuum is compared with the cost of a vessel designed for vacuum but without the extra equipment, the difference may be small or negligible, and the vessel designed for vacuum will be inherently safer. If a vessel is designed for vacuum, precautions should be taken to ensure that internal or external corrosion will not destroy the integrity of the vessel. Dimpled jackets may provide an economical way of providing vacuum protection when jacketed vessels are involved.

Personnel Hazards The following case history illustrates how vacuum can be harmful and dangerous to personnel. A plant superintendent was checking an open nozzle on a glass-lined reactor on which there was a vacuum pump pulling vacuum, when suddenly his arm was sucked into the nozzle, up to his shoulder. He could not remove his arm until help arrived to release the vacuum on the vessel. He was injured painfully, though not seriously. The injury could have been very serious if help had not been nearby. Personnel hazards can also result from vacuum conveyor systems for solids handling.

Examples of Vacuum-Related Accidents Figure 26-47 shows a jacketed tank, where the jacket was designed for low-pressure steam. When the steam was turned off and the drain valve and trap were closed, the steam condensed, causing the jacket to collapse. The jacket should have been designed for full vacuum, or a suitable vacuum relief device should have been installed on the jacket.

Figure 26-48 shows the collapse of a large storage tank containing acetone. The overflow and vent line had recently been changed, so it would vent through a vapor seal of water to remove acetone emissions from the vent when the tank was being filled. When the tank was being emptied, water was sucked into the vent pipe, creating a vacuum in the tank, which collapsed the top of the tank. A suitable vacuum relief device on the tank should have been installed to prevent this incident. Venting the tank through a liquid seal of this type is probably not very effective and a better method of controlling emissions should have been selected.

Low-Pressure Storage Tanks Low-pressure storage tanks are fragile. Even an eggshell can withstand more pressure and vacuum (Sanders, "Don't Be Another Victim of Vacuum," *Chemical Eng. Prog.*, September 1993, pp. 54–57). Low-pressure storage tanks do not require much pressure difference between the inside of the tank and the atmosphere to buckle the relatively thin tank walls. Pressure

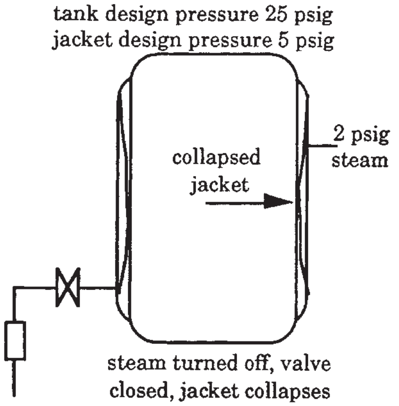


FIG. 26-47 Collapse of vessel jacket due to condensation of steam. (*W. T. Allen, Michigan Engineering, The Dow Chemical Company, Midland, Mich., personal communication, May 1988.*)

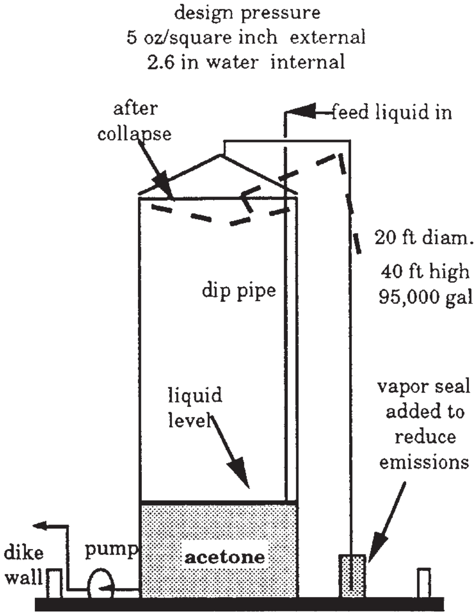


FIG. 26-48 Collapse of storage tank due to adding a liquid vapor seal to reduce vapor emissions. (*Allen, 1988.*)

differences as low as 10 mbar (0.01 atm, or 0.15 psig, or 0.7 in H_2O) between the inside and outside of the tank can buckle some tanks. The rate of handling of product and the breathing volume flow rate due to weather effects must be taken into account in designing the necessary pressure compensation devices.

A critical situation arises in summer when the tank is heated by strong radiation, then cooled by sudden rainfall. Heavy rainfall results in a rapid drop in ambient temperature and the formation of a rainwater film that flows on the top of the tank and down the tank wall. The wall and, with a certain lag, the gas in the tank are cooled, and air must flow into the tank to prevent a significant pressure difference from arising between the inside and outside of the tank. If vapors in the tank are condensed, more air must flow into the tank.

The initial gas temperature in a tank can reach a value of 55°C (131°F) as a result of strong solar radiation. Ambient rainfall is assumed to be 15°C (59°F). The maximum flow rate of air into the tank is reached some minutes later. At the start of the rainfall, after a certain lag, the flow rate at first increases, then reaches a maximum, then decreases.

A study has been made to allow the prediction of the rate at which air must enter a tank with and without internal condensation to prevent a pressure difference from arising (Fullarton, Evripidis, and Schlünder, Institut für Thermische Verfehrenstechnik, Universität Karlsruhe (TH), "Influence of Product Vapour Condensation on Venting of Storage Tanks," *Chem. Eng. Process.*, **22**(3), 1987, published by Elsevier-Sequoia, New York). The results are too involved to be presented in detail here. The reader is referred to this paper for details of the calculations.

The results of a specific case study are shown in Fig. 26-49. This depicts the change in inbreathing volume flow rate as a function of time. The middle curve describes the case when the tank is filled with dry air: that is, no condensation occurs. When the air is saturated with water vapor at 55°C (131°F) and condensation occurs, the top curve is obtained. The bottom line represents the volume flow rate brought about by thermal contraction alone, not including the amount condensed. Because of the heat of condensation released, this fraction is less than the volume flow rate without condensation, but this effect is more than compensated for by the additional volume flow rate due to condensation.

Experimental data in small equipment has shown that condensation of water vapor causes a twofold increase in the maximum flow rate compared to dry air, and a fourfold increase in condensation of methanol vapor.

API 2000 lists the venting capacity for inbreathing (vacuum relief) and outbreathing (pressure relief) for oil tanks up to 180,000 barrels (7,560,000 gal or 2.86×10^4 m^3) capacity at 14.7 psia and 60°F. Tanks larger than 180,000 barrels require individual study (API 2000, "Venting Atmospheric and Low-Pressure Storage Tanks, Non-Refrigerated and Refrigerated," *API Standard 2000,* 3d ed., American Petroleum Institute, Washington D.C., January 1983).

Vacuum Requirements for Draining Tanks (Wintner, 1991, by permission.) A shortcut method of calculating the vacuum that can occur when a tank is being drained while the vent line is closed can be performed by measuring the head in the tank, assuming it is completely full. This is the maximum vacuum that would exist in a gravity-drain tank before air would begin to enter it. If the tank's overall height is designated H, then this vacuum is $2.036H\rho(g/g_cP_o)$ in Hg.

If the tank has some headspace, as is usually the case, it is desirable to get a better estimate of the actual level, since tanks usually have some gas headspace even when filled with liquid. Two tank configurations are considered: the gravity discharge tank (discharge is open to the atmosphere) and the pumped discharge tank. These calculations assume that the process is so rapid that an adiabatic model for the gas in the headspace is the correct choice. This is true when the drainage

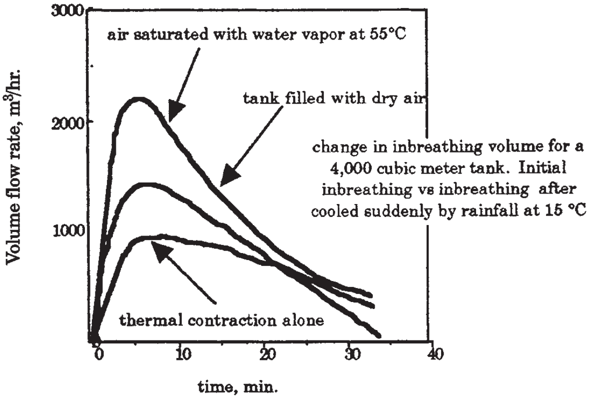


FIG. 26-49 Effect of water vapor condensation on volume flow rate of air into tank. (*Fullarton, Evripidis, and Schlünder, 1987, by permission of Elsevier Science S.A., Lausanne, Switzerland.*)

time is short (on the order of a few minutes for a tank of several thousand gallons capacity). An isothermal model is the best choice when the drain time is long.

For the gravity discharge case, the height of the fluid at maximum vacuum, which is the point at which air would begin to backflow into the tank, is determined by Eq. (26-54). Equation (26-55) calculates the corresponding vacuum in the tank's headspace at this liquid height. Since the drain nozzle is open to the atmosphere, this solution is a static force balance that is satisfied when the sum of the internal pressure and the remaining fluid head is equal to the atmospheric pressure.

$$h_f = \frac{144P_o(1 - \{V_o/[V_o + \pi R^2(h_o - h_f)]\}^\gamma)}{\rho g/g_c} \qquad (26\text{-}54)$$

$$P = \frac{29.92\, h_f \rho g}{144 P_o g_c} \qquad (26\text{-}55)$$

$$h_f = \text{NPSH} + F_1 + VP - h_i - \frac{144P_o\,(1 - \{V_o/[V_o + \pi R^2(h_o - h_f)]\}^\gamma)}{\rho g/g_c} \qquad (26\text{-}56)$$

$$P = 2.036P_o[1 - \{V_o/(V_o + \pi R^2 h_o)\}^\gamma] \qquad (26\text{-}57)$$

For the pumped-discharge case, internal pressure and final fluid height are calculated by Eqs. (26-56) and (26-57). The final fluid level is the point at which the net positive suction head (NPSH) equation is satisfied.

The solutions of Eqs. (26-54) and (26-56) involve a trial-and-error technique or a numerical method. This can be solved using a computer program for multivariable equations, or it can be calculated by hand. In either equation, assume a reasonable value for h_f and insert it on the right-hand side of the equation. The left-hand value obtained is then substituted until the values guessed at and those calculated are in close agreement. The number of trials is strongly dependent on the initial guess; for realistic tank dimensions, between four and ten iterations should produce good agreement.

The pumped-discharge case is generally more difficult to solve because of the uncertainty in dealing with negative numerical results. As a final answer, a negative value could indicate that the pump has completely emptied the tank; however, as an intermediate value, it could mean that it is not a true solution. A simple check is to try a different initial estimate and see if the intermediate negative results disappear.

Example Assume the tank in Fig. 26-50 has a diameter of 4 ft and a capacity of 1000 gal, is filled with water, and discharges to the atmosphere. The shortcut calculation (tank is initially completely full) indicates that the internal pressure would be 10.65 in Hg. An initial fillage of 70 percent of the tank's volume would produce a vacuum of 6.93 in Hg, which is 65 percent of the shortcut result.

In the case of pumped discharge, assume that a centrifugal pump is used. Its NPSH will determine the height at which vacuum is released by the backflow of air through the pump. Detailed information about the pump characteristics is needed to evaluate the potential vacuum. For these design calculations, assume that the pump will stop delivering liquid and air backflow will begin when the pump's NPSH requirements are no longer met (Sommerfield, "Tank Draining Revisited," *Chem. Eng.,* May 1990, p. 171).

The precise flow-decay pattern will depend on the type, size, and dimensions of the pump. Flow for a typical centrifugal pump will begin to decay at the NPSH point, but some additional fluid transfer will usually occur before a steady backflow of air through the pump begins. At that point, the pump's priming is completely lost.

The mathematical solution for maximum vacuum is based on Eq. (26-56), which solves the NPSH equation for this value of the fluid height. The nomenclature used contains only positive numbers for elevation, with the base point being set at the tank's discharge nozzle (analogous to the gravity-discharge case).

For this example, assume the following parameters:

Pump capacity = 50 gal/min
Pipe = 100 ft of 2-in pipe

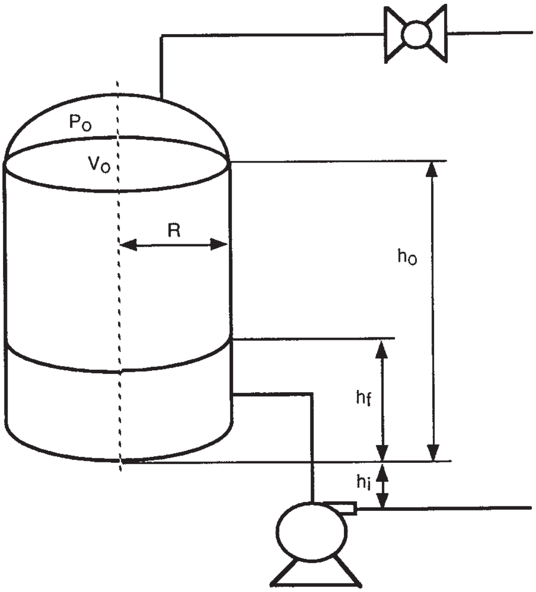


FIG. 26-50 Tank configuration used in example calculation.

NPSH = 4 ft
Elevation H_i = 1 ft
R = 2 ft
Liquid = water at 190°F
P_o = 14.7 psia

For these parameters, the equations predict a much higher vacuum (24.5 in Hg or 230 percent of the shortcut method) than the gravity-discharge case. Of course, different tank dimensions and pump characteristics could give different comparisons between cases. If conditions are such that the pump can completely empty the tank before backflow occurs, the vacuum is best calculated from Eq. (26-57).

If proper instruments are provided, the tank and pump can be interlocked, so the pump will stop when abnormal conditions are detected. This may help keep the tank from collapsing, but the gravity-discharge case should also be checked to ensure that failure will not occur after the interlock stops the pump. In all cases where instrumentation is used, the consequences of potential failure should be considered.

HAZARDS OF INERT GASES

General References: Air Products and Chemicals Co., *Dangers of Oxygen Deficient Atmospheres,* Allentown, Pa., 1988. ASHRAE Standard 34, "Fluorocarbon Numbering for Methane, Ethane and Cycloalkane Refrigerants," 1978. ASHRAE Standard 62-1989, American Society of Heating Refrigerating and Air-Conditioning Engineers, Inc., Atlanta, Ga., 1989. Bartknecht, *Dust Explosions,* Springer-Verlag, Berlin, 1989. Bartknecht, *Explosion Course Prevention, Protection,* Springer-Verlag, Berlin, 1981. Bodurtha, *Industrial Explosion Prevention and Protection,* McGraw-Hill, 1980. Generon Systems (membrane systems for producing moderate- to high-purity nitrogen), 400 W. Sam Houston Parkway South, Houston, Tex., 1993. *Guidelines for Engineering Design for Process Safety,* CCPS-AIChE, New York, 1993. Lees, *Loss Prevention in the Process Industries,* Butterworths, London, 1980. Nagy, Dorsett, and Jacobson, "Preventing Ignition of Dust Dispersions by Inerting," *U.S. Bur. Mines Rep. Invest. 6543,* 1964. NFPA 68, *Venting of Deflagrations,* National Fire Protection Association, Quincy, Mass., 1988. NFPA 69, *Explosion Prevention Systems,* National Fire Protection Association, Quincy, Mass., 1992. NFPA 654, *Standard for Fire and Dust Explosion Prevention in the Chemical, Dye, Pharmaceutical and Plastics Industries,* National Fire Protection Association, Quincy, Mass. 1982. Niida et al., *Some Expert System Experiments in Process Engineering,* Chem. Eng. Res. Des., vol. 64, September 1986, p. 374. *Ventilation for Acceptable Indoor Air Quality,* American Society of Heating, Refrigerating and Air-Conditioning Engineers, Inc., Atlanta, Ga. Zabetakis, *Flammability Characteristics of Combustible Gases and Vapors,* Bulletin 627, Bureau of Mines, 1965.

Introduction The use of inert atmospheres should be considered to prevent fires and deflagrations when using flammable materials. However, inert atmospheres can be dangerous to personnel. One of the most important concerns in the use of an inert atmosphere is that it can kill if a person breathes it. The air we normally inhale contains about 21 percent O_2, 79 percent N_2, and small amounts of other components. Inhaling air containing less than about 16 percent oxygen causes dizziness, rapid heartbeat, and headache. One or two breaths of pure nitrogen and some other gases containing no oxygen can be lethal. Other gases of this type include methane, ethane, acetylene, carbon dioxide, nitrous oxide, hydrogen, argon, neon, helium, and some others. Oxygen in the lungs is washed out and replaced by gas containing no oxygen. Blood from the lungs receives insufficient oxygen and flows to the brain, where tissues rapidly become deficient. Within five seconds of inhaling only a few breaths of oxygen-free gas, there can be mental failure and coma. Symptoms or warnings are generally absent. Death follows in two to four minutes. However, a coma due to lack of oxygen is not always fatal. Cardiopulmonary resuscitation techniques should be used on persons who are not breathing due to lack of oxygen (*Ventilation for Acceptable Indoor Air Quality,* American Society of Heating, Refrigerating and Air-Conditioning Engineers, Inc., Atlanta, Ga.; Zabetakis, *Flammability Characteristics of Combustible Gases and Vapors,* Bulletin 627, Bureau of Mines, 1965).

Gases which act as simple asphyxiants, such as nitrogen and helium, merely displace oxygen in the atmosphere so that the concentration falls below that needed to maintain consciousness. There are also chemical asphyxiants, such as carbon monoxide, hydrogen sulfide, and hydrogen cyanide, which have a specific blocking action and prevent a sufficient supply of oxygen from reaching the body. Most deaths due to short-term gassing are caused by carbon monoxide (Lees, *Loss Prevention in the Process Industries,* Butterworths, London, 1980, p. 646).

Effects of Low Oxygen Levels There are many factors which can affect the ability of human beings to adjust to lower oxygen levels. For example, two men were accidentally exposed to a low oxygen level in a vessel. One of them died, and one survived without permanent injury. The one who died had been in poorer general health and it is believed that this factor may have made the low oxygen level fatal for him, while the other person, who was in good health, survived.

It is well known that people accustomed to living near sea level can take several days to adjust fully to the lower amount of oxygen available in mountainous regions such as Denver, Colorado. Anyone who has traveled to the top of Pike's Peak knows how the altitude can make one tired, lethargic, and even sick. People react differently, however, and one cannot generalize as to exactly how a person will react to lower oxygen levels and higher altitudes. Table 26-25 gives the signs and symptoms of reduced oxygen content on persons at rest.

Minimum Oxygen Limits Oxygen limits are set at 19.5 percent minimum as recommended by OSHA and the American Standards Institute. Michigan has adopted these guidelines as well and has defined grade D air for O_2 to be 19.5 percent to 23.5 percent as an obligation to the employee by their employer. The Ontario Ministry of Labour designates enclosures containing less than 18 percent O_2 as hazardous.

Confined-Space Entry by the Dow Chemical Company The Dow Chemical Company Safety Standard on Confined-Space Entry states the following regarding confined space entry.

1. Check all test instruments to assure they are operable before and after use.
2. Readings acceptable for entry shall be recorded on the Safe Work Permit and shall assure that the oxygen content is 21 percent plus or minus 0.5 percent.
3. Toxic materials shall be at or below the threshold limit value, permissible exposure limit, or other approved industrial hygiene guideline.
4. The combustible gas indicator must be calibrated using the appropriate calibrating gas, such as methane or pentane.
5. The analysis shall be in the following sequence: oxygen concentration, then the combustible gas or vapor.

Confined-Space Entry as Defined by OSHA (Taylor, Shoemaker, and Sasse, "Confined Space Entry," *AIChE 1990 Summer National Meeting,* San Diego, Calif., August 19–22, 1990.) Occupational Safety and Health Administration (OSHA), in Section 1926.21(b)(6)(ii), has defined confined space as space having a limited means of egress, which is subject to the accumulation of toxic or flammable contaminants or has an oxygen-deficient atmosphere. For the purpose of this section, confined-space entry is discussed only as it pertains to process vessels, catalytic reactors, and storage tanks. OSHA classifies confined-space entry into two categories: immediately dangerous to life and health (IDLH) and non-IDLH as follows:

Class A—immediately dangerous to life and health based on oxygen level less than 19.5 percent and/or airborne presence of toxic or poisonous substances in concentration constituting IDLH conditions; flammability up to 20 percent of lower flammable limit.

Class B—Non-IDLH based on oxygen level between 19.5 and 21 percent, but classified as dangerous due to the airborne presence of toxic or poisonous substance below IDLH level, but greater than the protection factor offered by air-purifying respirators.

In addition, there is a non-IDLH class based on oxygen level between 19.5 and 21 percent, but classified as hazardous due to the presence of nuisance dusts or vapors below the IDLH level, but not greater than the protection factor of air-purifying respirators or low concentration of toxic or flammable substances.

Case Histories Following are examples of fatal accidents resulting from lack of oxygen:

- In a chemical plant, compressed nitrogen was temporarily being used to supply a control room, which was usually closed, containing pneumatic process control instruments that normally used instrument air. With the normal venting of nitrogen by the instruments in the control room, the air in the room was gradually replaced. An instrument man entered the control room for maintenance and was overcome by the lack of oxygen and died.
- Two men were inspecting a large tank in which other equipment was installed. The tank had two large manways attached to it, one near the bottom and one near the top. Ventilation was provided by air entering the bottom manway and leaving the top manway. A sheet of plastic had temporarily been placed over the top manway, which decreased the amount of air circulation. One of the inspectors climbed a ladder in the tank, became dizzy, and fell to the tank floor below. He died from the injuries received in the fall. It was found that

TABLE 26-25 Effects of Breathing Oxygen-Deficient Atmospheres

Oxygen content of air, %	Signs and symptoms of persons at rest
19.5–23.5	Recommended by OSHA.
15–19	Decreased ability to work strenuously. May impair coordination and may induce early symptoms in persons with coronary, pulmonary, or circulatory problems.
12–17	Loss of balance, dizziness. Respiration deeper, increased pulse rate, impaired coordination, perception, and judgment.
10–12	Further increase in rate and depth of respiration, further increase in pulse rate, performance failure, giddiness, poor judgment, lips blue, prolonged exposure possibly results in brain damage.
8–10	Mental failure, nausea, vomiting, fainting, unconsciousness, ashen face, blueness of lips. 8 minutes: 100% fatal. 6 minutes: 50% fatal. 4 to 5 minutes: recovery with treatment; brain damage and death are possible.
4	Coma in 40 s, convulsions, respiration ceases, death.

SOURCE: Air Products and Chemicals Co., "Dangers of Oxygen Deficient Atmospheres," Allentown, Pa., 1988, and American Standards Institute, Report No. 788.

the oxygen level in the upper part of the tank was 12.3 percent, which was low enough to cause dizziness and loss of balance. When the plastic sheet was removed, the oxygen content quickly rose to 21 percent. It was concluded that steel inside the tank had corroded, causing low oxygen content in the tank. Impaired ventilation caused by the plastic sheet had reduced circulation so that the air in the upper part of the tank remained at a low oxygen concentration.

Inerting Monomer Storage Tanks with Nitrogen It is good practice to keep the vapor space of flammable liquids out of the flammable range. Monomers that can potentially polymerize require special consideration. The vapor space above some monomers, such as styrene and methyl acrylate, should be kept below about 10 percent oxygen in warm weather to be below the flammable range. For many of these monomers, a small amount of oxygen is required to maintain the activity of the inhibitor and to avoid polymerization in storage tanks, which could lead to overheating and explosions and fire. An oxygen concentration of 5 percent in the vapor space is recommended as a safety factor to stay out of the flammable range and maintain inhibitor activity.

Maintaining an inert atmosphere for these applications can be difficult, since usually nitrogen is available as a high-purity gas, and it is necessary to add a small amount of oxygen (usually air) to the nitrogen to achieve the desired oxygen concentration. Mixing air and nitrogen has not proven to be a reliable method of maintaining the proper inert pad in the past. This is because instrument failure has caused high nitrogen concentration, which in turn has caused storage vessels to polymerize. One alternative to consider is the use of membrane systems, such as those sold by Generon Systems and other suppliers. This system can produce 95/5 percent nitrogen/oxygen for inerting, using plant compressed air available at 65 psig (449 kPa gauge). This system has an inherently stable output when operating at a specific pressure drop because the pressure drop across the membrane module sets the nitrogen purity.

Halon Systems for Inerting The term *halon* is generic for a range of halogenated hydrocarbons in which one or more of the hydrogen atoms have been replaced by atoms from the halogen series. Fully halogenated hydrocarbons are considered *hard* halons because it is believed that they have a major effect on the ozone layer. They work as fire-extinguishing agents by interfering with the free radical chain reaction occurring in flames. However, they destroy ozone in the same way. Halons containing bromine are much more destructive of ozone than chlorofluorocarbons (CFCs). It has been reported that one atom of some halons can destroy 10^6 ozone molecules. Halon alternatives that have less effect on the ozone layer include HCFCs, which are halogenated hydrocarbons with at least one hydrogen atom. In 1987, the Montreal Protocol on Protection of the Stratospheric Ozone Layer was signed, which set a timetable for phasing out the production and use of CFCs, including halons. The date for phaseout of the manufacture of halons according to the latest Copenhagen Meeting was January 1, 1994 (UNEP, Montreal Protocol on Substances that Deplete the Ozone Layer—Final Act 1987, 1987).

Although there have been many materials under development to replace the halons, there is not a single material that is a drop-in replacement. Some HCFCs are low in ozone depletion allowance, compared to halons or other CFCs, but in the long term, the goal should be zero ozone depletion. It is probable that there are no absolutely essential applications for halon in the chemical industry. There may be essential uses in airplanes, submarines, etc. Suggested replacements are water, dry chemical, and carbon dioxide. A large use for halon systems is in the form of total halon flooding systems for computer centers. To reduce the need for halon systems for computer centers, modern computer centers have a minimum amount of combustible materials to cause heat generation and there is less cable insulation with the use of fiber optics. Smoke and heat detectors are first-line-of-defense measures, along with emergency electrical power shutoff switches.

Fine water spray systems may be potentially superior to CO_2 applications and may replace halon environments such as telephone central offices and computer rooms. In the fine spray delivery system, water is delivered at relatively high pressure (above 100 psi [0.689 MPa]) or by air atomization to generate droplets significantly smaller than those generated by sprinklers. Water flow from a fine spray nozzle potentially extinguishes the fire faster than a sprinkler because the droplets are smaller and vaporize more quickly. Preliminary information indicates that the smaller the droplet size, the lower the water flow requirements and the less chance of water damage.

Inert Gas Generation Nitrogen is often the preferred gas for providing an inert atmosphere. In general, most organic combustible compounds will not propagate flame if oxygen in the mixtures of the organic vapor, inert gas, and air is below about 10 percent and 13 percent, with nitrogen and carbon dioxide, respectively, as the inert gases. With carbon dioxide, the minimum oxygen concentration is higher than with nitrogen because carbon dioxide has a higher specific heat. Carbon dioxide is fairly soluble in many liquids and will react with alkaline materials, so its use as an inerting material is limited. Heavy gases such as carbon dioxide provide superior inerting of vent stacks to prevent air entry. Water vapor is a good inerting gas if the temperature is high enough (above about 80 to 85°C [176 to 185°F]). Water vapor has a higher specific heat than nitrogen, so less water vapor is required for inerting than nitrogen (*FMRC Update,* vol. 7, no. 3, Factory Mutual Engineering Corp., Norwood, Mass., December 1993, pp. 2, 3).

Table 26-26 lists some of the main commercial methods used to generate nitrogen or nitrogen-rich gas.

TABLE 26-26 Commercial Methods Used to Generate Nitrogen or Nitrogen-Rich Gas

Process	Purity	Capacity	Features
Cryogenic separation	Very high N_2 purity, 99.999%, by-products oxygen and argon	Can be high	Very high purity; high flexibility by storing liquid nitrogen; fairly high capital costs, modest operating costs; complicated process
Pressure swing adsorption using molecular sieves	High purity, 99 to 99.9% N_2	Moderate	High purity; high-pressure storage may be required; simple process; economical
Membrane separation	Medium to high purity N_2, 95 to 99.9%	Small; typical module produces 855 scfh at 175 lb/in^2 and 77°F	Can use plant air as air source; simple and safe to operate; stable output; may be economical for low-capacity, medium- to high-purity requirements; excellent when some oxygen is required with the nitrogen; temperature and pressure sensitive
Hydrocarbon combustion	Contaminated with other gases: N_2 ~ 85% CO_2 ~ 14% CO ~ 0.5% O_2 ~ 0.5% H_2O ~ saturated	Small	Simple process; can use combustion products from engines or boilers, or dedicated burner; less reliability of O_2 control; may be very economical; used on tanker ships
Ammonia decomposition	Contaminated with H_2, water; N_2 ~ 75–99.5%, very low O_2	Small	Used only when cheap NH_3 is available

SOURCE: K. Niida, et al., Some Expert System Experiments in Process Engineering, *Chem. Eng. Res. Des,* vol. 64, September 1986, p. 374; Generon Systems, 400 W. Sam Houston Parkway South, Houston, Tex., 1993.

Conclusions The use of an inert atmosphere can virtually eliminate the possibility of explosions and fire with flammable materials. However, inerting systems can be quite expensive and difficult to operate successfully and can be hazardous to personnel. Before using inert systems, alternatives should be explored, such as using nonflammable materials or operating below the flammable range.

GAS DISPERSION

Nomenclature

A	Area affected by release, length^2
A^*	Dimensionless impact area
C	Concentration, mass/volume
$\langle C \rangle$	Time-averaged concentration, mass/volume
$\langle C \rangle^*$	Concentration of interest, mass/volume
D_c	Characteristic source dimension for continuous releases of dense gases, defined by Eq. (26-72), length
D_i	Characteristic source dimension for instantaneous releases of dense gases, defined by Eq. (26-73), length
g	Acceleration due to gravity, length/time^2
g_o	Initial buoyancy factor, defined by Eq. (26-71), length/time^2
H_r	Height of release above ground level, length
K	Eddy diffusivity, area/time
L^*	Scaled length, defined by Eq. (26-66), length
M	Molecular weight, mass/mole
P	Pressure, force/area
q_o	Initial plume volume flux for dense gas dispersion, volume/time
Q_m	Continuous release rate of material, mass/time
Q_m^*	Instantaneous release of material, mass
R_d	Release duration, time
T	Absolute temperature, K
t	Time, s
u	Wind speed, length/time
V_o	Initial volume of released dense gas material, length^3
x,y,z	Distance in dimensional space, length
x_v,y_v,z_v	Virtual distances for plume, length
x^*	Dimensionless downwind distance

Greek symbols

$\sigma_x,\sigma_y,\sigma_z$	Dispersion coefficients, length
ρ_a	Density of ambient air, mass/volume
ρ_o	Initial density of released material, mass/volume

Subscripts

a	Ambient
j	Either x, y, or z length dimensions
o	Initial
v	Virtual

Superscripts

$'$	Stochastic or fluctuating quantity

GENERAL REFERENCES: Crowl and Louvar, *Chemical Process Safety: Fundamentals with Applications,* Prentice Hall, Englewood Cliffs, NJ, 1990, pp. 121–155. Hanna and Drivas, *Guidelines for Use of Vapor Cloud Dispersion Models,* AIChE, New York, 1987. Hanna and Strimaitis, *Workbook of Test Cases for Vapor Cloud Source Dispersion Models,* AIChE, New York, 1989. Lees, *Loss Prevention in the Process Industries,* Butterworths, London, 1986, pp. 428–463. Seinfeld, *Atmospheric Chemistry and Physics of Air Pollution,* Chaps. 12, 13, 14, Wiley, New York, 1986. Turner, *Workbook of Atmospheric Dispersion Estimates,* U.S. Department of Health, Education, and Welfare, Cincinnati, 1970.

Introduction Gas dispersion (or vapor dispersion) is used to determine the consequences of a release of a toxic or flammable material. Typically, the calculations provide an estimate of the area affected and the average vapor concentrations expected. In order to make this determination, one must know the release rate of the gas (or the total quantity released) and the atmospheric conditions (wind speed, time of day, cloud cover).

The steps required to utilize a gas dispersion model are:

1. Identify the scenario. What can go wrong to result in the loss of containment of the material?
2. Develop an appropriate source model to calculate the release rate or total quantity released based on the specified scenario (see Discharge Rates from Punctured Lines and Vessels).
3. Use an appropriate gas dispersion model to estimate the consequences.
4. Determine if the resulting consequence is acceptable. If not, then something must be changed to reduce the consequence.

The entire procedure is shown in Fig. 26-51. If the consequence is not acceptable, then some of the options available to reduce the consequence are shown in Table 26-27.

Calculations and experiments have demonstrated that even the release of a small quantity of toxic or flammable material can have a significant consequence. Thus, it is clear that the best procedure is to prevent the release in the first place. However, release mitigation must be a part of any process safety program. Release mitigation involves: (1) detecting the release as early as possible, (2) stopping the release as quickly as possible, and (3) invoking a mitigation/emergency response procedure to reduce the consequences of the release.

Parameters Affecting Gas Dispersion A wide variety of parameters affect the dispersion of gases. These include: (1) wind speed, (2) atmospheric stability, (3) local terrain characteristics, (4) height of the release above the ground, (5) release geometry, i.e. from a point, line, or area source, (6) momentum of the material released, and (7) buoyancy of the material released.

As the wind speed is increased, the material is carried downwind faster, but the material is also diluted faster by a larger quantity of air.

Atmospheric stability depends on the wind speed, the time of day, and the solar energy input. During the day, the air temperature is at a maximum at the ground surface as a result of radiative heating of the ground from the sun. At night, radiative cooling of the ground occurs, resulting in an air temperature which is low at ground level, increases with height until a maximum is reached, and then decreases with further height.

Terrain characteristics affect the mechanical mixing of the air as it flows over the ground. Thus, the dispersion over a lake is different from the dispersion over a forest or a city of tall buildings.

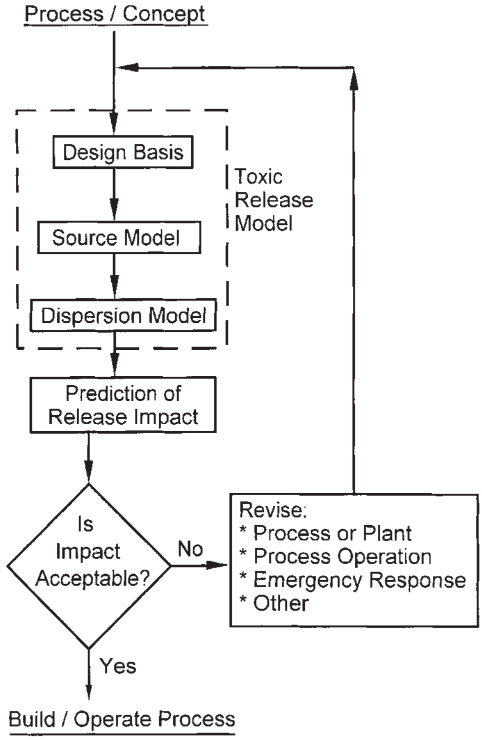


FIG. 26-51 The procedure for using a gas dispersion model to estimate the release impact.

TABLE 26-27 Release Mitigation Approaches

Major area	Examples
Inherent safety	*Inventory reduction:* Fewer chemicals inventoried or fewer in process vessels. *Chemical substitution:* Substitute a less hazardous chemical for one more hazardous. *Process attenuation:* Use lower temperatures and pressures.
Engineering design	*Plant physical integrity:* Use better seals or materials of construction. *Process integrity:* Ensure proper operating conditions and material purity. *Process design features for emergency control:* Emergency relief systems. *Spill containment:* Dikes and spill vessels.
Management	Operating policies and procedures Training for vapor release prevention and control Audits and inspections Equipment testing Maintenance program Management of modifications and changes to prevent new hazards Security
Early vapor detection and warning	Detection by sensors Detection by personnel
Countermeasures	Water sprays Water curtains Steam curtains Air curtains Deliberate ignition of explosive cloud Dilution Foams
Emergency response	On-site communications Emergency shutdown equipment and procedures Site evacuation Safe havens Personal protective equipment Medical treatment On-site emergency plans, procedures, training, and drills

SOURCE: Adapted from Prugh and Johnson, *Guidelines for Vapor Release Mitigation,* AIChE, New York, 1988.

Figure 26-52 shows the effect of height on the downwind concentrations due to a release. As the release height increases, the ground concentration downwind decreases since the resulting plume has more distance to mix with fresh air prior to contacting the ground.

The geometry of the release also affects the resulting consequence. An ideal release would occur at a point source. Real releases are more likely to occur as a line source (from an escaping jet of material) or as an area source (from a boiling pool of liquid).

Figure 26-53 shows the affect of initial momentum and buoyancy of the release. If the material is released as a jet, then the effective height of the release is increased. Furthermore, if the material released is heavier than air (which is the usual case for the release of most hydrocarbons), the plume initially slumps toward the ground until subsequent dilution by air results in a neutrally buoyant cloud.

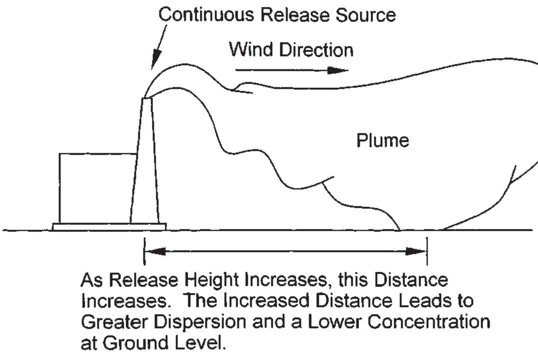


FIG. 26-52 Effect of increased release height on the downwind ground-level concentration. (*Reprinted from D. A. Crowl and J. F. Louvar,* Chemical Process Safety, Fundamentals with Applications, *1990, p. 127. Used by permission of Prentice Hall.*)

Gaussian Dispersion Gaussian dispersion is the most common method for estimating dispersion due to a release of vapor. The method applies only for neutrally buoyant clouds and provides an estimate of average downwind vapor concentrations. Since the concentrations predicted are time averages, it must be considered that local concentrations might be greater than this average; this result is important when estimating dispersion of highly toxic materials where local concentration fluctuations might have a significant impact on the consequences.

Fundamental Equations A complete development of the fundamental equations is presented elsewhere (Crowl and Louvar, 1990, pp. 129–144). The model begins by writing an equation for the conservation of mass of the dispersing material:

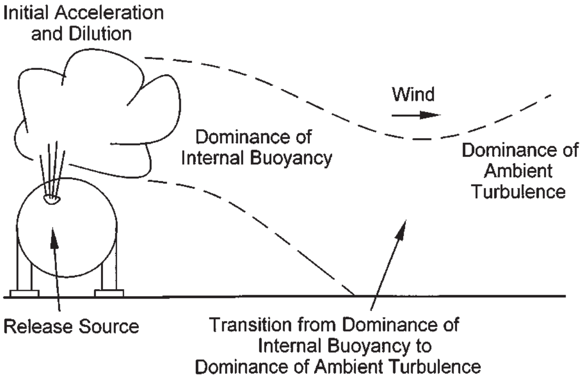


FIG. 26-53 Effect of initial acceleration and buoyancy on the release of gases. (*Adapted from S. R. Hanna and P. J. Drivas,* Guidelines for Use of Vapor Cloud Dispersion Models, *1987. Used by permission of the American Institute of Chemical Engineers, Center for Chemical Process Safety.*)

$$\frac{\partial C}{\partial t} + \frac{\partial}{\partial x_j}(u_j C) = 0 \tag{26-58}$$

where C is the concentration of dispersing material; j represents the summation over all three coordinates, x, y, and z; and u is the velocity of the air.

The difficulty with Eq. (26-58) is that it is impossible to determine the velocity u at every point, since an adequate turbulence model does not currently exist. The solution is to rewrite the concentration and velocity in terms of an average and stochastic quantity: $C = \langle C \rangle + C'$; $u_j = \langle u_j \rangle + u_j'$, where the brackets denote the average value and the prime denotes the stochastic, or deviation variable. It is also helpful to define an eddy diffusivity K_j (with units of area/time) as

$$-K_j \frac{\partial \langle C \rangle}{\partial x_j} = \langle u_j' C' \rangle \tag{26-59}$$

By substituting the stochastic equations into Eq. (26-58), taking an average, and then using Eq. (26-59), the following result is obtained:

$$\frac{\partial \langle C \rangle}{\partial t} + \langle u_j \rangle \frac{\partial \langle C \rangle}{\partial x_j} = \frac{\partial}{\partial x_j}\left(K_j \frac{\partial \langle C \rangle}{\partial x_j}\right) \tag{26-60}$$

The problem with Eq. (26-60) is that the eddy diffusivity changes with position, time, wind velocity, and prevailing atmospheric conditions, to name a few, and must be specified prior to a solution to the equation. This approach, while important theoretically, does not provide a practical framework for the solution of vapor dispersion problems.

Sutton (*Micrometeorology*, McGraw-Hill, 1953, p. 286) developed a solution to the above difficulty by defining dispersion coefficients, σ_x, σ_y, and σ_z, defined as the standard deviation of the concentrations in the downwind, crosswind, and vertical (x, y, z) directions, respectively. The dispersion coefficients are a function of atmospheric conditions and the distance downwind from the release. The atmospheric conditions are classified into six stability classes (A through F) for continuous releases and three stability classes (unstable, neutral, and stable) for instantaneous releases. The stability classes depend on wind speed and the amount of sunlight, as shown in Table 26-28.

Pasquill (*Atmospheric Diffusion*, Van Nostrand, 1962) recast Eq. (26-60) in terms of the dispersion coefficients and developed a number of useful solutions based on either continuous (plume) or instantaneous (puff) releases. Gifford (*Nuclear Safety*, vol. 2, no. 4, 1961, p. 47) developed a set of correlations for the dispersion coefficients based on available data (see Table 26-29 and Figs. 26-54 to 26-57). The resulting model has become known as the *Pasquill-Gifford model.*

The *puff model* describes near-instantaneous releases of material. The solution depends on the total quantity of material released, the atmospheric conditions, the height of the release above ground, and the distance from the release. The equation for the average concentration for this case is (Crowl and Louvar, 1990, p. 143):

$$\langle C \rangle(x,y,z,t) = \frac{Q_m^*}{(2\pi)^{3/2}\sigma_x\sigma_y\sigma_z} \exp\left[-\frac{1}{2}\left(\frac{y}{\sigma_y}\right)^2\right]$$
$$\times \left\{\exp\left[-\frac{1}{2}\left(\frac{z-H_r}{\sigma_z}\right)^2\right] + \exp\left[-\frac{1}{2}\left(\frac{z+H_r}{\sigma_z}\right)^2\right]\right\} \tag{26-61}$$

TABLE 26-28 Atmospheric Stability Classes for Use with the Pasquill-Gifford Dispersion Model

Wind speed, m/s	Day radiation intensity			Night cloud cover	
	Strong	Medium	Slight	Cloudy	Calm and Clear
<2	A	A–B	B		
2–3	A–B	B	C	E	F
3–5	B	B–C	C	D	E
5–6	C	C–D	D	D	D
>6	C	D	D	D	D

Stability classes for puff model:
A, B: unstable
C, D: neutral
E, F: stable

TABLE 26-29 Equations and Data for Pasquill-Gifford Dispersion Coefficients

Equations for continuous plumes

Stability class	σ_y, m
A	$\sigma_y = 0.493x^{0.88}$
B	$\sigma_y = 0.337x^{0.88}$
C	$\sigma_y = 0.195x^{0.90}$
D	$\sigma_y = 0.128x^{0.90}$
E	$\sigma_y = 0.091x^{0.91}$
F	$\sigma_y = 0.067x^{0.90}$

Stability class	x, m	σ_z, m
A	100–300	$\sigma_z = 0.087x^{1.10}$
	300–3000	$\log_{10}\sigma_z = -1.67 + 0.902 \log_{10}x + 0.181(\log_{10}x)^2$
B	100–500	$\sigma_z = 0.135x^{0.95}$
	$500–2 \times 10^4$	$\log_{10}\sigma_z = -1.25 + 1.09 \log_{10}x + 0.0018(\log_{10}x)^2$
C	$100–10^5$	$\sigma_z = 0.112x^{0.91}$
D	100–500	$\sigma_z = 0.093x^{0.85}$
	$500–10^5$	$\log_{10}\sigma_z = -1.22 + 1.08 \log_{10}x - 0.061(\log_{10}x)^2$
E	100–500	$\sigma_z = 0.082x^{0.82}$
	$500–10^5$	$\log_{10}\sigma_z = -1.19 + 1.04 \log_{10}x - 0.070(\log_{10}x)^2$
F	100–500	$\sigma_z = 0.057x^{0.80}$
	$500–10^5$	$\log_{10}\sigma_z = -1.91 + 1.37 \log_{10}x - 0.119(\log_{10}x)^2$

Data for puff releases

Stability condition	$x = 100$ m		$x = 4000$ m	
	σ_y, m	σ_z, m	σ_y, m	σ_z, m
Unstable	10	15	300	220
Neutral	4	3.8	120	50
Very stable	1.3	0.75	35	7

SOURCE: Frank P. Lees, *Loss Prevention in the Process Industries*, Butterworths, London, 1986, p. 443).

The center of the puff is located at $x = ut$. Here x is the downwind direction, y is the crosswind direction, and z is the height above ground level. The initial release occurs at a height H_r above the ground point at $(x,y,z) = (0,0,0)$, and the center of the coordinate system remains at the center of the puff as it moves downwind.

Notice that the wind speed does not appear explicitly in Eq. (26-61). It is implicit through the dispersion coefficients since these are a function of distance downwind from the initial release and the atmospheric stability conditions.

A typical requirement is to determine the cloud boundary at a fixed concentration. These boundaries, or lines, are called *isopleths.* The

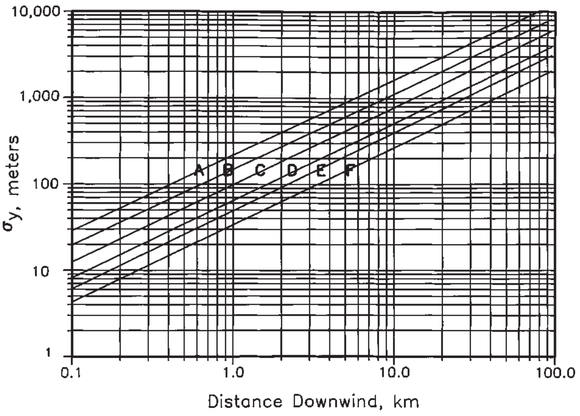


FIG. 26-54 Horizontal dispersion coefficient for Pasquill-Gifford plume model. (*Reprinted from D. A. Crowl and J. F. Louvar,* Chemical Process Safety, Fundamentals with Applications, *1990, p. 138. Used by permission of Prentice Hall.*)

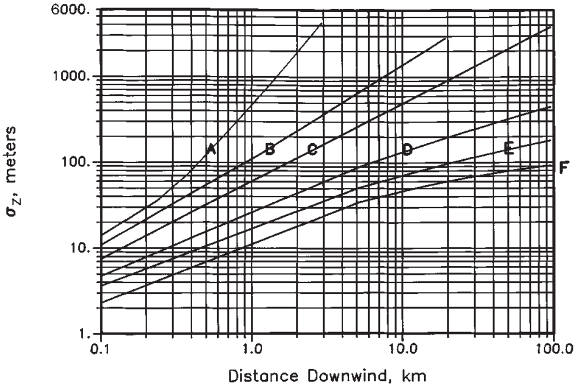


FIG. 26-55 Vertical dispersion coefficient for Pasquill-Gifford plume model. (*Reprinted from D. A. Crowl and J. F. Louvar,* Chemical Process Safety, Fundamentals with Applications, *1990, p. 138. Used by permission of Prentice Hall.*)

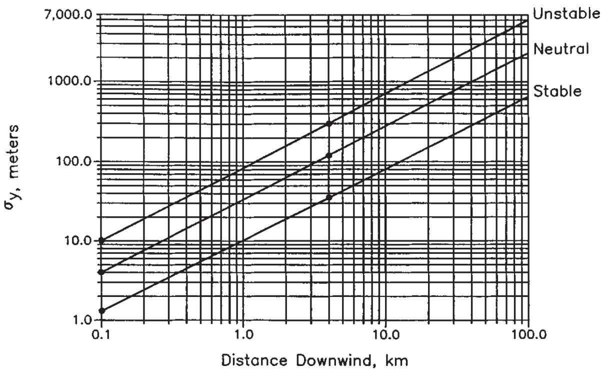


FIG. 26-56 Horizontal dispersion coefficient for Pasquill-Gifford puff model. These data are based on only the data points shown and should not be considered reliable elsewhere. (*Reprinted from D. A. Crowl and J. F. Louvar,* Chemical Process Safety, Fundamentals with Applications, *1990, p. 140. Used by permission of Prentice Hall.*)

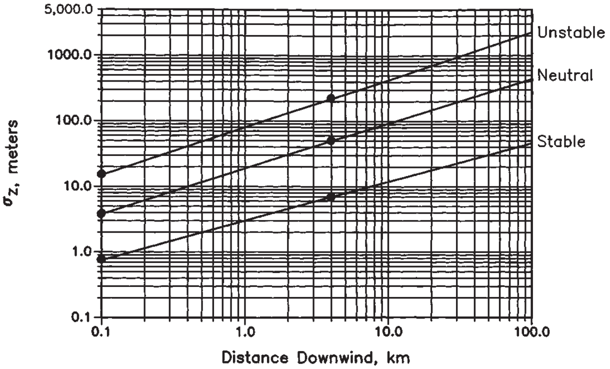


FIG. 26-57 Vertical dispersion coefficient for Pasquill-Gifford puff model. These data are based only on the data points shown and should not be considered reliable elsewhere. (*Reprinted from D. A. Crowl and J. F. Louvar,* Chemical Process Safety, Fundamentals with Applications, *1990, p. 140. Used by permission of Prentice Hall.*)

locations of these are found by dividing the equation for the centerline concentration, i.e., $\langle C\rangle(x,0,0,t)$, by the general ground-level concentration provided by Eq. (26-61). The resulting equation is solved for y to give

$$y = \sigma_y \sqrt{2 \ln \left(\frac{\langle C\rangle(x,0,0,t)}{\langle C\rangle(x,y,0,t)} \right)} \tag{26-62}$$

The procedure to determine an isopleth at any specified time is:

1. Specify a concentration $\langle C\rangle^*$ for the isopleth.
2. Determine the concentrations $\langle C\rangle(x,0,0,t)$, along the x axis directly downwind from the release. Define the boundary of the cloud along this axis.
3. Set $\langle C\rangle(x,y,0,t) = \langle C\rangle^*$ in Eq. (26-62) and determine the value of y at each centerline point determined in step 2. Plot the y values to define the isopleth, using symmetry around the centerline.

The *plume model* describes continuous release of material. The solution depends on the rate of release, the atmospheric conditions, the height of the release above ground, and the distance from the release. In this case, the wind is moving at a constant speed u in the x direction. The equation for the average concentration for this case is (Crowl and Louvar, 1990, p. 142):

$$\langle C\rangle(x,y,z) = \frac{Q_m}{2\pi\sigma_y\sigma_z u} \exp\left[-\frac{1}{2}\left(\frac{y}{\sigma_y}\right)^2\right]$$
$$\times \left\{ \exp\left[-\frac{1}{2}\left(\frac{z-H_r}{\sigma_z}\right)^2\right] + \exp\left[-\frac{1}{2}\left(\frac{z+H_r}{\sigma_z}\right)^2\right] \right\} \tag{26-63}$$

For releases at ground level, the maximum concentration occurs at the release point. For releases above ground level, the maximum ground concentration occurs downwind along the centerline. The location of the maximum is found using

$$\sigma_z = \frac{H_r}{\sqrt{2}} \tag{26-64}$$

and the maximum concentration is found from

$$\langle C\rangle_{\max} = \frac{2Q_m}{e\pi u H_r^2}\left(\frac{\sigma_z}{\sigma_y}\right) \tag{26-65}$$

The procedure for finding the maximum concentration and the downwind distance for the maximum is to

1. Use Eq. (26-64) to determine the dispersion coefficient σ_z at the maximum.
2. Use Fig. 26-56 to determine the downwind location of the maximum.
3. Use Eq. (26-65) to determine the maximum concentration.

Nomograph Method By defining a scaled length

$$L^* = \left(\frac{Q_m}{u\langle C\rangle^*}\right)^{1/2} \tag{26-66}$$

a dimensionless downwind distance

$$x^* = \frac{x}{L^*} \tag{26-67}$$

and a dimensionless area

$$A^* = \frac{A}{(L^*)^2} \tag{26-68}$$

nomographs can be developed for determining the downwind distance and the total area affected at the concentration of interest $\langle C\rangle^*$. These nomographs are shown in Figs. 26-58 and 26-59.

Virtual Sources The previous equations apply to point source releases. Real releases, such as a boiling pool of liquid or a streaming jet of flashing liquid, involve a more complex geometry. One approach (*Guidelines for Chemical Process Quantitative Risk Analysis,* AIChE, 1989, p. 87) is to define a virtual source upwind from the actual source such that the computed plume matches the real plume. However, to achieve this, a concentration at a centerline point directly downwind must be known.

There are several ways to determine the location of the virtual source for a plume:

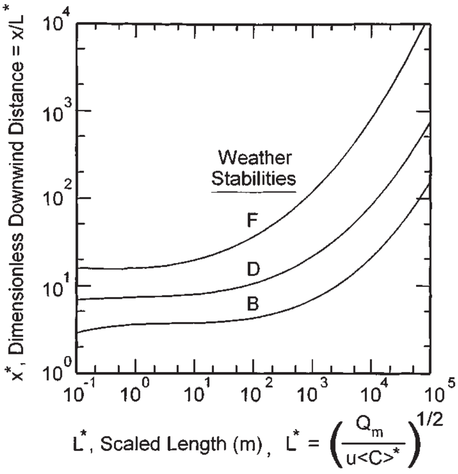


FIG. 26-58 Nomograph to determine the downwind distance affected by a release. (*Adapted from* Guidelines for Chemical Process Quantitative Risk Analysis, *1989, p. 90. Used by permission of the American Institute of Chemical Engineers.*)

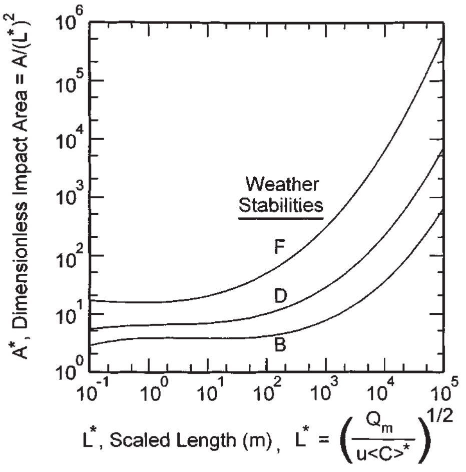


FIG. 26-59 Nomograph to determine the area affected by a release. (*Adapted from* Guidelines for Chemical Process Quantitative Risk Analysis, *1989, p. 91. Used by permission of the American Institute of Chemical Engineers.*)

1. Assume that all of the dispersion coefficients become equal at the virtual source. Then, from Eq. (26-63)

$$\sigma_y(y_v) = \sigma_z(z_v) = \left(\frac{Q_m}{\pi u \langle C \rangle^*}\right)^{1/2} \tag{26-69}$$

The virtual distances, y_v and z_v, determined using Eq. (26-69) are added to the actual downwind distance x to determine the dispersion coefficients σ_y and σ_z for subsequent computations.

2. Assume that $x_v = y_v = z_v$. Then, from Eq. (26-63)

$$\sigma_y(x_v) \cdot \sigma_z(x_v) = \frac{Q_m}{\pi u \langle C \rangle^*} \tag{26-70}$$

x_v is determined from Eq. (26-70) using a trial-and-error approach. The effective distance downwind for subsequent calculations using Eq. (26-63) is determined from $(x + x_v)$.

3. For large downwind distances, the virtual distances will be negligible and the point source models are used directly.

Strengths and Weaknesses The major strength to the gaussian approach is that the method is easy to apply. For most cases of interest, i.e., centerline concentrations along the ground, the equations reduce to a very simple form.

The primary weakness of the approach is that it does not apply to dense vapor releases, a category which includes most hydrocarbon materials. Furthermore, the concentrations predicted are time-weighted averages, with instantaneous values potentially exceeding the average. Finally, the range of applicability is typically from 0.1 to 10 km downwind from the release.

Example 1: Continuous Release What continuous release of chlorine is required to result in a concentration of 0.5 ppm at 300 m directly downwind on the ground? Also, estimate the total area affected. Assume that the release occurs at ground level and that the atmospheric conditions are worst case.

From Eq. (26-63), with $H_r = 0$, $z = 0$, and $y = 0$,

$$\langle C \rangle(x,0,0) = \frac{Q_m}{\pi \sigma_y \sigma_z u}$$

Worst-case atmospheric conditions occur to maximize $\langle C \rangle$. This occurs with minimum dispersion coefficients and minimum wind speed u within a stability class. By inspection of Figs. 26-54 and 26-55 and Table 26-28, this occurs with F-stability and $u = 2$ m/s. At 300 m = 0.3 km, from Figs. 26-54 and 26-55, $\sigma_y = 11$ m and $\sigma_z = 5$ m. The concentration in ppm is converted to kg/m^3 by application of the ideal gas law. A pressure of 1 atm and temperature of 298 K are assumed.

$$\text{mg/m}^3 = \left(\frac{\text{gm-mole K}}{0.08206 \text{ L atm}}\right)\left(\frac{PM}{T}\right)C_{\text{ppm}}$$

Using a molecular weight of 70.91 gm/gm-mole, the preceding equation gives a concentration of 1.45 mg/m^3. The release rate required is computed directly:

$$Q_m = \langle C \rangle^* \pi \sigma_y \sigma_z u = (1.45 \text{ mg/m}^3)(3.14)(11 \text{ m})(5 \text{ m})(2 \text{ m/s}) = 500 \text{ mg/s}$$

This is a very small release rate and demonstrates that it is much more effective to prevent the release than to mitigate it after the fact.

The area affected is determined from Fig. 26-59. For this case,

$$L^* = \left[\frac{5 \times 10^{-4} \text{ kg/s}}{(2 \text{ m/s})(1.45 \times 10^{-6} \text{ kg/m}^3)}\right]^{1/2} = 13.1 \text{ m}$$

From Fig. 26-59, $A^* = 20$ and it follows that

$$A = A^*(L^*)^2 = (20)(13.1 \text{ m})^2 = 3430 \text{ m}^2$$

Dense Gas Dispersion A dense gas is defined as any gas whose density is greater than the density of the ambient air through which it is being dispersed. This result can be due to a gas with a molecular weight greater than that of air, or a gas with a low temperature due to autorefrigeration during release, or other processes.

Dense gases behave considerably differently from neutrally buoyant gases. When they are initially released, these gases slump toward the ground and move both upwind and downwind. Furthermore, the mechanisms for mixing with air are completely different from neutrally buoyant releases.

As dense clouds move downwind, they are diluted with air until they eventually become neutrally buoyant. Thus, the gaussian models presented earlier are applicable for dense cloud releases at distances far downwind from the release.

A complete analysis of dense gas dispersion is much beyond the scope of this treatise. More detailed references are available (Britter and McQuaid, *Workbook on the Dispersion of Dense Gases,* Health and Safety Executive Report No. 17/1988, England, 1988; Lees, 1986, pp. 455–461; Hanna and Drivas, 1987; *Workbook of Test Cases for Vapor Cloud Source Dispersion Models,* AIChE, 1989; *Guidelines for Chemical Process Quantitative Risk Analysis,* 1989, pp. 96–103).

Many computer codes, both public and private, are available to model dense cloud dispersion. A detailed review of these codes, and how they perform relative to actual field test data, is available (Hanna, Chang, and Strimaitis, *Atmospheric Environment,* vol. 27A, no. 15, 1993, pp. 2265–2285). An interesting result of this review is that a simple nomograph method developed by Britter and McQuaid (1988) matches the available data as well as any of the computer codes. This method will be presented here.

The Britter and McQuaid model was developed by performing a dimensional analysis and correlating existing data on dense cloud dispersion. The model is best suited for instantaneous or continuous ground-level area or volume source releases of dense gases. Atmospheric stability was found to have little effect on the results and is not a part of the model. Most of the data came from dispersion tests in remote, rural areas, on mostly flat terrain. Thus, the results would not be applicable to urban areas or highly mountainous areas.

The model requires a specification of the initial cloud volume, the initial plume volume flux, the duration of release, and the initial gas density. Also required is the wind speed at a height of 10 m, the distance downwind, and the ambient gas density.

The first step is to determine if the dense gas model is applicable. If an initial buoyancy is defined as

$$g_o = \frac{g(\rho_o - \rho_a)}{\rho_a} \tag{26-71}$$

and a characteristic source dimension as, for continuous releases,

$$D_c = \left(\frac{q_o}{u}\right)^{1/2} \tag{26-72}$$

and for instantaneous releases:

$$D_i = V_o^{1/3} \tag{26-73}$$

then the criteria for a sufficiently dense cloud to require a dense cloud representation are, for continuous releases:

$$\left(\frac{g_o q_o}{u^3 D_c}\right)^{1/3} \geq 0.15 \tag{26-74}$$

and for instantaneous releases:

$$\frac{(g_o V_o)^{1/2}}{u D_i} \geq 0.20 \tag{26-75}$$

If these criteria are satisfied, then Figs. 26-60 and 26-61 are used to estimate the downwind concentrations.

The criteria for determining whether the release is continuous or instantaneous is calculated using the following group:

$$\frac{u R_d}{x} \tag{26-76}$$

If the group has a value greater than or equal to 2.5, then the dense gas release is considered continuous. If the group value is less than or equal to 0.6, then the release is considered instantaneous. If the value lies in between, then the concentrations are calculated using both continuous and instantaneous models and the minimum concentration result is selected.

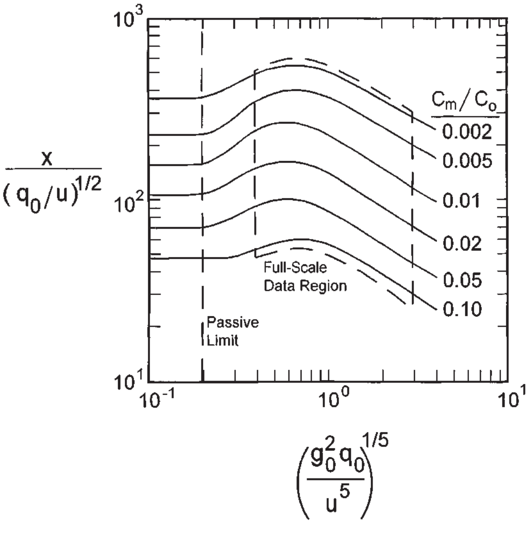


FIG. 26-60 Nomograph to estimate downwind concentrations due to continuous dense gas release based on the Britter-McQuaid correlation.

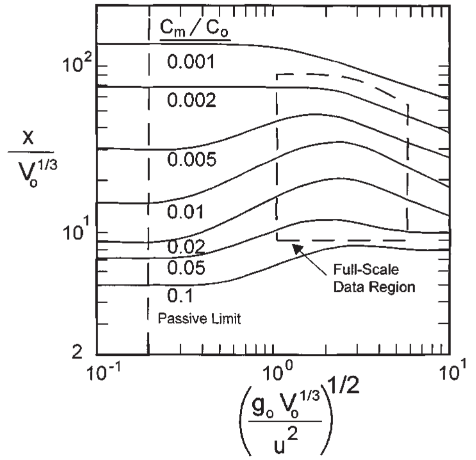


FIG. 26-61 Nomograph to estimate downwind concentrations due to an instantaneous dense gas release based on the Britter-McQuaid correlation.

The Britter and McQuaid model is not appropriate for jets or two-phase plume releases. However, it would be appropriate at a minimal distance of 100 m from these types of releases since the initial release effect is usually minimal beyond these distances.

Example 2: LNG Dispersion Tests Britter and McQuaid (1988, p. 70) report on the Burro LNG dispersion tests. Compute the distance downwind from the following LNG release to obtain a concentration equal to the lower flammability limit (LFL) of 5 percent vapor concentration by volume. Assume ambient conditions of 298 K and 1 atm. The following data are available:

Spill rate of liquid	$0.23\ \text{m}^3/\text{s}$
Spill duration R_d	174 s
Windspeed at 10 m above ground (u)	10.9 m/s
LNG density	$425.6\ \text{kg/m}^3$
LNG vapor density at boiling point of −162°C	$1.76\ \text{kg/m}^3$

Solution. The volumetric discharge rate is given by:

$$q_o = \frac{(0.23\ \text{m}^3/\text{s})(425.6\ \text{kg/m}^3)}{1.76\ \text{kg/m}^3} = 55.6\ \text{m}^3/\text{s}$$

The ambient air density is computed from the ideal gas law and gives a result of $1.22\ \text{kg/m}^3$. Thus

$$g_o = g\left(\frac{\rho_o - \rho_a}{\rho_a}\right) = (9.8\ \text{m/s}^2)\left(\frac{1.76 - 1.22}{1.22}\right) = 4.29\ \text{m/s}^2$$

Step 1: Determine if the release is considered continuous or instantaneous. For this case, Eq. (26-76) applies and the quantity must be greater than 2.5 for a continuous release. Thus

$$\frac{u R_d}{x} = \frac{(10.9\ \text{m/s})(174\ \text{s})}{x} \geq 2.5$$

and it follows that for a continuous release

$$x \leq 758\ \text{m}$$

Our final distance must be less than this for application of the continuous release model.

Step 2: Determine if a dense cloud model applies. For this case, Eqs. (26-69) and (26-74) apply. Substituting the appropriate numbers,

$$D_c = \left(\frac{q_o}{u}\right)^{1/2} = \left(\frac{55.6\ \text{m}^3/\text{s}}{10.9\ \text{m/s}}\right)^{1/2} = 2.26\ \text{m}$$

$$\left(\frac{g_o q_o}{u^3 D_c}\right)^{1/3} = \left[\frac{(4.29\ \text{m/s}^2)(55.6\ \text{m}^3/\text{s})}{(10.9\ \text{m/s})^3(2.26\ \text{m})}\right]^{1/3} = 0.43 \geq 0.15$$

and it is clear that the dense cloud model applies.

Step 3: Adjust the concentration for non-isothermal release. Britter and MacQuaid (1988, p. 61) provide an adjustment to the concentration to account for non-isothermal release of the vapor. If the original, non-isothermal concentration is C^*, then the equivalent isothermal concentration is given by

$$C = \frac{C^*}{C^* + (1 - C^*)(T_a/T_o)}$$

where T_a is the ambient temperature and T_o is the source temperature. For our required concentration of 0.05, the preceding equation gives an effective concentration of 0.019.

Step 4: Compute the dimensionless groups for Fig. 26-61.

$$\left(\frac{g_o^2 q_o}{u^5}\right)^{1/5} = \left[\frac{(4.29\ \text{m/s}^2)^2(55.6\ \text{m}^3\text{/s})}{(10.9\ \text{m/s})^5}\right]^{1/5} = 0.367$$

and

$$\left(\frac{q_o}{u}\right)^{1/2} = \left(\frac{55.6\ \text{m}^3\text{/s}}{10.9\ \text{m/s}}\right)^{1/2} = 2.25\ \text{m}$$

Step 5: Apply Fig. 26-60 to determine the downwind distance. The initial concentration of gas C_o is essentially pure LNG. Thus, $C_o = 1.0$ and it follows that $C_m/C_o = 0.019$. From Fig. 26-60,

$$\frac{x}{\left(\frac{q_o}{u}\right)^{1/2}} = 126$$

and it follows that $x = (2.25\ \text{m})(126) = 283$ m. This compares to an experimentally determined distance of 200 m. This demonstrates that dense gas dispersion estimates can easily be off by a factor of 2. A gaussian plume model assuming worst-case weather conditions (*F*-stability, 2 m/s wind speed) predicts a downwind distance of 14 km. Clearly, the dense cloud model provides a much better result.

DISCHARGE RATES FROM PUNCTURED LINES AND VESSELS

Nomenclature

a, b, c	Constants
A	Cross-sectional area perpendicular to flow, m^2
C_D	Overall discharge coefficient (–)
C_{DG}	Discharge coefficient for gas flow (–)
C_{DL}	Discharge coefficient for liquid flow (–)
C_p	Heat capacity at constant pressure, J·kg^{-1}·K^{-1}
C_v	Heat capacity at constant volume, J·kg^{-1}·K^{-1}
D	pipe diameter, m
D_T	tank diameter, m
f	Fanning friction factor (–)
F_I	Pipe inclination factor, Eq. (26-87)
g	Gravitational acceleration, ms^{-2}
G	Mass flux, kg·m^{-2}, s^{-1}
H	Specific enthalpy, J·kg^{-1}
H_{GL}	Heat of vaporization, $(H_G - H_L)$ sat, J·kg^{-1}
k	Value near C_p/C_v
K	Slip velocity ratio, u_G/u_L
K_e	Number of velocity heads for fittings, expansions, contractions, and bends
L	Length of pipe
N	$4fL/D + K_e$
P	Pressure, N·m^{-2}
q	Constant
Q	Heat transfer rate, W/kg
R	Gas constant, Jk mole^{-1}K^{-1}
Re	Reynolds number, $G{\cdot}D/\mu$ (–)
S	Entropy, J·kg^{-1}·K^{-1}
t	Time, s
T	Temperature, K
u	Velocity, ms^{-1}
v	Specific volume, m^3·kg^{-1}
w	Mass discharge rate, kg·s^{-1}
x	Vapor quality, kg vapor/kg mixture
X_m	Lockhart Martinelli parameter
z	Vertical distance, m

Greek	
α	Vapor void fraction, m^3 vapor/m^3 mixture
γ	Heat capacity ratio, C_p/C_v
ε	Dimensionless specific volume, v/v_o
η	Pressure ratio, P/P_o
θ	Inclination angle of pipe to horizontal
μ	Two-phase viscosity, P
ρ	Density, kg·m^{-3}
σ	Area ratio
ϕ	Two-phase multiplier, pressure drop for two-phase flow divided by pressure drop for single-phase flow
ω	Parameter defined by Eqs. (26-90) or (26-91)

Subscripts	
a	Ambient
c	Choked
d	Discharge
g, G	Gas or vapor
GL	Gas minus liquid
H	Homogeneous
L	Liquid
N	Nonequilibrium or puncture area
o	Area initial, stagnation conditions
p	Pipe flow
s	Saturation
1	Point at which backpressure from pipe is felt after entrance from tank
2	Plane at vena contracta or at pipe puncture
*	Dimensionless

GENERAL REFERENCES: Cheremisinoff and Gupta, eds., *Handbook of Fluids in Motion,* Ann Arbor Science, Ann Arbor, Michigan, 1983. Chisholm, *Two-phase Flow in Pipelines and Heat Exchangers,* George Godwin, New York, in association with the Institution of Chemical Engineers, 1983. Fisher et al., *Emergency Relief System Design Using DIERS Technology,* AIChE, New York, 1992. Graham, “The Flow of Air-Water Mixtures Through Nozzles,” National Engineering Laboratories (NEL) Report No. 308, East Kilbride, Glasgow, 1967. Jobson, “On the Flow of Compressible Fluids Through Orifices,” *Proc. Instn. Mech. Engrs.* **169**(37): 767–776, 1955. “The Two-Phase Critical Flow of One-Component Mixtures in Nozzles, Orifices, and Short Tubes,” *Trans. ASME, J. Heat Transfer* **93**(5): 179–N87, 1976. Lee and Sommerfeld, “Maximum Leakage Times Through Puncture Holes for Process Vessels of Various Shapes,” *J. Hazardous Materials* **38**(1): 27–40, July 1994. Lee and Sommerfeld, “Safe Drainage or Leakage Considerations and Geometry in the Design of Process Vessels,” *Trans. IChemE* **72,** part B: 88–89, May 1994. Leung, “A Generalized Correlation for One-Component Homogeneous Equilibrium Flashing Choked Flow,” *AIChE J.* **32**(10): 1743–1746, 1986. Leung, “Similarity Between Flashing and Non-flashing Two-Phase Flow,” *AIChE J.* **36**(5): 797, 1990. Leung, “Size Safety Relief Valves for Flashing Liquids,” *Chem. Eng. Prog.* **88**(2): 70–75, February 1992. Leung, “Two-Phase Flow Discharge in Nozzles and Pipes—A Unified Approach,” *J. Loss Prevention Process Ind.* **3**(27): 27–32, January 1990. Leung and Ciolek, “Flashing Flow Discharge of Initially Subcooled Liquid in Pipes,” *ASME Trans. J. Fluids Eng.* **116**(3), September 1994. Leung and Epstein, “Flashing Two-Phase Flow Including the Effects of Noncondensable Gases,” *ASME Trans. J Heat Transfer* **113**(1): 269, February 1991. Leung and Epstein, “A Generalized Correlation for Two-Phase Non-flashing Homogeneous Choked Flow,” *ASME J. Heat Transfer* **112**(2), May 1990. Leung and Grolmes, “The Discharge of Two-Phase Flashing Flow in a Horizontal Duct,” *AIChE J.* **33**(3): 524–527, 1987; also errata, **34**(6): 1030, 1988. Leung and Grolmes, “A Generalized Correlation for Flashing Choked Flow of Initially Subcooled Liquid,” *AIChE J.* **34**(4): 688–691, 1988. Levenspiel, “The Discharge of Gases from a Reservoir Through a Pipe,” *AIChE J.* **23**(3): 402–403, 1977. Lockhart and Martinelli, “Proposed Correlation of Data for Isothermal Two-Phase, Two-Component Flow in Pipes,” *Chem. Eng. Prog.* **45**(1): 39–48, January 1949. Sozzi and Sutherland, “Critical Flow of Saturated and Subcooled Water at High Pressure, General Electric Co. Report No. NEDO-13418, July 1975; also *ASME Symp. on Non-equilibrium Two-Phase Flows,* 1975. Tangren, Dodge, and Siefert, “Compressibility Effects in Two-Phase Flow,” *J. Applied Physics* **20:** 637–645, 1949. Uchida and Narai, “Discharge of Saturated Water Through Pipes and Orifices,” *Proc. 3d Intl. Heat Transfer Conf.,* ASME, Chicago, **5:** 1–12, 1966. Van den Akker, Snoey, and Spoelstra, “Discharges of Pressurized Liquefied Gases Through Apertures and Pipes,” *I. Chem. E. Symposium Ser.* (London), **80:** E23–35, 1983. Watson, Vaughan, and McFarlane, “Two-Phase Pressure Drop with a Sharp-Edged Orifice,” National Engineering Laboratories (NEL) Report No. 290, East Kilbride, Glasgow, 1967. Woodward, “Discharge Rates Through Holes in Process Vessels and Piping,” in V. Fthenakis, ed., *Prevention and Control of Accidental Releases of Hazardous Gases,* Van Nostrand Reinhold, New York, pp. 94–159, 1993. Woodward and Mudan, “Liquid and Gas Discharge Rates Through Holes in Process Vessels,” *J. Loss Prevention:* **4**(3): 161–165, 1991.

Overview Modeling the consequences of accidental releases of hazardous materials begins with the calculation of discharge rates. In the most general case, the discharged material is made up of a volatile flashing liquid and vapor along with noncondensable gases and solid particles. For efficiency, the treatment here is of two-phase flow, which reduces as a special case to single-phase all gas or all liquid flow. Solid particulate discharge is usually not particularly hazardous and is not considered here.

If the puncture occurs on a pipe which is at least 0.5 m from a vessel, it is justifiable to use a *homogeneous equilibrium model* (HEM) for which an analytical solution is available. The discharge rate predictions by the HEM beyond this range are within 10 percent of measured values for single-component liquids which are either subcooled or saturated.

If the puncture occurs on the vessel or on a line shorter than 0.5 m, the discharge is likely to be nonhomogeneous, meaning the gas and liquid velocities are not equal and the phases are not likely to be in equilibrium. For this case, various models have been developed, including some of considerable complexity, accounting for interphase heat, mass, and momentum transfer. These are generally used in the nuclear power industry. For most engineering applications, simpler models suffice. A reasonably simple *nonequilibrium model* (NEM) is developed here. We also provide an HEM for orifice flow, since it helps to develop the HEM for pipe flow, and its inaccuracies may at times be tolerable.

The energy and momentum balances common to both situations are stated first, along with some useful general concepts, followed by a development of an HEM for orifice and pipe discharge by Leung (1986; 1990; 1992) and Leung et al. (Leung and Ciolek, 1994; Leung and Epstein, 1990; Leung and Grolmes, 1988) and then the NEM for short pipe, orifice, and nozzle flow summarized by Chisholm.

Discharge Flow Regimes Upon developing a puncture in either the vessel or a line attached to the vessel, as in Fig. 26-62, the subsequent depressurization can cause a volatile liquid to flash and develop bubbles in the liquid. These bubbles cause an expansion, or *swell,* which raises the two-phase, or *frothy,* level. If the puncture is in the vapor space of a vessel or on a line from the vapor space, the discharge will be at least initially all vapor. This is the simplest discharge case and is treated here as a special case.

In the more general and more difficult case, either the puncture is initially in the liquid space, or in a line attached to it, or the liquid swells to reach the puncture or punctured line, giving two-phase or all-liquid discharge. For these cases the discharge model solutions must treat four regimes, which are defined by the initial void (vapor) fraction α_o and by the pressure ratios:

$$\eta_s = \frac{P_s}{P_o} \qquad \eta_a = \frac{P_a}{P_o}$$

where P_s is the saturation vapor pressure and P_a is ambient pressure.

Regime 1. If the tank is initially saturated (usually pressurized with volatile contents) there is no padding gas contributing noncondensables, so $\eta_s = 1$ and $\alpha_o = 0$. In this case, a discharge in the liquid space is a flashing liquid.

If the initial tank conditions are subcooled, $\eta_s < 1$, tank pressure must be maintained with padding gas (which could be air), typically introducing noncondensables, so $\alpha_o > 0$. These noncondensables may or may not become involved in the discharge. Furthermore, the subcooled liquid may flash ($\eta_s > \eta_a$) or not ($\eta_s < \eta_a$). In addition, some reacting systems generate noncondensable gases, giving Regimes 3 or 4.

Regime 2. If the puncture is below the initial liquid level, the padding gas will not be discharged, so there will be no noncondensables in the discharge ($\alpha_o = 0$). With low or moderate subcooling, $\eta_s > \eta_a$, the subcooled liquid will flash when the pressure ratio at some point drops below η_s. This point could be beyond the choke point, though. With high subcooling, $\eta_s < \eta_a$, and no flashing occurs (single-phase flow).

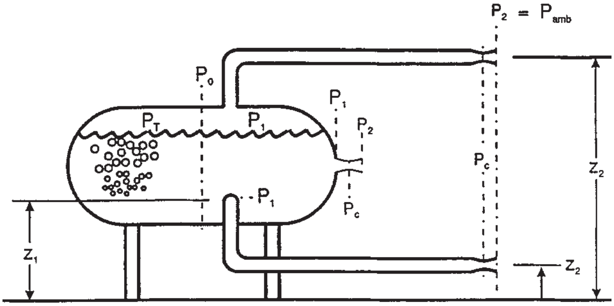


FIG. 26-62 Definition of terms for puncture of a vessel or line attached to a vessel.

Regime 3. If the puncture is above the initial liquid level but becomes covered by the swell, there will be noncondensables mixed with the liquid ($\alpha_o > 0$). If also $\eta_s < \eta_a$, no flashing occurs. This is called a *frozen flow situation,* since the mass fraction of compressible component x_o is constant during discharge.

Regime 4. This is the same as Regime 3 ($\alpha_o > 0$) except $1 < \eta_s < \eta_a$, so flashing occurs, giving two sources of compressible gases and vapors.

Solutions are given here for only the first three regimes. For Regime 4, see Leung and Epstein (1991).

Figures 26-63 and 26-64 illustrate the significant differences between subcooled and saturated-liquid discharge rates. Discharge rate decreases with increasing pipe length in both cases, but the drop in discharge rate is much more pronounced with saturated liquids. This is because the flashed vapor effectively chokes the flow and decreases the two-phase density.

General Two-Phase Flow Relationships For flow across an orifice or nozzle, the equilibrium mass fraction of flashed vapor x can be found for single components from either an entropy or an enthalpy balance. For multicomponents, use a standard flash routine. Since orifice discharge follows a more nearly isentropic thermodynamic path, the appropriate balance to use for single components in this case is the entropy balance (Van den Akker, Snoey, and Spoelstra, 1983). This balance is written from the initial stagnation point inside the vessel with temperature T_o to the saturation temperature T_s at a given pressure (of greatest interest are the choke pressure or ambient pressure). This gives:

$$x = \frac{S_{Lo}\,(T_o) - S_L\,(T_s)}{S_{\mathrm{GL}}\,(T_s)} \tag{26-77}$$

At ambient pressure, T_s is the normal boiling point.

Since pipe flow is more nearly isenthalpic, the flash fraction x is found from an enthalpy balance between the stagnation point and a point z downstream. Accounting for changes in potential energy, kinetic energy, and heat added or removed from the pipe Q, x is given by:

$$x = \frac{H_{Lo}\,(T_o) - H_{L2}\,(T_{S2}) - \tfrac{1}{2}u_{L2}^2 - gz \sin\theta + Q}{H_{\mathrm{GL}}\,(T_{s2}) + \tfrac{1}{2}u_{G2}^2 - \tfrac{1}{2}u_{L2}^2} \tag{26-78}$$

If the potential energy, kinetic energy, and heat added terms are negligible, this reduces to:

$$x = \frac{H_{Lo}\,(T_o) - H_L\,(T_s)}{H_{\mathrm{GL}}\,(T_s)} \tag{26-79}$$

These equations apply also to multicomponent systems, where the enthalpies are found for each phase from the component enthalpies.

Figure 26-62 depicts a flow system, which is described by the following differential momentum balance:

$$v dP + G^2 v dv + \left[4 f_{Lo}\frac{dz}{D} + K_e\right]\frac{1}{2}\,G^2 v_{Lo}^2 \phi_{Lo}^2 + g \sin\theta dz = 0 \tag{26-80}$$

where the terms represent the effect of pressure gradient, acceleration, line friction, and potential energy (static head), respectively. The effect of fittings, bends, entrance effects, etc., is included in the term K_e by standard methods. The inclination angle θ is the angle to the horizontal of a line from the pipe connection at the vessel to the discharge point. The term ϕ_{Lo}^2 is the two-phase multiplier which corrects the liquid-phase friction pressure loss to a two-phase pressure loss. Converting Eq. (26-80) to the dimensionless variables:

$$G_*^2 = \frac{G^2}{P_o \rho_o}, \qquad \eta = \frac{P}{P_o}, \qquad \varepsilon = \frac{v}{v_o} \tag{26-81}$$

gives:

$$\varepsilon d\eta + G_*^2 \varepsilon d\varepsilon + N\,\frac{1}{2}\,G_*^2 \varepsilon^2 \phi_{Lo}^2 + \frac{g \sin\theta dz}{P_o v_o} = 0 \tag{26-82}$$

where N is the number of equivalent velocity heads, given by:

$$N = 4 f_{Lo}\frac{dz}{D} + K_e \tag{26-83}$$

For homogeneous flow, the two-phase multiplier is simply:

$$\phi_{FLO}^2 = \frac{v_H}{v_L} \tag{26-84}$$

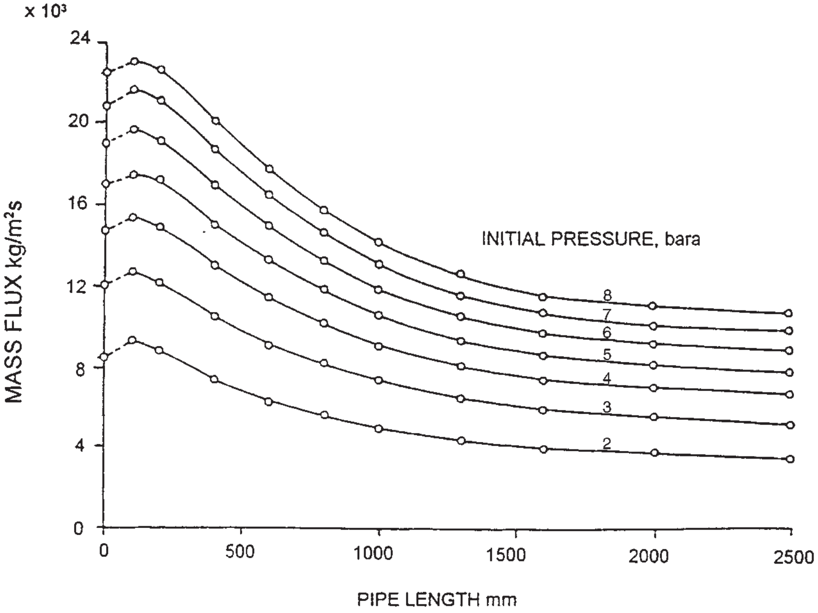


FIG. 26-63 Discharge mass flux for highly subcooled water (20°C) from orifice and 4-mm pipe of various lengths. (*Data of Uchida and Narai, 1966; reproduced by permission of ASME.*)

where v_H is the homogeneous specific volume given by:

$$v_H = xv_G + (1 - x)\, v_L \tag{26-85}$$

The momentum balance for homogeneous flow can be factored to a form which enables integration as:

$$-N = \frac{G^2_{\ast p}\varepsilon_H d\varepsilon_H + \varepsilon_H d\eta}{\tfrac{1}{2}G^2_{\ast p}\,\varepsilon^2_H + F_I} \tag{26-86}$$

by defining a pipe inclination factor F_I:

$$F_I = \frac{gD \sin \theta}{4f_{Lo}P_o v_o} \tag{26-87}$$

F_I is positive for upflow, negative for downflow, and zero for horizontal flow.

The energy balance across a pipe from the stagnation point 0 to a point 2 downstream is:

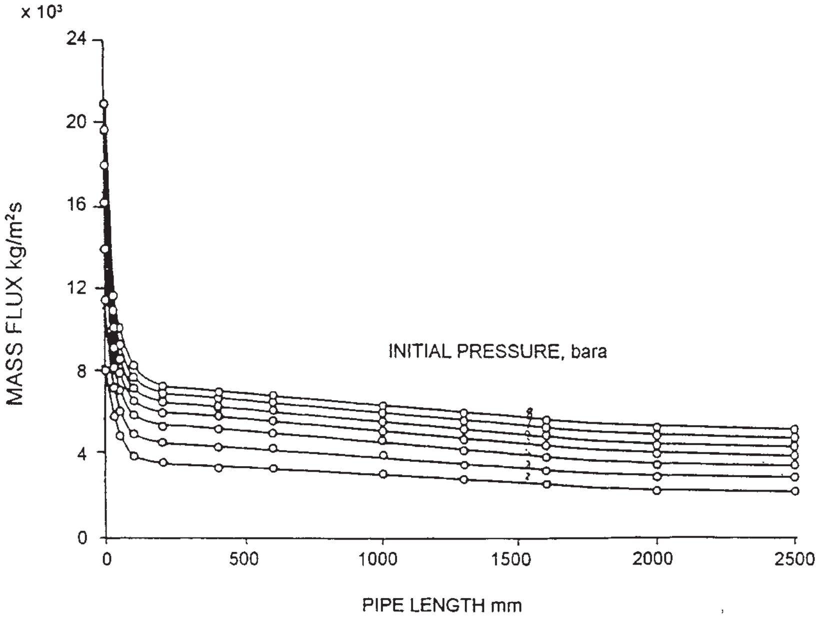


FIG. 26-64 Discharge mass flux for saturated water from orifice and 4-mm pipe of various lengths. (*Data of Uchida and Narai, 1966; reproduced by permission of ASME.*)

$$H_o + \frac{1}{2}u_o^2 = \frac{1}{2}(G^2 v_e^2)_2 + H_2 + Q \tag{26-88}$$

For homogeneous flow, the equivalent specific volume v_e is the same as the homogeneous specific volume v_H, and the enthalpy is given by:

$$H_2 = [xH_G + (1-x)\,H_L]_2 \tag{26-89}$$

Omega Method HEM Equation (26-86) can be integrated after first relating the dimensionless specific volume ε to the dimensionless pressure ratio η. A simple reciprocal relationship, designated the *omega method,* was suggested by Leung (1986) and by Leung and Grolmes (1988):

$$\varepsilon_H = \begin{cases} \omega\left[\dfrac{\eta_s}{\eta} - 1\right] + 1 & \text{if } \dfrac{\eta_s}{\eta} > 1 \\ 1.0 & \text{if } \dfrac{\eta_s}{\eta} \le 1 \end{cases} \tag{26-90}$$

Figure 26-65 illustrates that Eq. (26-90) provides a linear approximation to the nonlinear relationship between two-phase specific volume and reciprocal pressure (v_H vs. P^{-1} or ε_H vs. η^{-1}). For single components, the initial slope of the ε_H curve is found using the Clapeyron equation to give:

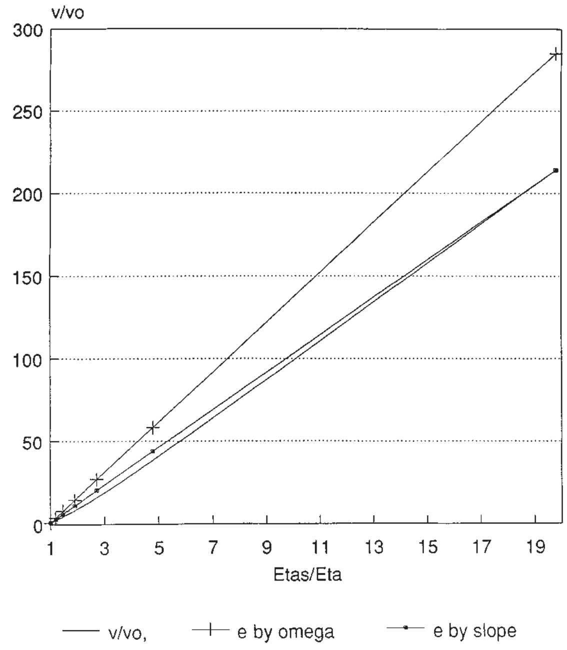
$$\omega = \alpha_o + (1-\alpha_o)\,\omega_s$$

$$\alpha_o = x_o\,\frac{v_{vo}}{v_o}$$

$$\omega_s = \frac{C_{PL}\,T_o P_s}{v_{LO}}\left[\frac{v_{VLO}\,(P_s)}{h_{VLO}\,(P_s)}\right]^2 \tag{26-91}$$

To generalize for multicomponents and, in fact, to find a better fit for single components, use known information about the value of ε_H at some lower pressure, $\eta = \eta_2$, where η_2 is a rough approximation to the choking pressure ratio. That is, use the slope over the largest pressure interval of interest to give:

$$\omega = \frac{\varepsilon_2 - 1}{(\eta_s/\eta_2) - 1} \tag{26-92}$$



NH3, Po =23.75 atm.

FIG. 26-65 Comparison of predictions for two-phase specific volume as a function of pressure by the omega method for two alternative formulas to calculate omega.

Equation (26-91) gives values which are often high or low at the low-pressure end of the curve, whereas Eq. (26-92) is in error only insofar as the true ε curve is nonlinear. However, in practice, either approach provides adequate predictions for discharge rate.

HEM for Two-Phase Orifice Discharge For orifice or nozzle flow, the friction term and the potential energy term in Eq. (26-82) are negligible, so it can be integrated in general across both subcooled and flashing regions thusly:

$$\frac{1}{2}\,\frac{G_{*\mathrm{ori}}^2}{C_D^2}\,\varepsilon_2^2 = \int_1^{\eta_s}\varepsilon_H\,d\eta + \int_{\eta_s}^{\eta_2}\varepsilon_H\,d\eta \tag{26-93}$$

For the highly subcooled subset of Regime 2, ($\eta_s < \eta_a$), flow is single-phase (liquid), and integration of Eq. (26-93) gives what is commonly referred to as the *orifice equation:*

Subcooled Liquid Orifice Discharge

$$G_{*\mathrm{ori}}^2 = C_D^2\,2\,(1-\eta_2) \tag{26-94}$$

For the compressible flow cases, Regimes 1 and 3, and Regime 2 with $\eta_s > \eta_a$, making use of Eq. (26-90), integration of Eq. (26-93) gives:

Compressible Fluid Orifice Discharge by HEM

$$\frac{G_{*\mathrm{ori}}^2}{C_D^2} = \frac{2\,\{(1-\eta_{\mathrm{sp}}) + (1-\omega)\,(\eta_{\mathrm{sp}}-\eta_2) + \omega\eta_{\mathrm{sp}}\ln(\eta_{\mathrm{sp}}/\eta_2)\}}{\varepsilon_2^2} \tag{26-95}$$

This is written with the general notation η_{sp} to avoid repetition of similar equations. For Regime 1, $\alpha_o = 0$, so $\omega = \omega_s$, and $\eta_{\mathrm{sp}} = \eta_s$. For Regime 3, $\omega = \alpha_o$, and the integration is developed with $\eta_{\mathrm{sp}} = 1$, so the above solution applies with $\eta_{\mathrm{sp}} = 1$. This emphasizes the essential unity of the solution for Regimes 1 and 3. Equation (26-95) is plotted in Fig. 26-66 with Regime 1 to the right of $\omega = 1$ and Regime 3 to the left.

Equation (26-95) applies for subsonic as well as choked flow. Choked flow occurs at the pressure ratio $\eta_2 = \eta_c$, which maximizes $G_{*\mathrm{ori}}$. To maximize $G_{*\mathrm{ori}}$, differentiate Eq. (26-95) and set:

$$\left[\frac{\partial G_*}{\partial \eta_2}\right]_{\eta_2 = \eta_c} = 0 \tag{26-96}$$

This gives a transcendental equation in η, the root of which occurs when $\eta = \eta_c$:

$$\frac{(1-\omega)^2}{2\omega\eta_s}\,\eta^2 + 2\,(1-\omega)\,\eta + \left(\frac{3}{2}\omega\eta_s - 1\right) - \omega\eta_s\ln\frac{\eta_s}{\eta} = 0 \tag{26-97}$$

Use a root-finding algorithm to discover the value of η_c which satisfies Eq. (26-97). These values are also plotted in Fig. 26-66.

For Regime 2, $\alpha_o = 0$ and $\omega = \omega_s$. Regime 2 requires using the incompressible solution for highly subcooled liquids and the compressible flow solutions for liquids of a low degree of subcooling. Essentially, these provide two branches to the solution, and by the flow maximization principle, we must choose the larger of the two. Empirically, the point at which these branches of the solution cross is given by:

$$\eta_{\mathrm{st}} = \frac{2\omega\eta_s}{1 + 2\omega\eta_s} \tag{26-98}$$

So, when $\eta_s > \eta_{\mathrm{st}}$ (low subcooling, flashing before the choke print), use the compressible solution, Eq. (26-95) with $\eta_{\mathrm{sp}} = \eta_s$. Otherwise (for high subcooling, no flashing before the choke point), use the liquid orifice equation, Eq. (26-94).

The solution for Regime 2 is plotted in Fig. 26-67. The high subcooling branch given by the liquid orifice equation goes through $G_{*\mathrm{ori}} = 0$ when $\eta_s = 1$. The moderate subcooling branch parts with the former branch at η_{st} and matches values shown in Figure 26-66 when $\eta_s = 1$.

Choked Flow by Two-Phase Energy Balance From the energy balance, Eq. (26-88), taking $u_o = 0$ (stagnation) and $Q = 0$:

$$G_{\mathrm{ori}} = \frac{[2\,(H_o - H_2)]^{1/2}}{v_e} \tag{26-99}$$

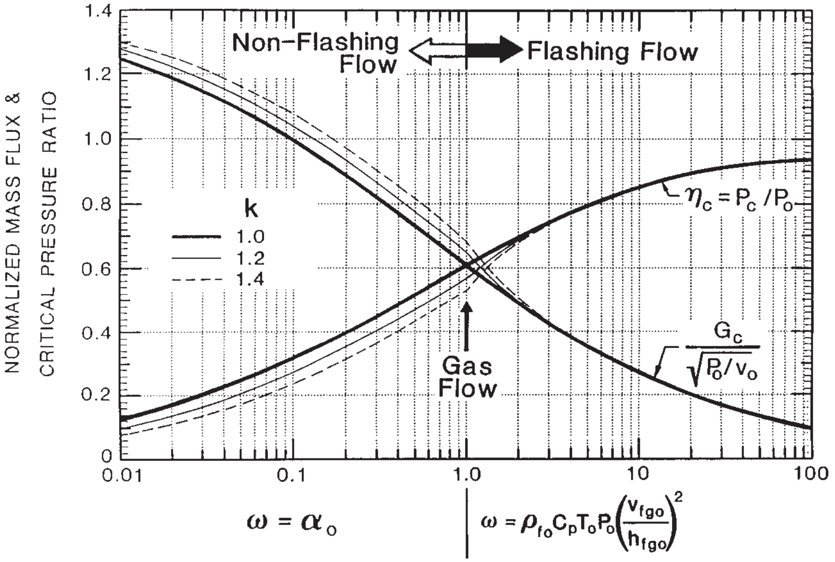


FIG. 26-66 Normalized mass flux and choked flow pressure ratio for frozen flow (left side) and for flashing liquid flow (right side) from orifice or nozzle discharge by the homogeneous equilibrium model. (*Leung, J.C.,* Chem. Eng. Progress *88(2), pp. 70–75, 1992, Reproduced with permission of AIChE. Copyright 1992 AIChE. All rights reserved.*)

where v_e is an equivalent specific volume. This provides a simple alternative HEM for finding mass flux. Simply decrement pressure and search for the maximum value of G given by Eq. (26-99). This method requires good physical properties tables.

Differentiating with respect to pressure and invoking the first law of thermodynamics gives:

$$G^2_{\text{ori}} = \frac{-1}{v_e}\left(\frac{\partial H}{\partial v_e}\right)_s = -\left[\frac{\partial P}{\partial v_e}\right]_s \tag{26-100}$$

or equivalently, differentiating Eq. (26-90) with respect to (η_2) gives:

$$G^2_{*\text{ori}} = -\left[\frac{\partial \varepsilon}{\partial \eta}\right]_S^{-1} = \frac{\eta_2^2}{\omega \eta_s} \tag{26-101}$$

When the flow is choked, this equation gives the same value for $G_{*\text{ori}}$ as does Eq. (26-95), as long as the root of Eq. (26-97) η_c is substituted for η_2.

Full-Bore and Punctured Pipe Discharge With a pipe puncture, the mass flux at the discharge point G_{*d} is larger than the mass flux in the pipe G_{*p}, by the puncture–to–pipe area ratio A_N/A_p, or $(D/D_p)^2$, defined as σ. Specifically:

$$G_{*p} = \sigma\, G_{*d} \tag{26-102}$$

Since this correction is readily made, the following discussion assumes a full-bore pipe rupture, or σ = 1.

HEM for Two-Phase Pipe Discharge With a pipe present, the backpressure experienced by the orifice is no longer η_2, but rather an intermediate pressure ratio η_1. Thus η_1 replaces η_2 in the orifice solution for mass flux $G_{*\text{ori}}$ Eq. (26-95). Correspondingly, the momentum balance is integrated between η_1 and η_2 to give the pipe flow solution for G_{*p}. The solutions for orifice and pipe flow must be solved simultaneously to make $G_{*\text{ori}} = G_{*p}$ and to find η_1 and η_2. This can be done explicitly for the simple case of incompressible single-phase (liquid) inclined or horizontal pipe flow. The solution is implicit for compressible regimes.

For incompressible orifice flow, $\varepsilon_H = 1$ and Eq. (26-86) is integrated between 1 and η_1 to give Eq. (26-94), with η_1 replacing η_2. Equation (26-86) integrated between η_1 and η_2 gives:

$$G^2_{*p} = \frac{2\,(\eta_1 - \eta_2)}{N} - 2F_i \tag{26-103}$$

Eliminating η_1 using Eq. (26-94) and setting $G_{*\text{ori}} = G_{*p}$ and $C_D = 1$ gives:

Subcooled Liquid Inclined Pipe Discharge

$$G^2_{*p} = \frac{2\,(1 - \eta_2) - NF_I}{N + 1} \tag{26-104}$$

For horizontal pipe flow, $F_I = 0$.

The general-case solution for compressible, inclined pipe flow is next stated, then the solution is developed for the special case of horizontal compressible flow.

Using the omega equation, Eq. (26-90), to eliminate $d\varepsilon_H$ in Eq. (26-86) enables Eq. (26-86) to be integrated to the following:

HEM for Inclined Pipe Discharge For = $\eta_1 > \eta_s > \eta_2$ (flashing within the pipe):

$$\begin{aligned} N + \ln\left[\frac{X(\eta_2)}{X(\eta_{\text{sp}})}\left[\frac{\eta_{\text{sp}}}{\eta_2}\right]^2\right] &= \frac{(\eta_1 - \eta_{\text{sp}}) + (1-\omega)(\eta_{\text{sp}} - \eta_2)}{c} \\ &\quad + \left[\frac{c\omega\eta_s - b\,(1-\omega)}{2c^2}\right]\ln\left[\frac{X(\eta_{\text{sp}})}{X(\eta_2)}\right] \\ &= \left[\frac{(1-\omega)(b^2 - 2ac) - bc\omega\eta_s}{2c^2}\right][I_o(\eta_{\text{sp}}) - I_o(\eta_2)] \end{aligned} \tag{26-105}$$

where:

$$X(\eta) = a + b\eta + c\eta^2 \tag{26-106}$$

$$a = \frac{1}{2}\, G^2_{*p}\, \omega^2 \eta_s^2 \tag{26-107}$$

$$b = \frac{1}{2}\, G^2_{*p}\, \omega\,(1-\omega)\,\eta_s \tag{26-108}$$

$$c = \frac{1}{2}\, G^2_{*p}\,(1-\omega)^2 + F_I \tag{26-109}$$

$$q = 4ac - b^2 \tag{26-110}$$

Defining:

$$I_o(\eta) = \int \frac{d\eta}{X(\eta)} \tag{26-111}$$

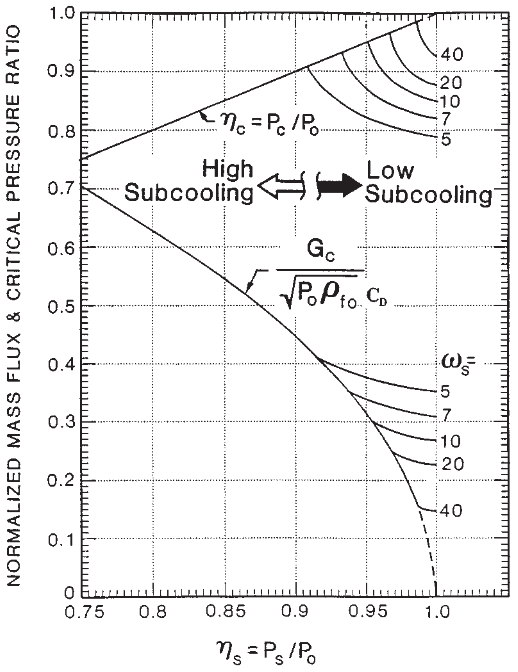


FIG. 26-67 Normalized mass flux and choked flow pressure ratio for flashing liquid discharge from orifices or nozzles by the homogeneous equilibrium model.*(Leung, J.C. and M.A. Grolmes,* AIChE J. ***33****(3) pp. 524–527 (1987); Leung, J.C.,* Chem. Eng. Prog. ***92****(12), pp. 28–50 (1996). Reproduced with permission of AIChE, Copyright 1987, 1996. All rights reserved.)*

we obtain:

$$I_o(\eta) = \begin{cases} \dfrac{2}{q^{1/2}} \tan^{-1}\left[\dfrac{2c\eta + b}{q^{1/2}}\right] & \text{if } q > 0 \text{ (upflow)} \\[2ex] \dfrac{1}{(-q)^{1/2}} \ln\left[\dfrac{2c\eta + b - (-q)^{1/2}}{2c\eta + b + (-q)^{1/2}}\right] & \text{if } q < 0 \text{ (downflow)} \end{cases} \qquad (26\text{-}112)$$

This solution is implicit in mass flux G_{*p}. To illustrate its application, first consider the special case of horizontal pipe flow. The term η_{sp} is defined as follows for both horizontal and inclined pipe flow.

HEM for Horizontal Pipe Discharge For horizontal pipe flow, $F_I = q = 0$, and:

$$I_o(\eta) = \frac{-1}{\frac{1}{2}b + c\eta} \qquad (26\text{-}113)$$

The general compressible flow solution simplifies for horizontal pipe flow to:

$$G_{*p}^2 = 2\,\frac{\left\{(\eta_1 - \eta_{sp}) + \dfrac{(\eta_{sp} - \eta_2)}{1 - \omega} + \dfrac{\omega\eta_s}{(1-\omega)^2} \ln\left[\dfrac{\varepsilon_2\eta_2}{\varepsilon_{sp}\eta_{sp}}\right]\right\}}{N + 2\ln\left[\dfrac{\varepsilon_2}{\varepsilon_{sp}}\right]} \qquad (26\text{-}114)$$

The solution is again generalized with the term η_{sp} and $\varepsilon_{sp} = \varepsilon(\eta_{sp})$. For Regimes 1 and 2, $\alpha_o = 0$, so $\omega = \omega_s$. Regime 2 is again split, depending on where the flashing occurs, in the orifice or in the line. The division between low and moderate subcooling is found by:

$$\eta_{st} = \frac{2\omega_s}{1 + 2\omega_s + N} \qquad (26\text{-}115)$$

Regime 1 is included in the following two subcases of Regime 2:

- For the low subcooling case, which includes Regime 1, $\eta_s > \eta_{st}$ and $\eta_s > \eta_1$ (flashing occurs in the vessel or pipe entrance). Set $\eta_{sp} = \eta_1$.
- For the moderate subcooling case, $\eta_s > \eta_{st} > \eta_2$ (flashing occurs in the pipe). Set $\eta_{sp} = \eta_s$.
- For the high subcooling case, $\eta_s < \eta_{st}$, use the single-phase orifice equation, Eq. (26-104).

For Regime 3, $\omega = \alpha_o$, and the integration is developed letting $\eta_s = 1$, so the above solution applies with $\eta_{sp} = 1$.

The solution of these equations requires a root-finding algorithm which iterates on assumed values of η_1. At each value of η_1, solve Eq. (26-95) (with η_1 replacing η_2) for G_{*ori}. Find η_2 from Eq. (26-101), subject also to:

$$\eta_2 \geq \eta_a$$

Solve Eq. (26-114) for G_{*p}. The function:

$$f(\eta_1) = G_{*ori} - G_{*p} \qquad (26\text{-}116)$$

always has a root in the interval $1 < \eta_1 < \eta_a$ since G_{*ori} increases with decreasing η_1 and G_{*p} decreases with decreasing η_1.

The maximum value for G_{*p} is G_{*ori} evaluated with zero pipe length. Denoting this value as G_{*max}, Fig. 26-68 plots the dimensionless mass

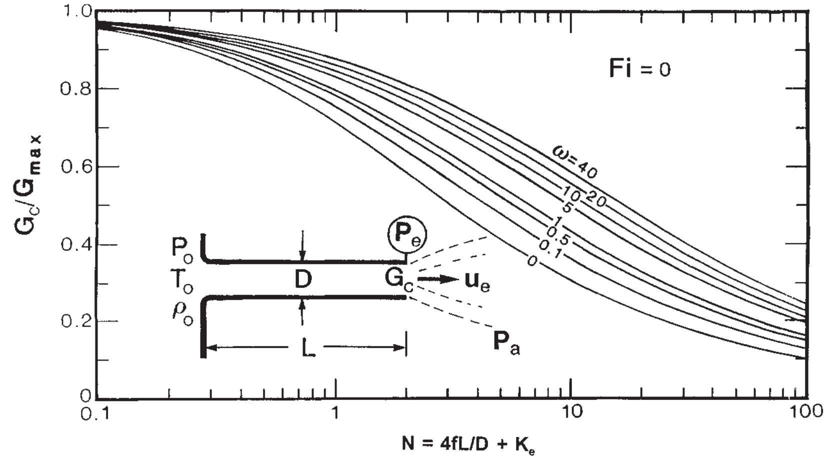


FIG. 26-68 Ratio of mass flux for horizontal pipe flow to that for orifice discharge for flashing liquids by the homogeneous equilibrium model. (*Leung and Grolmes,* AIChE J, ***33*** *(3), pp. 524–527, 1987; reproduced by permission of AIChE. copyright 1987. All rights reserved.)*

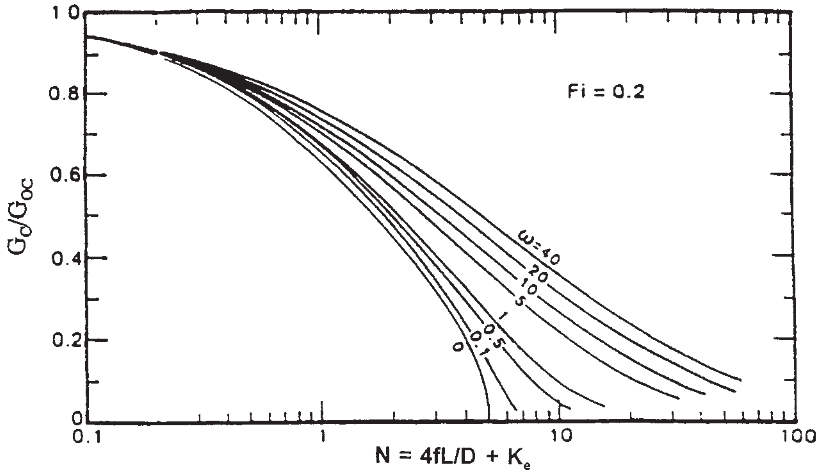


FIG. 26-69 Ratio of mass flux for inclined pipe flow to that for orifice discharge for flashing liquids by the homogeneous equilibrium model. (*Leung,* J. of Loss Prev. Process Ind. **3** *pp. 27–32, with kind permission of Elsevier Science, Ltd, The Boulevard, Langford Lane, Kidlington, OX5 IGB U.K., 1990.*)

flux discharge for horizontal pipe flow $G_{\circ p}$ as a ratio $G_{\circ p}/G_{\circ \max}$. Similar design charts were developed by Levenspiel (1977).

Figure 26-69 plots $G_{\circ p}/G_{\circ \max}$ for an upwardly inclined pipe flow [Eq. (26-105)] for a specific value of the pipe inclination factor F_I = 0.2. Comparing Figs. 26-68 and 26-69 shows that discharge rates decrease with upflow. For downflow, the curves are higher than in horizontal flow. In fact, a minimum flow occurs, regardless of how much pipe length is added, quite similar to the terminal velocity of free-falling objects. These charts are useful for design calculations up to a reduced temperature (ratio of temperature to the critical temperature) of about 0.90.

Accuracy of Omega Method HEM Figures 26-70 and 26-71 illustrate the accuracy to be expected with the omega method HEM. For slightly subcooled (flashing) or saturated water, using the data of Sozzi and Sutherland (1975) and the ASME Symposium on Non-Equilibrium Two-Phase Flows (1975), predictions improve to within 10 percent error when the pipe length is larger than about 0.5 m.

NEM for Two-Phase Orifice Discharge With flow through an orifice or nozzle, the flash is delayed, and the delay time depends on the initial concentration of nucleation sites for vaporization. A simplified approach to represent nonequilibrium orifice or nozzle flow has been suggested by Henry and Fauske ("The Two-Phase Critical Flow of One-Component Mixtures in Nozzles, Orifices, and Short Tubes," *Trans. ASME, J. Heat Transfer* **93**(5): 179–N87, 1976) and by Chisholm (1983).

For orifice flow, Eq. (26-80) reduces to:

$$-vdP = G^2vdv \tag{26-117}$$

or, differentiating the definition of *G:*

$$-vdP = udu = \frac{1}{2}\,du^2 \tag{26-118}$$

This can be readily integrated numerically as long as we use the appropriate nonequilibrium equivalent specific volume v_e in the integration. A reasonably simple form for v_e has been suggested by Chisholm (1983), which makes use of established correlations for the slip velocity *K,* which depends on the Lockhart-Martinelli parameter *X.* Integrating Eq. (26-118) gives:

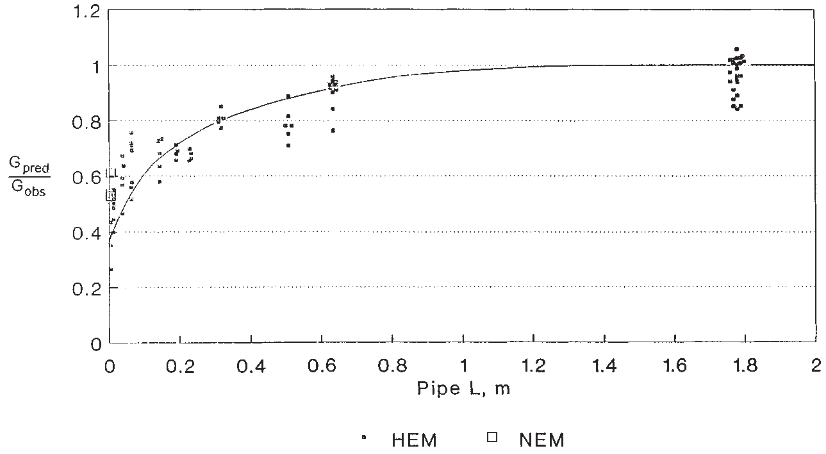


FIG. 26-70 Accuracy in HEM predictions for slightly to moderately subcooled flashing flow. Comparison with data for water by Sozzi and Sutherland (1975); also ASME Symposium on Non-Equilibrium Two-Phase Flows (1975) (Nozzle type 2).

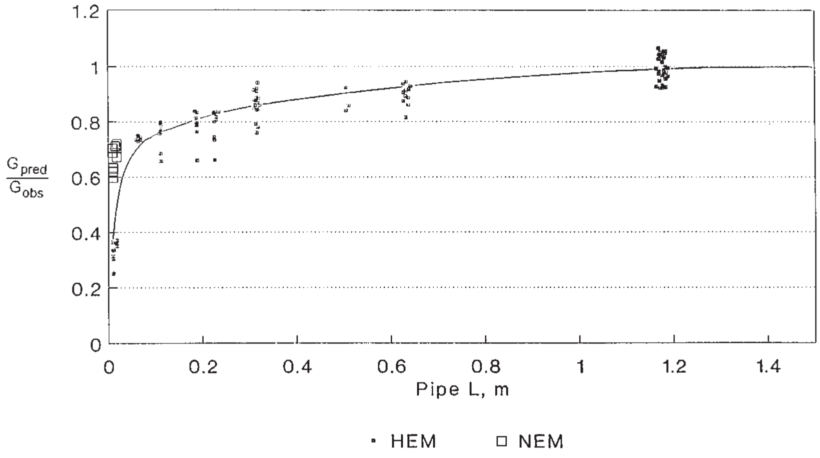


FIG. 26-71 Accuracy in HEM predictions for saturated, flashing flow. Comparison with data for water by Sozzi and Sutherland (1975), (Nozzle type 2).

$$-\int_{P_o}^{P_2} v\,dP = u_2^2\left[1-\left(\frac{u_o}{u_2}\right)^2\right] \tag{26-119}$$

Making use of continuity:

$$w = A_o\frac{u_o}{v_o} = A_2\frac{u_2}{v_2} \tag{26-120}$$

Equation (26-119) can be rearranged and written in dimensionless variables as:

$$G_{*2}^2 = \frac{-2\displaystyle\int_1^{\eta_2}\varepsilon_e\,d\eta}{\varepsilon_{e2}^2\left[1-\left(\dfrac{A_2\varepsilon_{e1}}{A_1\varepsilon_{e2}}\right)^2\right]} = \frac{-2\displaystyle\int_1^{\eta_2}\varepsilon_e\,d\eta}{\varepsilon_{e2}^2 - C_D^2} \tag{26-121}$$

since $C_D = A_2/A_o$ at the vena contracta, $G_{*2} = G_{*C}$. Equation (26-131) gives $G_{*\text{ori}}$.

The integral of Eq. (26-121) is evaluated in increments of pressure ratio $d\eta$, using the following procedure. At the next pressure given by:

$$P_i = P_{i-1} - \Delta\eta P_o \tag{26-122}$$

use an equation of state to find v_G, v_L. Use an isentropic flash to find the equilibrium flash fraction x. The initial vapor mass fraction x_o can include noncondensables as well as an initial flash fraction. If this is the case, add the noncondensable portion to x.

Find the Lockhart-Martinelli coefficient as defined by Lockhart and Martinelli (1949):

$$X_m^2 = \frac{dP_L}{dP_G} = \frac{f_L(1-x)^2}{f_G x^2}\,\frac{v_L}{v_G} \tag{26-123}$$

or the ratio of the pressure drop for liquid flowing alone to that for gas flowing alone. The liquid and gas friction factors are usually justifiably taken as equal (unless one phase is in laminar flow while the other is in turbulent).

Find the equilibrium, homogeneous specific volume v_H given by Eq. (26-85) and estimate the slip velocity ratio using the following correlation:

$$K_o = \begin{cases}\left[\dfrac{v_H}{v_L}\right]^{1/2} & \text{if } X_m > 1\\[2ex] \left[\dfrac{v_G}{v_L}\right]^{1/4} & \text{if } X_m < 1\end{cases} \tag{26-124}$$

The slip velocity ratio is adequately represented by:

$$K = \frac{u_G}{u_L} = K_o^{0.4} \tag{26-125}$$

Find the coefficient in the equivalent specific volume B using:

$$B = \frac{(1/K)\,(v_G/v_L) + K - 2}{(v_G/v_L) - 1} \tag{26-126}$$

or, if $\dfrac{v_G}{v_L} >> K\,(K-2)$

$$B = \frac{1}{K} \tag{26-127}$$

Find the transition flash fraction x_t:

$$x_t = \frac{1}{1+(v_G/v_L)^{1/2}} \tag{26-128}$$

The nonequilibrium flash fraction x_N is interpolated nonlinearly between x_o and x_t by:

$$x_N = \begin{cases} x_o + \left(\dfrac{x-x_o}{x_t-x_o}\right)^2 (x-x_o) & x < x_t\\[2ex] x & x > x_t\end{cases} \tag{26-129}$$

So when $x > x_t$, thermal equilibrium is assumed.

Find the equivalent nonequilibrium specific volume as:

$$\varepsilon_e = \frac{v_e}{v_o} = 1 + \left(\frac{v_G}{v_L} - 1\right)\left[Bx_N\,(1-x_N) + x_N^2\right] \tag{26-130}$$

The integration proceeds stepwise until the integral begins to decrease. This occurs at the choked pressure ratio η_c, giving a maximum mass flux G_{*2c}.

As shown in Figs. 26-70 and 26-71, the orifice flow predictions by the NEM (open points) are larger than those of the HEM, although still low compared with these particular data.

Discharge Coefficients and Gas Discharge A compressible fluid, upon discharge from an orifice, accelerates from the puncture point and the cross-sectional area contracts until it forms a minimum at the vena contracta. If flow is choked, the mass flux G_{*c} can be found at the vena contracta, since it is a maximum at that point. The mass flux at the orifice is related to the mass flux at the vena contracta by the discharge coefficient, which is the area contraction ratio (A_c at the vena contracta to A_N at the orifice):

$$G_{*\text{ori}} = C_D G_{*c} \tag{26-131}$$

For two-phase flow, the phase contraction coefficients C_{DG} and C_{DL} relate the area of each phase A_G and A_L at the vena contracta to the known area of the orifice A_N. Thus:

$$C_{DG} = \frac{A_G}{A_N}, \qquad C_{DL} = \frac{A_L}{A_N} \tag{26-132}$$

The two-phase discharge coefficient is:

$$C_D = \frac{A_G + A_L}{A_N} = \frac{xv_G + K(1-x)v_L}{\dfrac{xv_G}{C_{DG}} + \dfrac{K(1-x)v_L}{C_{DL}}} \qquad (26\text{-}133)$$

where K is the slip velocity ratio, u_G/u_L given by Eq. (26-125). The contraction coefficient for liquids is generally accepted as $C_{DL} = 0.61$. For the gas phase, as developed by Jobson (1955):

$$C_{DG} = \frac{1}{2b_1\eta_{2c}^{1/k}}\left\{a_1 - \left[a_1^2 - \frac{4\eta_{2c}^{2/k}(1-\eta_2)\,b_1}{G_{*g}^2}\right]^{1/2}\right\} \qquad (26\text{-}134)$$

$$b_1 = \frac{1}{C_{DL}} - \frac{1}{2C_{DL}^2} \qquad (26\text{-}135)$$

$$a_1 = 1 + \frac{(\eta_{2c} - \eta_2)\,\eta_{2c}^{1/k}}{G_{*g}^2} \qquad (26\text{-}136)$$

where: $$G_{*g}^2 = \frac{2k}{(k-1)}\,\eta_2^{2/k}\left(1 - \eta_2^{(k-1)/k}\right) \qquad (26\text{-}137)$$

and for vapor or gas flow:

$$G_{*\mathrm{ori}} = C_{DG}\,G_{*g} \qquad (26\text{-}138)$$

Equation (26-137) is recognized as the expression for all-gas flow by adiabatic expansion across an orifice or nozzle. The factor k is the expansion coefficient for the adiabatic flow equation of state:

$$\frac{P}{P_o} = \left[\frac{\rho}{\rho_o}\right]^k = \left[\frac{T}{T_o}\right]^{k/(k-1)} \qquad (26\text{-}139)$$

For an ideal gas:

$$k = \frac{C_p}{C_v} \qquad (26\text{-}140)$$

Fortunately, for most operating pressure ranges, k is nearly constant with temperature and pressure. For wider ranges where this might not hold it is often adequate to replace k by a value slightly smaller than C_p/C_v. A rationale for this is that heat exchange with the surroundings can shift the behavior slightly toward the isothermal solution, which is a limiting case with $k = 1$.

TABLE 26-30 Variation in Two-Phase Discharge Coefficients by Jobson Equations

Exit pressure ratio, η_2	$\dfrac{C_{DG}}{C_{DL}}$	C_{DG}
1.0	1.0	0.61
0.8	1.07	0.653
0.6	1.18	0.720
0.4	1.31	0.799
0.2	1.40	0.854
0.0	1.44	0.878

A further generalization for two-phase flow as suggested by Tangren et al. (1949) is to use the generalized value of k as:

$$k = \frac{xC_{pG} + (1-x)\,C_{PL}}{xC_{vG} + (1-x)\,C_{PL}} \qquad (26\text{-}141)$$

For gas-phase choked flow, the pressure ratio at the vena contracta is:

$$\eta_{2c} = \left(\frac{2}{k+1}\right)^{k/(k-1)} \qquad (26\text{-}142)$$

and $$\eta_2 = \text{maximum}(\eta_{2c}, \eta_a)$$

reaching η_a when the flow becomes subsonic.

For choked flow, $a_1 = 1$ in Eq. (26-136). Typical values developed by Eqs. (26-133) and (26-134) are listed in Table 26-30 (Watson et al., 1983).

Blowdown Modeling Blowdown models incorporate not only the preceding discharge rate models but also a model of the tank and line contents to predict how the tank pressure and temperature decay in time. Analytical time-varying blowdown solutions are available for single-phase discharge, gas or liquid (Woodward and Mudan, 1991). Analytical liquid blowdown models have been developed for essentially all tank geometries of interest by Sommerfeld and coworkers (Lee and Sommerfeld, May 1994, July 1994). Vapor blowdown is readily modeled, using an energy and mass balance on the tank contents. The tank pressure decays along the vapor pressure curve as long as a liquid is present. Two-phase blowdown modeling is further discussed in Woodward (1993, pp. 94–159).