### CHAPTER 9

# Safety and Loss Prevention

#### 9.1. INTRODUCTION

Any organisation has a legal and moral obligation to safeguard the health and welfare of its employees and the general public. Safety is also good business; the good management practices needed to ensure safe operation will also ensure efficient operation.

The term "loss prevention" is an insurance term, the loss being the financial loss caused by an accident. This loss will not only be the cost of replacing damaged plant and third party claims, but also the loss of earnings from lost production and lost sales opportunity.

All manufacturing processes are to some extent hazardous, but in chemical processes there are additional, special, hazards associated with the chemicals used and the process conditions. The designer must be aware of these hazards, and ensure, through the application of sound engineering practice, that the risks are reduced to acceptable levels.

In this book only the particular hazards associated with chemical and allied processes will be considered. The more general, normal, hazards present in all manufacturing process such as, the dangers from rotating machinery, falls, falling objects, use of machine tools, and of electrocution will not be considered. General industrial safety and hygiene are covered in several books, King and Hirst (1998), Ashafi (2003) and Ridley (2003).

Safety and loss prevention in process design can be considered under the following broad headings:

- 1. Identification and assessment of the hazards.
- 2. Control of the hazards: for example, by containment of flammable and toxic materials.
- 3. Control of the process. Prevention of hazardous deviations in process variables (pressure, temperature, flow), by provision of automatic control systems, interlocks, alarms, trips; together with good operating practices and management.
- 4. Limitation of the loss. The damage and injury caused if an incident occurs: pressure relief, plant layout, provision of fire-fighting equipment.

In this chapter the discussion of safety in process design will of necessity be limited. A more complete treatment of the subject can be found in the books by Wells (1980) (1997), Lees (1996), Fawcett and Wood (1984), Green (1982) and Carson and Mumford (1988) (2002); and in the general literature, particularly the publications by the American Institute of Chemical Engineers and the Institution of Chemical Engineers. The proceedings of the symposia on safety and loss prevention organised by these bodies, and the European Federation of Chemical Engineering, also contain many articles of interest on general safety philosophy, techniques and organisation, and the hazards associated with specific

processes and equipment. The Institution of Chemical Engineers has published a book on safety of particular interest to students of Chemical Engineering, Marshall and Ruhemann (2000).

### 9.2. INTRINSIC AND EXTRINSIC SAFETY

Processes can be divided into those that are intrinsically safe, and those for which the safety has to be engineered in. An intrinsically safe process is one in which safe operation is inherent in the nature of the process; a process which causes no danger, or negligible danger, under all foreseeable circumstances (all possible deviations from the design operating conditions). The term inherently safe is often preferred to intrinsically safe, to avoid confusion with the narrower use of the term intrinsically safe as applied to electrical equipment (see Section 9.3.4).

Clearly, the designer should always select a process that is inherently safe whenever it is practical, and economic, to do so. However, most chemical manufacturing processes are, to a greater or lesser extent, inherently unsafe, and dangerous situations can develop if the process conditions deviate from the design values.

The safe operation of such processes depends on the design and provision of engineered safety devices, and on good operating practices, to prevent a dangerous situation developing, and to minimise the consequences of any incident that arises from the failure of these safeguards.

The term "engineered safety" covers the provision in the design of control systems, alarms, trips, pressure-relief devices, automatic shut-down systems, duplication of key equipment services; and fire-fighting equipment, sprinkler systems and blast walls, to contain any fire or explosion.

The design of inherently safe process plant is discussed by Kletz in a booklet published by the Institution of Chemical Engineers, Kletz (1984) and Keltz and Cheaper (1998). He makes the telling point that what you do not have cannot leak out: so cannot catch fire, explode or poison anyone. Which is a plea to keep the inventory of dangerous material to the absolute minimum required for the operation of the process.

### 9.3. THE HAZARDS

In this section the special hazards of chemicals are reviewed (toxicity, flammability and corrosivity); together with the other hazards of chemical plant operation.

### 9.3.1. Toxicity

Most of the materials used in the manufacture of chemicals are poisonous, to some extent. The potential hazard will depend on the inherent toxicity of the material and the frequency and duration of any exposure. It is usual to distinguish between the short-term effects (acute) and the long-term effects (chronic). A highly toxic material that causes immediate injury, such as phosgene or chlorine, would be classified as a safety hazard. Whereas a material whose effect was only apparent after long exposure at low concentrations, for instance, carcinogenic materials, such as vinyl chloride, would be classified as industrial

health and hygiene hazards. The permissible limits and the precautions to be taken to ensure the limits are met will be very different for these two classes of toxic materials. Industrial hygiene is as much a matter of good operating practice and control as of good design.

The inherent toxicity of a material is measured by tests on animals. It is usually expressed as the lethal dose at which 50 per cent of the test animals are killed, the  $LD_{50}$  (lethal dose fifty) value. The dose is expressed as the quantity in milligrams of the toxic substance per kilogram of body weight of the test animal.

Some values for tests on rats are given in Table 9.1. Estimates of the  $LD_{50}$  for man are based on tests on animals. The  $LD_{50}$  measures the acute effects; it gives only a crude indication of the possible chronic effects.

Table 9.1. Some LD<sub>50</sub> values

Compound	mg/kg
Potassium cyanide	10
Tetraethyl lead	35
Lead	100
DDT	150
Aspirin	1500
Table salt	3000

Source: Lowrance (1976).

There is no generally accepted definition of what can be considered toxic and non-toxic. A system of classification is given in the *Classification*, *Packaging and Labelling of Dangerous Substances*, *Regulations*, 1984 (United Kingdom), which is based on European Union (EU) guidelines; for example:

 $LD_{50}$ , absorbed orally in rats, mg/kg  $\leq$ 25 very toxic 25 to 200 toxic 200 to 2000 harmful

These definitions apply only to the short-term (acute) effects. In fixing permissible limits on concentration for the long-term exposure of workers to toxic materials, the exposure time must be considered together with the inherent toxicity of the material. The "Threshold Limit Value" (TLV) is a commonly used guide for controlling the long-term exposure of workers to contaminated air. The TLV is defined as the concentration to which it is believed the average worker could be exposed to, day by day, for 8 hours a day, 5 days a week, without suffering harm. It is expressed in ppm for vapours and gases, and in mg/m³ (or grains/ft³) for dusts and liquid mists. A comprehensive source of data on the toxicity of industrial materials is Sax's handbook, Lewis (2004); which also gives guidance on the interpretation and use of the data. Recommended TLV values are published in bulletins by the United States Occupational Safety and Health Administration. Since 1980 the United Kingdom Health and Safety Executive (HSE) has published values for the Occupational Exposure Limits (OEL), for both long and short term exposure, in place of TLV values.

Fuller details of the methods used for toxicity testing, the interpretation of the result and their use in setting standards for industrial hygiene are given in the more specialised texts on the subject; see Carson and Mumford (1988) and Lees (1996).

#### Control of substances hazardous to health

In the United Kingdom the use of substances likely to be harmful to employees is covered by regulations issued by the Health and Safety Executive (HSE), under the Health and Safety at Work Act, 1974 (HSAWA). The principal set of regulations in force is the *Control of Substances Hazardous to Health* regulations, 2002; known under the acronym: the *COSHH* regulations. The *COSHH* regulations apply to any hazardous substance in use in any place of work.

The employer is required to carry out an assessment to evaluate the risk to health, and establish what precautions are needed to protect employees. A written record of the assessment would be kept, and details made available to employees.

A thorough explanation of the regulations is not within the scope of this book, as they will apply more to plant operation and maintenance than to process design. The HSE has published a series of booklets giving details of the regulations and their application (see www.hse.gov.uk/pubns). A comprehensive guide to the *COSHH* regulations has also been published by the Royal Society of Chemistry, Simpson and Simpson (1991).

The designer will be concerned more with the preventative aspects of the use of hazardous substances. Points to consider are:

- 1. Substitution: of the processing route with one using less hazardous material. Or, substitution of toxic process materials with non-toxic, or less toxic materials.
- 2. Containment: sound design of equipment and piping, to avoid leaks. For example, specifying welded joints in preference to gasketed flanged joints (liable to leak).
- 3. Ventilation: use open structures, or provide adequate ventilation systems.
- 4. Disposal: provision of effective vent stacks to disperse material vented from pressure relief devices; or use vent scrubbers.
- 5. Emergency equipment: escape routes, rescue equipment, respirators, safety showers, eye baths.

In addition, good plant operating practice would include:

- 1. Written instruction in the use of the hazardous substances and the risks involved.
- 2. Adequate training of personnel.
- 3. Provision of protective clothing.
- 4. Good housekeeping and personal hygiene.
- 5. Monitoring of the environment to check exposure levels. Consider the installation of permanent instruments fitted with alarms.
- Regular medical check-ups on employees, to check for the chronic effects of toxic materials.

# 9.3.2. Flammability

The term "flammable" is now more commonly used in the technical literature than "inflammable" to describe materials that will burn, and will be used in this book. The hazard caused by a flammable material depends on a number of factors:

- 1. The flash-point of the material.
- 2. The autoignition temperature of the material.
- 3. The flammability limits of the material.
- 4. The energy released in combustion.

### Flash-point

The flash-point is a measure of the ease of ignition of the liquid. It is the lowest temperature at which the material will ignite from an open flame. The flash-point is a function of the vapour pressure and the flammability limits of the material. It is measured in standard apparatus, following standard procedures (BS 2000). Both open- and closed-cup apparatus is used. Closed-cup flash-points are lower than open cup, and the type of apparatus used should be stated clearly when reporting measurements. Flash-points are given in Sax's handbook, Lewis (2004). The flash-points of many volatile materials are below normal ambient temperature; for example, ether  $-45^{\circ}$ C, petrol (gasoline)  $-43^{\circ}$ C (open cup).

### Autoignition temperature

The autoignition temperature of a substance is the temperature at which it will ignite spontaneously in air, without any external source of ignition. It is an indication of the maximum temperature to which a material can be heated in air; for example, in drying operations.

### Flammability limits

The flammability limits of a material are the lowest and highest concentrations in air, at normal pressure and temperature, at which a flame will propagate through the mixture. They show the range of concentration over which the material will burn in air, if ignited. Flammability limits are characteristic of the particular material, and differ widely for different materials. For example, hydrogen has a lower limit of 4.1 and an upper limit of 74.2 per cent by volume, whereas for petrol (gasoline) the range is only from 1.3 to 7.0 per cent.

The Flammability limits for a number of materials are given in Table 9.2.

The limits for a wider range of materials are given in Sax's handbook, Lewis (2004).

A flammable mixture may exist in the space above the liquid surface in a storage tank. The vapour space above highly flammable liquids is usually purged with inert gas (nitrogen) or floating-head tanks are used. In a floating-head tank a "piston" floats on top of the liquid, eliminating the vapour space.

# Flame traps

Flame arresters are fitted in the vent lines of equipment that contains flammable material to prevent the propagation of flame through the vents. Various types of proprietary flame arresters are used. In general, they work on the principle of providing a heat sink, usually expanded metal grids or plates, to dissipate the heat of the flame. Flame arrestors and their applications are discussed by Rogowski (1980), Howard (1992) and Mendoza *et al.* (1988).

Traps should also be installed in plant ditches to prevent the spread of flame. These are normally liquid U-legs, which block the spread of flammable liquid along ditches.

Table 9.2. Flammability ranges

Material	Lower limit	Upper limit
Hydrogen	4.1	74.2
Ammonia	15.0	28.0
Hydrocyanic acid	5.6	40.0
Hydrogen sulphide	4.3	45.0
Carbon disulphide	1.3	44.0
Carbon monoxide	12.5	74.2
Methane	5.3	14.0
Ethane	3.0	12.5
Propane	2.3	9.5
Butane	1.9	8.5
Isobutane	1.8	8.4
Ethylene	3.1	32.0
Propylene	2.4	10.3
n-Butene	1.6	9.3
Isobutene	1.8	9.7
Butadiene	2.0	11.5
Benzene	1.4	7.1
Toluene	1.4	6.7
Cyclohexane	1.3	8.0
Methanol	7.3	36.0
Ethanol	4.3	19.0
Isopropanol	2.2	12.0
Formaldehyde	7.0	73.0
Acetaldehyde	4.1	57.0
Aetone	3.0	12.8
Methylethyl ketone	1.8	10.0
Dimethylamine (DEA)	2.8	184
Trimethylamine (TEA)	2.0	11.6
Petrol (gasoline)	1.3	7.0
Paraffin (kerosene)	0.7	5.6
Gas oil (diesel)	6.0	13.5

Volume percentage in air at ambient conditions

# Fire precautions

Recommendations on the fire precautions to be taken in the design of chemical plant are given in the British Standard, BS 5908.

# 9.3.3. Explosions

An explosion is the sudden, catastrophic, release of energy, causing a pressure wave (blast wave). An explosion can occur without fire, such as the failure through over-pressure of a steam boiler or an air receiver.

When discussing the explosion of a flammable mixture it is necessary to distinguish between detonation and deflagration. If a mixture detonates the reaction zone propagates at supersonic velocity (approximately 300 m/s) and the principal heating mechanism in the mixture is shock compression. In a deflagration the combustion process is the same as in the normal burning of a gas mixture; the combustion zone propagates at subsonic

velocity, and the pressure build-up is slow. Whether detonation or deflagration occurs in a gas-air mixture depends on a number of factors; including the concentration of the mixture and the source of ignition. Unless confined or ignited by a high-intensity source (a detonator) most materials will not detonate. However, the pressure wave (blast wave) caused by a deflagration can still cause considerable damage.

Certain materials, for example, acetylene, can decompose explosively in the absence of oxygen; such materials are particularly hazardous.

### Confined vapour cloud explosion (CVCE)

A relatively small amount of flammable material, a few kilograms, can lead to an explosion when released into the confined space of a building.

### Unconfined vapour cloud explosions (UCVCE)

This type of explosion results from the release of a considerable quantity of flammable gas, or vapour, into the atmosphere, and its subsequent ignition. Such an explosion can cause extensive damage, such as occurred at Flixborough, HMSO (1975). Unconfined vapour explosions are discussed by Munday (1976) and Gugan (1979).

### Boiling liquid expanding vapour explosions (BLEVE)

Boiling liquid expanding vapour explosions occur when there is a sudden release of vapour, containing liquid droplets, due to the failure of a storage vessel exposed to fire. A serious incident involving the failure of a LPG (Liquified Petroleum Gas) storage sphere occurred at Feyzin, France, in 1966, when the tank was heated by an external fire fuelled by a leak from the tank; see Lees (1996) and Marshall (1987).

# **Dust explosions**

Finely divided combustible solids, if intimately mixed with air, can explode. Several disastrous explosions have occurred in grain silos.

Dust explosions usually occur in two stages: a primary explosion which disturbs deposited dust; followed by the second, severe, explosion of the dust thrown into the atmosphere. Any finely divided combustible solid is a potential explosion hazard. Particular care must be taken in the design of dryers, conveyors, cyclones, and storage hoppers for polymers and other combustible products or intermediates. The extensive literature on the hazard and control of dust explosions should be consulted before designing powder handling systems: Field (1982), Cross and Farrer (1982), Barton (2001), and Eckhoff (2003).

# 9.3.4. Sources of ignition

Though precautions are normally taken to eliminate sources of ignition on chemical plants, it is best to work on the principle that a leak of flammable material will ultimately find an ignition source.

### Electrical equipment

The sparking of electrical equipment, such as motors, is a major potential source of ignition, and flame proof equipment is normally specified. Electrically operated instruments, controllers and computer systems are also potential sources of ignition of flammable mixtures.

The use of electrical equipment in hazardous areas is covered by British Standards BS 5345 and BS 5501. The code of practice, BS 5345, Part 1, defines hazardous areas as those where explosive gas-air mixtures are present, or may be expected to be present, in quantities such as to require special precautions for the construction and use of electrical apparatus. Non-hazardous areas are those where explosive gas-air mixtures are not expected to be present.

Three classifications are defined for hazardous areas:

Zone 0: explosive gas-air mixtures are present continuously or present for long periods.

Specify: intrinsically safe equipment.

Zone 1: explosive gas-air mixtures likely to occur in normal operation.

Specify: intrinsically safe equipment, or flame-proof enclosures: enclosures with pressurizing and purging.

Zone 3: explosive gas-air mixtures not likely to occur during normal operation, but could occur for short periods.

Specify: intrinsically safe equipment, or total enclosure, or non-sparking apparatus.

Consult the standards for the full specification before selecting equipment for use in the designated zones.

The design and specification of intrinsically safe control equipment and systems is discussed by MacMillan (1998) and Cooper and Jones (1993).

# Static electricity

The movement of any non-conducting material, powder, liquid or gas, can generate static electricity, producing sparks. Precautions must be taken to ensure that all piping is properly earthed (grounded) and that electrical continuity is maintained around flanges. Escaping steam, or other vapours and gases, can generate a static charge. Gases escaping from a ruptured vessel can self-ignite from a static spark. For a review of the dangers of static electricity in the process industries, see the article by Napier and Russell (1974); and the books by Pratt (1999) and Britton (1999). A code of practice for the control of static electricity is given in BS 5938 (1991).

### Process flames

Open flames from process furnaces and incinerators are obvious sources of ignition and must be sited well away from plant containing flammable materials.

#### Miscellaneous sources

It is the usual practice on plants handling flammable materials to control the entry on to the site of obvious sources of ignition; such as matches, cigarette lighters and battery-operated

equipment. The use of portable electrical equipment, welding, spark-producing tools and the movement of petrol-driven vehicles would also be subject to strict control.

Exhaust gases from diesel engines are also a potential source of ignition.

### 9.3.5. lonising radiation

The radiation emitted by radioactive materials is harmful to living matter. Small quantities of radioactive isotopes are used in the process industry for various purposes; for example, in level and density-measuring instruments, and for the non-destructive testing of equipment.

The use of radioactive isotopes in industry is covered by government legislation, see hse.gov.uk/pubns.

A discussion of the particular hazards that arise in the chemical processing of nuclear fuels is outside the scope of this book.

### 9.3.6. Pressure

Over-pressure, a pressure exceeding the system design pressure, is one of the most serious hazards in chemical plant operation. Failure of a vessel, or the associated piping, can precipitate a sequence of events that culminate in a disaster.

Pressure vessels are invariably fitted with some form of pressure-relief device, set at the design pressure, so that (in theory) potential over-pressure is relieved in a controlled manner.

Three basically different types of relief device are commonly used:

Directly actuated valves: weight or spring-loaded valves that open at a predetermined pressure, and which normally close after the pressure has been relieved. The system pressure provides the motive power to operate the valve.

*Indirectly actuated valves*: pneumatically or electrically operated valves, which are activated by pressure-sensing instruments.

Bursting discs: thin discs of material that are designed and manufactured to fail at a predetermined pressure, giving a full bore opening for flow.

Relief valves are normally used to regulate minor excursions of pressure; and bursting discs as safety devices to relieve major over-pressure. Bursting discs are often used in conjunction with relief valves to protect the valve from corrosive process fluids during normal operation. The design and selection of relief valves is discussed by Morley (1989a,b), and is also covered by the pressure vessel standards, see Chapter 13. Bursting discs are discussed by Mathews (1984), Askquith and Lavery (1990) and Murphy (1993). In the United Kingdom the use of bursting discs is covered by BS 2915. The discs are manufactured in a variety of materials for use in corrosive conditions; such as, impervious carbon, gold and silver; and suitable discs can be found for use with all process fluids.

Bursting discs and relief valves are proprietary items and the vendors should be consulted when selecting suitable types and sizes.

The factors to be considered in the design of relief systems are set out in a comprehensive paper by Parkinson (1979) and by Moore (1984); and in a book published by the Institution of Chemical Engineers, Parry (1992).

### Vent piping

When designing relief venting systems it is important to ensure that flammable or toxic gases are vented to a safe location. This will normally mean venting at a sufficient height to ensure that the gases are dispersed without creating a hazard. For highly toxic materials it may be necessary to provide a scrubber to absorb and "kill" the material; for instance, the provision of caustic scrubbers for chlorine and hydrochloric acid gases. If flammable materials have to be vented at frequent intervals; as, for example, in some refinery operations, flare stacks are used.

The rate at which material can be vented will be determined by the design of the complete venting system: the relief device and the associated piping. The maximum venting rate will be limited by the critical (sonic) velocity, whatever the pressure drop (see Volume 1, Chapter 4). The design of venting systems to give adequate protection against over-pressure is a complex and difficult subject, particularly if two-phase flow is likely to occur. For complete protection the venting system must be capable of venting at the same rate as the vapour is being generated. For reactors, the maximum rate of vapour generation resulting from a loss of control can usually be estimated. Vessels must also be protected against over-pressure caused by external fires. In these circumstances the maximum rate of vapour generation will depend on the rate of heating. Standard formulae are available for the estimation of the maximum rates of heat input and relief rates, see ROSPA (1971) and NFPA (1987a,b).

For some vessels, particularly where complex vent piping systems are needed, it may be impractical for the size of the vent to give complete protection against the worst possible situation.

For a comprehensive discussion of the problem of vent system design, and the design methods available, see the papers by Duxbury (1976, 1979).

The design of relief systems has been studied by the Design Institute for Emergency Relief Systems (DIERS), established by the American Institute of Chemical Engineers; Fisher (1985). DIERS has published recommended design methods; see Poole (1985) and AIChemE (1992a,b). Computer programs based on the work by DIERS are also available.

### Under-pressure (vacuum)

Unless designed to withstand external pressure (see Chapter 13) a vessel must be protected against the hazard of under-pressure, as well as over-pressure. Under-pressure will normally mean vacuum on the inside with atmospheric pressure on the outside. It requires only a slight drop in pressure below atmospheric pressure to collapse a storage tank. Though the pressure differential may be small, the force on the tank roof will be considerable. For example, if the pressure in a 10-m diameter tank falls to 10 millibars below the external pressure, the total load on the tank roof will be around 80,000 N (8 tonne). It is not an uncommon occurrence for a storage tank to be sucked in (collapsed) by the suction pulled by the discharge pump, due to the tank vents having become blocked. Where practical, vacuum breakers (valves that open to atmosphere when the internal pressure drops below atmospheric) should be fitted.

# 9.3.7. Temperature deviations

Excessively high temperature, over and above that for which the equipment was designed, can cause structural failure and initiate a disaster. High temperatures can arise from loss

of control of reactors and heaters; and, externally, from open fires. In the design of processes where high temperatures are a hazard, protection against high temperatures is provided by:

- 1. Provision of high-temperature alarms and interlocks to shut down reactor feeds, or heating systems, if the temperature exceeds critical limits.
- 2. Provision of emergency cooling systems for reactors, where heat continues to be generated after shut-down; for instance, in some polymerisation systems.
- Structural design of equipment to withstand the worst possible temperature excursion.
- 4. The selection of intrinsically safe heating systems for hazardous materials.

Steam, and other vapour heating systems, are intrinsically safe; as the temperature cannot exceed the saturation temperature at the supply pressure. Other heating systems rely on control of the heating rate to limit the maximum process temperature. Electrical heating systems can be particularly hazardous.

### Fire protection

To protect against structural failure, water-deluge systems are usually installed to keep vessels and structural steelwork cool in a fire.

The lower section of structural steel columns are also often lagged with concrete or other suitable materials.

### 9.3.8. Noise

Excessive noise is a hazard to health and safety. Long exposure to high noise levels can cause permanent damage to hearing. At lower levels, noise is a distraction and causes fatigue.

The unit of sound measurement is the decibel, defined by the expression:

Sound level = 20 
$$\log_{10} \left[ \frac{\text{RMS sound pressure (Pa)}}{2 \times 10^{-5}} \right]$$
, dB (9.1)

The subjective effect of sound depends on frequency as well as intensity.

Industrial sound meters include a filter network to give the meter a response that corresponds roughly to that of the human ear. This is termed the "A" weighting network and the readings are reported as dB(A).

Permanent damage to hearing can be caused at sound levels above about 90 dB(A), and it is normal practice to provide ear protection in areas where the level is above 80 dB(A).

Excessive plant noise can lead to complaints from neighbouring factories and local residents. Due attention should be given to noise levels when specifying, and when laying out, equipment that is likely to be excessively noisy; such as, compressors, fans, burners and steam relief valves.

Several books are available on the general subject of industrial noise control, Bias and Hansen (2003), and on noise control in the process industries, Cheremisnoff (1996), ASME (1993).

### 9.4. DOW FIRE AND EXPLOSION INDEX

The hazard classification guide developed by the Dow Chemical Company and published by the American Institute of Chemical Engineering, Dow (1994) (www.aiche.org), gives a method of evaluating the potential risk from a process, and assessing the potential loss.

A numerical "Fire and explosion index" (F & EI) is calculated, based on the nature of the process and the properties of the process materials. The larger the value of the F & EI, the more hazardous the process, see Table 9.3.

Table 9.3. Assessment of hazard

Fire and explosion index range	Degree of hazard
1-60	Light
61-96	Moderate
97-127	Intermediate
128-158	Heavy
>159	Severe

Adapted from the Dow F & EI guide (1994).

To assess the potential hazard of a new plant, the index can be calculated after the Piping and Instrumentation and equipment layout diagrams have been prepared. In earlier versions of the guide the index was then used to determine what preventative and protection measures were needed, see Dow (1973). In the current version the preventative and protection measures, that have been incorporated in the plant design to reduce the hazard–are taken into account when assessing the potential loss; in the form of loss control credit factors.

It is worthwhile estimating the F & EI index at an early stage in the process design, as it will indicate whether alternative, less hazardous, process routes should be considered.

Only a brief outline of the method used to calculate the Dow F & EI will be given in this section. The full guide should be studied before applying the technique to a particular process. Judgement, based on experience with similar processes, is needed to decide the magnitude of the various factors used in the calculation of the index, and the loss control credit factors.

#### 9.4.1. Calculation of the Dow F & El

The procedure for calculating the index and the potential loss is set out in Figure 9.1.

The first step is to identify the units that would have the greatest impact on the magnitude of any fire or explosion. The index is calculated for each of these units.

The basis of the F & EI is a *Material Factor* (MF). The MF is then multiplied by a *Unit Hazard Factor*, F<sub>3</sub>, to determine the F & EI for the process unit. The Unit Hazard factor is the product of two factors which take account of the hazards inherent in the operation of the particular process unit: the general and special process hazards, see Figure 9.2.

#### Material factor

The material factor is a measure of the intrinsic rate of energy release from the burning, explosion, or other chemical reaction of the material. Values for the MF for over 300 of

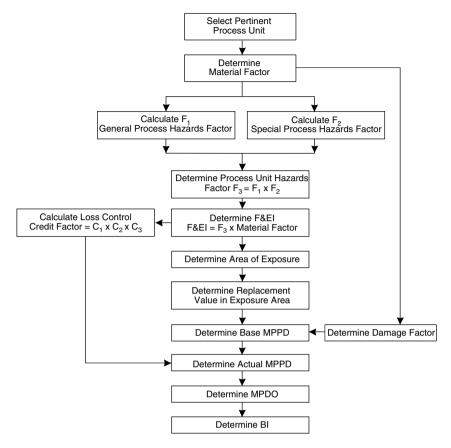


Figure 9.1. Procedure for calculating the fire and explosion index and other risk analysis information. From Dow (1994) reproduced by permission of the American Institute of Chemical Engineers. © 1994 AIChE. All rights reserved.

the most commonly used substances are given in the guide. The guide also includes a procedure for calculating the MF for substances not listed: from a knowledge of the flash points, (for dusts, dust explosion tests) and a reactivity value,  $N_r$ . The reactivity value is a qualitative description of the reactivity of the substance, and ranges from 0 for stable substances, to 4 for substances that are capable of unconfined detonation.

Some typical material factors are given in Table 9.4.

In calculating the F & EI for a unit the value for the material with the highest MF, which is present in significant quantities, is used.

### General process hazards

The general process hazards are factors that play a primary role in determining the magnitude of the loss following an incident.

Six factors are listed on the calculation form, Figure 9.2.

	MF	Flash point°C	Heat of combustion MJ/kg
Acetaldehyde	24	-39	24.4
Acetone	16	-20	28.6
Acetylene	40	gas	48.2
Ammonia	4	gas	18.6
Benzene	16	-11	40.2
Butane	21	gas	45.8
Chlorine	1	_	0.0
Cyclohexane	16	-20	43.5
Ethyl alcohol	16	13	26.8
Hydrogen	21	gas	120.0
Nitroglycerine	40	_	18.2
Sulphur	4	_	9.3
Toluene	16	40	31.3
Vinyl Chloride	21	gas	18.6

Table 9.4. Some typical material factors

- A. *Exothermic chemical reactions*: the penalty varies from 0.3 for a mild exotherm, such as hydrogenation, to 1.25 for a particularly sensitive exotherm, such as nitration.
- B. *Endothermic processes*: a penalty of 0.2 is applied to reactors, only. It is increased to 0.4 if the reactor is heated by the combustion of a fuel.
- C. *Materials handling and transfer*: this penalty takes account of the hazard involved in the handling, transfer and warehousing of the material.
- D. Enclosed or indoor process units: accounts for the additional hazard where ventilation is restricted.
- E. Access of emergency equipment: areas not having adequate access are penalised. Minimum requirement is access from two sides.
- F. *Drainage and spill control*: penalises design conditions that would cause large spills of flammable material adjacent to process equipment; such as inadequate design of drainage.

# Special process hazards

The special process hazards are factors that are known from experience to contribute to the probability of an incident involving loss.

Twelve factors are listed on the calculation form, Figure 9.2.

- A. *Toxic materials*: the presence of toxic substances after an incident will make the task of the emergency personnel more difficult. The factor applied ranges from 0 for non-toxic materials, to 0.8 for substances that can cause death after short exposure.
- B. *Sub-atmospheric pressure*: allows for the hazard of air leakage into equipment. It is only applied for pressure less than 500 mmHg (9.5 bara).
- C. Operation in or near flammable range: covers for the possibility of air mixing with material in equipment or storage tanks, under conditions where the mixture will be within the explosive range.

# **FIRE & EXPLOSION INDEX**

AREA/COUNTRY	DIVISION		LOCATION		DATE		
SITE	MANUFACTURI	NG UNIT	PROCESS UNIT				
PREPARED BY:	AF	PPROVED BY:(Superin	tendent)	BUILDING			
REVIEWED BY:(Management)	RE	EVIEWED BY:(Technol	ogy Center)	REVIEWE	D BY:(Safety & Los	s Prevention)	
MATERIALS IN PROCESS UNIT							
STATE OF OPERATION			BASIC MATERIAL(S) FO	R MATERIA	L FACTOR		
- DESIGN - START UP I	NORMAL OPERAT	TION — SHUTDOWN					
MATERIAL FACTOR (See Table 1 or A	MATERIAL FACTOR (See Table 1 or Appendices A or B) Note requirements when unit temperature over 140 °F (60 °C)						
General Process Hazar	ds				Penalty Fac- tor Range	Penalty Fac- tor Used(1)	
Base Factor					1.00	1.00	
A. Exothermic Chemical F	Reactions				0.30 to 1.25		
<ul> <li>B. Endothermic Processe</li> </ul>	s				0.20 to 0.40		
C. Material Handling and	Transfer				0.25 to 1.05		
D. Enclosed or Indoor Pro	cess Units				0.25 to 0.90		
E. Access	E. Access						
F. Drainage and Spill Controlgal or cu.m.					0.25 to 0.50		
General Process Hazards Factor (F <sub>1</sub> )							
2. Special Process Hazard	ds						
Base Factor					1.00	1.00	
A. Toxic Material(s)					0.20 to 0.80		
B. Sub-Atmospheric Pres	sure (< 500 mn	n Hg)			0.50		
C. Operation In or Near F	lammable Rang	ge l	nerted Not In	erted			
_ 1. Tank Farms Stora	ge Flammable	Liquids			0.50		
Process Upset or 1	Purge Failure				0.30		
<ol><li>Always in Flamma</li></ol>	ble Range				0.80		
D. Dust Explosion (See Ta					0.25 to 2.00		
E. Pressure (See Figure 2	2)		psig or kP				
<u> </u>		Relief Setting	psig or kPa	a gauge			
F. Low Temperature					0.20 to 0.30		
G. Quantity of Flammable	/Unstable Mate		Quantity				
`	D (0		H <sub>C</sub> =BTU/lb or	kcal/kg			
Liquids or Gases in	<del></del>						
2. Liquids or Gases i			Figure 5)				
3. Combustible Solid		iust in Process (See	rigule 3)		0.10 to 0.75		
H. Corrosion and Erosion					0.10 to 0.73		
Leakage – Joints and F  J. Use of Fired Equipment				+	0.70 10 7.00		
J. Use of Fired Equipmen  K. Hot Oil Heat Exchange			<del></del>		0.15 to 1.15		
<del></del>	Cystern (366	1 4513 51			0.50		
L. Rotating Equipment				1.			
Special Process Hazard							
Process Unit Hazards F							
Fire and Explosion Ind	ex (F3 x MF	= F&EI)					

(1) For no penalty use 0.00.

Figure 9.2. Dow Fire and Explosion Index calculation form.

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Note: 1 m³ = 264.2 US gal; 1 kN/m² = 0.145 psi; 1 kg = 2.2 lbs; 1 kJ/Kg = 0.43 BTU/lb.

- D. *Dust explosion*: covers for the possibility of a dust explosion. The degree of risk is largely determined by the particle size. The penalty factor varies from 0.25 for particles above 175  $\mu$ m, to 2.0 for particles below 75  $\mu$ m.
- E. *Relief pressure*: this penalty accounts for the effect of pressure on the rate of leakage, should a leak occur. Equipment design and operation becomes more critical as the operating pressure is increased. The factor to apply depends on the relief device setting and the physical nature of the process material. It is determined from Figure 2 in the Dow Guide.
- F. Low temperature: this factor allows for the possibility of brittle fracture occurring in carbon steel, or other metals, at low temperatures (see Chapter 7 of this book).
- G. Quantity of flammable material: the potential loss will be greater the greater the quantity of hazardous material in the process or in storage. The factor to apply depends on the physical state and hazardous nature of the process material, and the quantity of material. It varies from 0.1 to 3.0, and is determined from Figures 3, 4 and 5 in the Dow Guide.
- H. *Corrosion and erosion*: despite good design and materials selection, some corrosion problems may arise, both internally and externally. The factor to be applied depends on the anticipated corrosion rate. The severest factor is applied if stress corrosion cracking is likely to occur (see Chapter 7 of this book).
- I. Leakage—joints and packing: this factor accounts for the possibility of leakage from gaskets, pump and other shaft seals, and packed glands. The factor varies from 0.1 where there is the possibility of minor leaks, to 1.5 for processes that have sight glasses, bellows or other expansion joints.
- J. *Use of fired heaters*: the presence of boilers or furnaces, heated by the combustion of fuels, increases the probability of ignition should a leak of flammable material occur from a process unit. The risk involved will depend on the siting of the fired equipment and the flash point of the process material. The factor to apply is determined with reference to Figure 6 in the Dow Guide.
- K. *Hot oil heat exchange system*: most special heat exchange fluids are flammable and are often used above their flash points; so their use in a unit increases the risk of fire or explosion. The factor to apply depends on the quantity and whether the fluid is above or below its flash point; see Table 5 in the Guide.
- L. *Rotating equipment*: this factor accounts for the hazard arising from the use of large pieces of rotating equipment: compressors, centrifuges, and some mixers.

#### 9.4.2 Potential loss

The procedure for estimating the potential loss that would follow an incident is set out in Table 9.5: the Unit analysis summary.

The first step is to calculate the *Damage factor* for the unit. The Damage factor depends on the value of the Material factor and the Process unit hazards factor  $(F_3$  in Figure 2). It is determined using Figure 8 in the Dow Guide.

An estimate is then made of the area (radius) of exposure. This represents the area containing equipment that could be damaged following a fire or explosion in the unit being considered. It is evaluated from Figure 7 in the Guide and is a linear function of the Fire and Explosion Index.

Table 9.5. Loss control credit factors

#### 1. Process Control Credit Factor (C<sub>1</sub>)

	Credit	Credit		Credit	Credit
Feature	Factor	Factor	Feature	Factor	Factor
	Range	Used(2)		Range	Used(2)
a. Emergency Power	0.98		f. Inert Gas	0.94 to 0.96	
b. Cooling	0.97 to 0.99		g. Operating Instructions/Procedures	0.91 to 0.99	
c. Explosion Control	0.84 to 0.98		h. Reactive Chemical Review	0.91 to 0.98	
d. Emergency Shutdown	0.96 to 0.99		i. Other Process Hazard Analysis	0.91 to 0.98	
e. Computer Control	0.93 to 0.99				

C<sub>1</sub>Value(3)

#### 2. Material Isolation Credit Factor (C<sub>2</sub>)

	Credit	Credit		Credit	Credit
Feature	Factor	Factor	Feature	Factor	Factor
	Range	Used(2)		Range	Used(2)
a. Remote Control Valves	0.96 to 0.98		c. Drainage	0.91 to 0.97	
b. Dump/Blowdown	0.96 to 0.98		d. Interlock	0.98	

C<sub>2</sub>Value(3)

#### 3. Fire Protection Credit Factor (C<sub>3</sub>)

	Credit	Credit		Credit	Credit
Feature	Factor	Factor	Feature	Factor	Factor
	Range	Used(2)		Range	Used(2)
a. Leak Detection	0.94 to 0.98		f. Water Curtains	0.97 to 0.98	
b. Structural Steel	0.95 to 0.98		g. Foam	0.92 to 0.97	
c. Fire Water Supply	0.94 to 0.97		h. Hand Extinguishers/Monitors	0.93 to 0.98	
d. Special Systems	0.91		i. Cable Protection	0.94 to 0.98	
e. Sprinkler Systems	0.74 to 0.97				

C3 value(3)	
Loss Control Credit Factor = $C_1 \times C_2 \times C_3(3)$ =	(enter on line 7 Table

C. Volue(2)

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An estimate of the replacement value of the equipment within the exposed area is then made, and combined with by the damage factor to estimate the *Base maximum probable property damage* (Base MPPD).

The *Maximum probable property damage* (MPPD) is then calculated by multiplying the Base MPPD by a *Credit control factor*. The Loss control credit control factors, see Table 9.6, allow for the reduction in the potential loss given by the preventative and protective measures incorporated in the design.

The MPPD is used to predict the maximum number of days which the plant will be down for repair, the *Maximum probable days outage* (MPDO). The MPDO is used to estimate

Table 9.6.	Process	unit	rick	analy	zeie	Summary
14016 9.0.	FIUCESS	umi	HISK	anary	V 212	Summary

5. Damage Factor (Figure 8)*	
4. Value of Area of Exposure       \$1         5. Damage Factor       (Figure 8)*         6. Base Maximum Probable Property Damage—(Base MPPD) [4 × 5]       \$1	
5. Damage Factor       (Figure 8)*         6. Base Maximum Probable Property Damage—(Base MPPD) [4 × 5]       \$1	
6. Base Maximum Probable Property Damage—(Base MPPD) [4 × 5]	SMM
7. Loss Control Credit Factor (See Above)	SMM
8. Actual Maximum Probable Property Damage — (Actual MPPD) $[6 \times 7]$	SMM
9. Maximum Probable Days Outage—(MPDO) (Figure 9)* days	
10. Business Interruption—(BI)	SMM

<sup>(2)</sup> For no credit factor enter 1.00. (3) Product of all factors used.

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the financial loss due to the lost production: the *Business interruption* (BI). The financial loss due to lost business opportunity can often exceed the loss from property damage.

### 9.4.3. Basic preventative and protective measures

The basic safety and fire protective measures that should be included in all chemical process designs are listed below. This list is based on that given in the Dow Guide, with some minor amendments.

- 1. Adequate, and secure, water supplies for fire fighting.
- 2. Correct structural design of vessels, piping, steel work.
- 3. Pressure-relief devices.
- 4. Corrosion-resistant materials, and/or adequate corrosion allowances.
- 5. Segregation of reactive materials.
- 6. Earthing of electrical equipment.
- 7. Safe location of auxiliary electrical equipment, transformers, switch gear.
- 8. Provision of back-up utility supplies and services.
- 9. Compliance with national codes and standards.
- 10. Fail-safe instrumentation.
- 11. Provision for access of emergency vehicles and the evacuation of personnel.
- 12. Adequate drainage for spills and fire-fighting water.
- 13. Insulation of hot surfaces.
- 14. No glass equipment used for flammable or hazardous materials, unless no suitable alternative is available.
- 15. Adequate separation of hazardous equipment.
- 16. Protection of pipe racks and cable trays from fire.
- 17. Provision of block valves on lines to main processing areas.
- 18. Protection of fired equipment (heaters, furnaces) against accidental explosion and fire.
- 19. Safe design and location of control rooms.

<sup>\*</sup>Refer to Fire & Explosion Index Hazard Classification Guide for details.

*Note*: the design and location of control rooms, particularly as regards protection against an unconfined vapour explosion, is covered in a publication of the Chemical Industries Association, CIA (1979a).

### 9.4.4. Mond fire, explosion, and toxicity index

The Mond index was developed from the Dow F and E index by personnel at the ICI Mond division. The third edition of the Dow index, Dow (1973), was extended to cover a wider range of process and storage installations; the processing of chemicals with explosive properties; and the evaluation of a toxicity hazards index. Also included was a procedure to allow for the off-setting effects of good design, and of control and safety instrumentation. Their revised, Mond fire, explosion and toxicity index was discussed in a series of papers by Lewis (1979a, 1979b); which included a technical manual setting out the calculation procedure. An extended version of the manual was issued in 1985, and an amended version published in 1993, ICI (1993).

#### **Procedure**

The basic procedures for calculating the Mond indices are similar to those used for the Dow index.

The process is first divided into a number of units which are assessed individually.

The dominant material for each unit is then selected and its material factor determined. The material factor in the Mond index is a function of the energy content per unit weight (the heat of combustion).

The material factor is then modified to allow for the effect of general and special process and material hazards; the physical quantity of the material in the process step; the plant layout; and the toxicity of process materials.

Separate fire and explosion indices are calculated. An aerial explosion index can also be estimated, to assess the potential hazard of aerial explosions. An equivalent Dow index can also be determined.

The individual fire and explosion indexes are combined to give an overall index for the process unit. The overall index is the most important in assessing the potential hazard.

The magnitude of the potential hazard is determined by reference to rating tables, similar to that shown for the Dow index in Table 9.2.

After the initial calculation of the indices (the initial indices), the process is reviewed to see what measures can be taken to reduce the rating (the potential hazard).

The appropriate off-setting factors to allow for the preventative features included in the design are then applied, and final hazard indices calculated.

#### Preventative measures

Preventative measures fall into two categories:

- 1. Those that reduce the number of incidents. Such as: sound mechanical design of equipment and piping; operating and maintenance procedures, and operator training.
- 2. Those that reduce the scale of a potential incident; such as: measures for fire protection, and fixed fire fighting equipment.

Many measures will not fit neatly into individual categories but will apply to both.

### Implementation

The Mond technique of hazard evaluation is fully explained in the ICI technical manual, ICI (1993)<sup>(1)</sup>, to which reference should be made to implement the method. The calculations are made using a standard form, similar to that used for the Dow index. A computer program is available for use with IBM compatible personal computers.

### **9.4.5. Summary**

The Dow and Mond indexes are useful techniques, which can be used in the early stages of a project design to evaluate the hazards and risks of the proposed process.

Calculation of the indexes for the various sections of the process will highlight any particularly hazardous sections and indicate where a detailed study is needed to reduce the hazards.

### Example 9.1

Evaluate the Dow F & EI for the nitric acid plant described in Chapter 4, Example 4.4.

#### Solution

The calculation is set out on the special form shown in Figure 9.2a. Notes on the decisions taken and the factors used are given below.

*Unit*: consider the total plant, no separate areas, but exclude the main storages.

Material factor: for ammonia, from Dow Guide, and Table 9.3.

$$MF = 4.0$$

*Note*: Hydrogen is present, and has a larger material factor (21) but the concentration is too small for it to be considered the dominant material.

### General process hazards:

- A. Oxidising reaction, factor = 0.5
- B. Not applicable.
- C. Not applicable.
- D. Not applicable.
- E. Adequate access would be provided, factor = 0.0.
- F. Adequate drainage would be provided, factor = 0.0.

# Special process hazards:

- A. Ammonia is highly toxic, likely to cause serious injury, factor = 0.6.
- B. Not applicable.

<sup>&</sup>lt;sup>(1)</sup> Published under licence from Imperial Chemical Industries plc by Dr P. Doran and T. R. Greig, 40 Mors Lane, Northwich, Cheshire, CW8 2PX, United Kingdom.

### **FIRE & EXPLOSION INDEX**

, ,,,	_ <del> </del>	0.011	1110-71					
AREA/C	COUNTRY	DIVISION	-	LOCATION	SLI	GO	DATE 20	JAN 1997
SITE	_		FURING UNIT EIC ACID	PROCESS	UNIT CO	MPLETE	PLANT	
PREPAR	RED BY: RKS	<u> </u>	APPROVED BY:(Superin	ntendent)	ent) BUILDING			
REVIEW	/ED BY:(Management) -		REVIEWED BY:(Technol	nology Center) REVIEWED BY:(Safety & Loss Prevent			s Prevention)	
MATERI	ALS IN PROCESS UNIT	AMMONIA,	AIR, OXIDES OF NITE	ROGEN, W	ATER			
STATE	OF OPERATION			BASIC MA	TERIAL(S) FOI	R MATERIA	L FACTOR	·
DE:	SIGN — START UP	NORMAL OP	ERATION — SHUTDOWN		АММС	NIA		
MATERI	AL FACTOR (See Table 1 or A	Appendices A	or B) Note requirements	when unit te	mperature ove	er 140 °F (60	o°C)	4
1. G	eneral Process Hazar	ds					Penalty Fac- tor Range	Penalty Fac- tor Used(1)
Ва	ase Factor						1.00	1.00
Α.							0.30 to 1.25	0.50
В.	Endothermic Processe	s					0.20 to 0.40	·
C.	Material Handling and	Transfer					0.25 to 1.05	
D.	Enclosed or Indoor Pro	cess Units		_			0,25 to 0.90	
E.	Access						0.20 to 0.35	
F.	Drainage and Spill Co.	ntroi			gal	or cu.m.	0.25 to 0.50	
G	eneral Process Hazar	ds Factor	(F <sub>1</sub> )					1.50
2. S	pecial Process Hazard	ds						
Ba	ase Factor						1.00	1.00
A.							0.20 to 0.80	0.60
B.	Sub-Atmospheric Pres	sure (< 500	mm Hg)				0.50	
C.	Operation in or Near F	lammable F	lange	Inerted	Not In	erted		
	<ol> <li>Tank Farms Stora</li> </ol>	ge Flamma	ble Liquids				0.50	
	<ol><li>Process Upset or</li></ol>	Purge Failu	re	,			0.30	0.80
	<ol><li>Always in Flamma</li></ol>	ble Range					0.80	
D.							0.25 to 2.00	
E.	Pressure (See Figure 2	2)	Operating Pressure Relief Setting		_ psig or kPa _ psig or kPa	!		0.35
F.	Low Temperature						0.20 to 0.30	
G.	. Quantity of Flammable	/Unstable N		Qu:	antity BTU/lb or	ib or kg kcai/kg		
	1. Liquids or Gases i	n Process (	See Figure 3)					
	2. Liquids or Gases i							
	<ol> <li>Combustible Solid</li> </ol>	s in Storage	e, Dust in Process (See	Figure 5)				
H.							0.10 to 0.75	0.10
i.	Leakage - Joints and I	Packing					0,10 to 1.50	0.10
J.	Use of Fired Equipmen	t (See Figu	re 6)					
K.	Hot Oil Heat Exchange	System (S	ee Table 5)				0.15 to 1.15	
L.							0.50	0.50
	pecial Process Hazar							3.45
Pı	rocess Unit Hazards F	actor (F1	x F <sub>2</sub> ) = F <sub>3</sub>					5.20
	re and Explosion Ind							21

(1) For no penalty use 0.00.

Figure 9.2a. Fire and explosion index calculation form, Example 9.1. From Dow (1994) reproduced by permission of the American Institute of Chemical Engineers. © 1994 AIChE. All rights reserved.

- C. Operation always is within the flammable limits, factor = 0.8.
- D. Not applicable.
- E. Operation pressure  $8 \text{ atm} = 8 \times 14.7 14.7 = 103 \text{ psig.}$  Set relief valve at 20% above the operating pressure (see Chapter 13 of this book) = 125 psig.

From Figure 2 in the guide, factor = 0.35.

*Note*: psig = pounds force per square inch, gauge.

- F. Not applicable.
- G. The largest quantity of ammonia in the process will be the liquid in the vaporiser, say around 500 kg.

Heat of combustion, Table 9.3 = 18.6 MJ/kg

Potential energy release =  $500 \times 18.6 = 9300 \text{ MJ}$ 

$$= 9300 \times 10^{6}/(1.05506 \times 10^{3}) = 8.81 \times 10^{6}$$
 Btu

which is too small to register on Figure 3 in the Guide, factor = 0.0.

- H. Corrosion resistant materials of construction would be specified, but external corrosion is possible due to nitric oxide fumes, allow minimum factor = 0.1.
- I. Welded joints would be used on ammonia service and mechanical seals on pumps. Use minimum factor as full equipment details are not known at the flow-sheet stage, factor = 0.1.
- J. Not applicable.
- K. Not applicable.
- L. Large turbines and compressors used, factor = 0.5.

The index works out at 21: classified as "Light". Ammonia would not normally be considered a dangerously flammable material; the danger of an internal explosion in the reactor is the main process hazard. The toxicity of ammonia and the corrosiveness of nitric acid would also need to be considered in a full hazard evaluation.

### 9.5. HAZARD AND OPERABILITY STUDIES

A hazard and operability study is a procedure for the systematic, critical, examination of the operability of a process. When applied to a process design or an operating plant, it indicates potential hazards that may arise from deviations from the intended design conditions.

The technique was developed by the Petrochemicals Division of Imperial Chemical Industries, see Lawley (1974), and is now in general use in the chemical and process industries.

The term "operability study" should more properly be used for this type of study, though it is usually referred to as a hazard and operability study, or HAZOP study. This can cause confusion with the term "hazard analysis", which is a technique for the quantitative assessment of a hazard, after it has been identified by an operability study, or similar technique. Numerous books have been written illustrating the use of HAZOP. Those by Hyatt (2003), AIChemE (2000), Taylor (2000) and Kletz (1999a) give comprehensive descriptions of the technique, with examples.

A brief outline of the technique is given in this section to illustrate its use in process design. It can be used to make a preliminary examination of the design at the flow-sheet stage; and for a detailed study at a later stage, when a full process description, final flow-sheets, P and I diagrams, and equipment details are available.

### 9.5.1. Basic principles

A formal operability study is the systematic study of the design, vessel by vessel, and line by line, using "guide words" to help generate thought about the way deviations from the intended operating conditions can cause hazardous situations.

The seven guide words recommended in the CIA booklet are given in Table 9.7. In addition to these words, the following words are also used in a special way, and have the precise meanings given below:

*Intention*: the intention defines how the particular part of the process was intended to operate; the intention of the designer.

*Deviations*: these are departures from the designer's intention which are detected by the systematic application of the guide words.

*Causes*: reasons why, and how, the deviations could occur. Only if a deviation can be shown to have a realistic cause is it treated as meaningful.

Consequences: the results that follow from the occurrence of a meaningful deviation. Hazards: consequences that can cause damage (loss) or injury.

The use of the guide words can be illustrated by considering a simple example. Figure 9.3 shows a chlorine vaporiser, which supplies chlorine at 2 bar to a chlorination reactor. The vaporiser is heated by condensing steam.

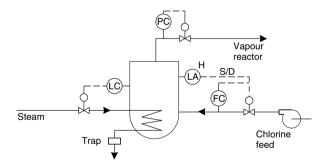


Figure 9.3. Chlorine vaporiser instrumentation

Consider the steam supply line and associated control instrumentation. The designer's intention is that steam shall be supplied at a pressure and flow rate to match the required chlorine demand.

Apply the guide word No:

Possible deviation—no steam flow.

Possible causes—blockage, valve failure (mechanical or power), failure of steam supply (fracture of main, boiler shut-down).

Clearly this is a meaningful deviation, with several plausible causes.

Consequences—the main consequence is loss of chlorine flow to the chlorination reactor.

The effect of this on the reactor operation would have to be considered. This would be brought out in the operability study on the reactor; it would be a possible cause of no chlorine flow.

Apply the guide word MORE:

Possible deviation—more steam flow.

Possible cause—valve stuck open.

Consequences—low level in vaporiser (this should activate the low level alarm), higher rate of flow to the reactor.

*Note:* to some extent the level will be self-regulating, as the level falls the heating surface is uncovered.

Hazard—depends on the possible effect of high flow on the reactor.

Possible deviation—more steam pressure (increase in mains pressure).

Possible causes—failure of pressure-regulating valves.

Consequences — increase in vaporisation rate. Need to consider the consequences of the heating coil reaching the maximum possible steam system pressure.

Hazard—rupture of lines (unlikely), effect of sudden increase in chlorine flow on reactor.

### 9.5.2. Explanation of guide words

The basic meaning of the guide words in Table 9.7. The meaning of the words No/Not, MORE and LESS are easily understood; the No/Not, MORE and LESS could, for example, refer to flow, pressure, temperature, level and viscosity. All circumstances leading to No flow should be considered, including reverse flow.

The other words need some further explanation:

As WELL As: something in addition to the design intention; such as, impurities, sidereactions, ingress of air, extra phases present.

PART OF: something missing, only part of the intention realized; such as, the change in composition of a stream, a missing component.

REVERSE: the reverse of, or opposite to, the design intention. This could mean reverse flow if the intention was to transfer material. For a reaction, it could mean the reverse reaction. In heat transfer, it could mean the transfer of heat in the opposite direction to what was intended.

OTHER THAN: an important and far-reaching guide word, but consequently more vague in its application. It covers all conceivable situations other than that intended; such as, start-up, shut-down, maintenance, catalyst regeneration and charging, failure of plant services.

When referring to time, the guide words SOONER THAN and LATER THAN can also be used.

Table 9.7. A list of guide words

Guide words	Meanings	Comments
No or Not	The complete negation of these intentions	No part of the intentions is achieved but nothing else happens
More Less	Quantitative increases or decreases	These refer to quantities and properties such as flow rates and temperatures, as well as activities like "HEAT" and
A	A constraint of the constraint	"REACT"
As well as	A qualitative increase	All the design and operating intentions are achieved together with some additional activity
PART OF	A qualitative decrease	Only some of the intentions are achieved; some are not
REVERSE	The logical opposite of the intention	This is mostly applicable to activities, for example reverse flow or chemical reaction. It can also be applied to substances, e.g. "Poison instead of "Antidote" or "D" instead of "L" optical isomers
OTHER THAN	Complete substitution	No part of the original intention is achieved. Something quite different happens

### 9.5.3. Procedure

An operability study would normally be carried out by a team of experienced people, who have complementary skills and knowledge; led by a team leader who is experienced in the technique.

The team examines the process vessel by vessel, and line by line, using the guide words to detect any hazards.

The information required for the study will depend on the extent of the investigation.

A preliminary study can be made from a description of the process and the process flow-sheets. For a detailed, final, study of the design, the flow-sheets, piping and instrument diagrams, equipment specifications and layout drawings would be needed. For a batch process information on the sequence of operation will also be required, such as that given in operating instructions, logic diagrams and flow charts.

A typical sequence of events is shown in Figure 9.4. After each line has been studied it is marked on the flow-sheet as checked.

A written record is not normally made of each step in the study, only those deviations that lead to a potential hazard are recorded. If possible, the action needed to remove the hazard is decided by the team and recorded. If more information, or time, is needed to decide the best action, the matter is referred to the design group for action, or taken up at another meeting of the study team.

When using the operability study technique to vet a process design, the action to be taken to deal with a potential hazard will often be modifications to the control systems and instrumentation: the inclusion of additional alarms, trips, or interlocks. If major hazards

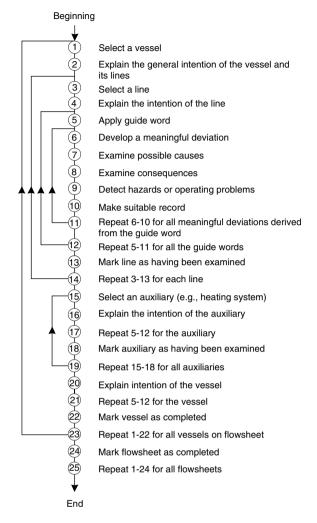


Figure 9.4. Detailed sequence of an operability study

are identified, major design changes may be necessary; alternative processes, materials or equipment.

# Example 9.2

This example illustrates how the techniques used in an operability study can be used to decide the instrumentation required for safe operation. Figure 9.5a shows the basic instrumentation and control systems required for the steady-state operation of the reactor section of the nitric acid process considered in Example 4.4. Figure 9.5b shows the

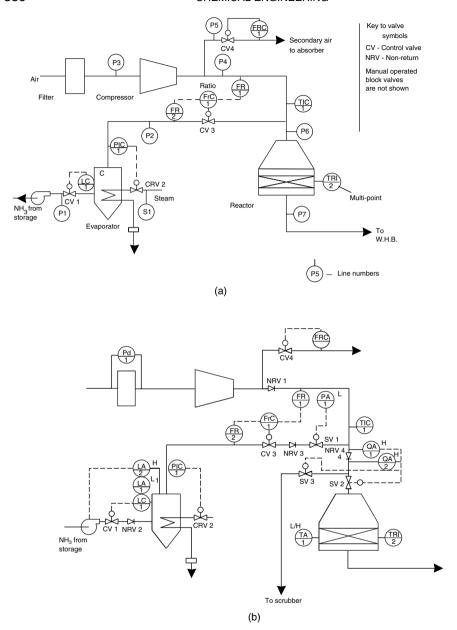


Figure 9.5. Nitric acid plant, reactor section (a) basic instrumentation (b) full instrumentation

additional instrumentation and safety trips added after making the operability study set out below. The instrument symbols used are explained in Chapter 5.

The most significant hazard of this process is the probability of an explosion if the concentration of ammonia in the reactor is inadvertently allowed to reach the explosive range, >14 per cent.

# Operability study

The sequence of steps shown in Figure 9.4 is followed. Only deviations leading to action, and those having consequences of interest, are recorded.

*Vessel* – **Air Filter**Intention – to remove particles that would foul the reactor catalyst

Guide word	Deviation	Cause	Consequences and action
		at atmospheric pressure a	and ambient
LESS OF	Flow	Partially blocked filter	Possible dangerous increase in NH <sub>3</sub> concentration: measure and log pressure differential
As WELL AS	Composition	Filter damaged, incorrectly installed	Impurities, possible poisoning of catalyst: proper maintenance
Vessel – Co	_	bar, 12,000 kg/h, 250°C,	, to the mixing tee
Line No. P		actor (mixing tee)	
No/None	Flow	Compressor failure	Possible dangerous NH <sub>3</sub> conc.: low flow pressure alarm (PA1) interlocked to shut-down NH <sub>3</sub> flow
More	Flow	Failure of compressor controls	High rate of reaction, high reactor temperature: high-temperature alarms (TA1)
REVERSE	Flow	Fall in line press. (compressor fails) high pressure at reactor	NH <sub>3</sub> in compressor — explosion hazard: fit non-return valve (NRV1); hot wet acid gas-corrosion; fit second valve (NRV4)
Line No. P.		v oir to obsorbor	
No	transfer secondar Flow	Compressor failure CV4 failure	Incomplete oxidation, air pollution from absorber vent: operating procedures
LESS	Flow	CV4 pluggage FRC1 failure	As no flow

*Vessel* – **Ammonia vaporiser** Intention – evaporate liquid ammonia at 8 bar, 25°C, 731 kg/h

Guide Deviation word		Cause	Consequences and action
Line No. P.	l transfer liquid N	Ho from storage	
No	Flow	Pump failure CV1 fails	Level falls in vaporiser: fit low-level alarm (LA1)
LESS	Flow	Partial failure pump/valve	(LA1) alarms
MORE	Flow	CV1 sticking, LC1 fails	Vaporiser floods, liquid to reactor: fit high-level alarm (LA2) with automatic pump shut-down
AS WELL AS	Water brine	Leakage into storages from refrigeration	Concentration of NH <sub>4</sub> OH in vaporiser: routine analysis, maintenance
REVERSE	Flow	Pump fails, vaporiser press. higher than delivery	Flow of vapour into storages: (LA1) alarms; fit non-return valve (NRV2)
Line No. P2			
	transfers vapour		
No	Flow	Failure of steam flow, CV3 fails closed	(LA1) alarms, reaction ceases: considered low flow alarm, rejected – needs resetting at each rate
LESS	Flow	Partial failure or blockage CV3	As no flow
	Level	LC1 fails	LA2 alarms
More	Flow	FR2/ratio control mis-operation	Danger of high ammonia concentration: fit alarm, fit analysers (duplicate) with high alarm 12 per cent NH <sub>3</sub> (QA1, QA2)
	Level	LC1 fails	LA2 alarms
REVERSE	Flow	Steam failure	Hot, acid gases from reactor – corrosion: fit non-return valve (NRV3)
Line S1 (auxiliary)		CRV2 fails, trap frozen	High level in vaporiser: LA2 actuated

Guide word	Deviation	Cause	Consequences and action
Vessel – R Intention –		th air, 8 bar, 900°C	
Line No. I	•	2500G	
No	- transfers mixture Flow	NRV4 stuck closed	Fall in reaction rate: fit low temp. alarm (TA1)
LESS	Flow	NRV4 partially closed	As No
	NH <sub>3</sub> conc.	Failure of ratio control	Temperatures fall: TA1 alarms (consider low conc. alarm on QA1, 2)
More	NH <sub>3</sub> conc.	Failure of ratio control, air flow restricted	High reactor temp.: TA1 alarms 14 per cent explosive mixture enters reactor – disaster: include automatic shut-down by-pass actuated by QA1, 2, SV2, SV3
	Flow	Control systems failure	High reactor temp.: TA1 alarms
Line No. I	•		
Intention -	- transfers reactor	products to waste-heat boil	ler
AS WELL AS	Composition	Refractory particles from reactor	Possible pluggage of boiler tubes: install filter up-stream of boiler

### 9.6. HAZARD ANALYSIS

An operability study will identify potential hazards, but gives no guidance on the likelihood of an incident occurring, or the loss suffered; this is left to the intuition of the team members. Incidents usually occur through the coincident failure of two or more items; failure of equipment, control systems and instruments, and mis-operation. The sequence of events that leads to a hazardous incident can be shown as a fault tree (logic tree), such as that shown in Figure 9.6. This figure shows the set of circumstances that would result in the flooding of the chloride vaporiser shown in Figure 9.3. The AND symbol is used where coincident inputs are necessary before the system fails, and the OR symbol where failure of any input, by itself, would cause failure of the system. A fault tree is analogous to the type of logic diagram used to represent computer operations, and the symbols are analogous to logic AND and OR gates.

The fault trees for even a simple process unit will be complex, with many branches. Fault trees are used to make a quantitive assessment of the likelihood of failure of a system, using data on the reliability of the individual components of the system. For example, if the following figures represent an estimate of the probability of the events

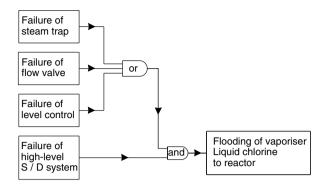


Figure 9.6. Simple fault chart (logic diagram)

shown in Figure 9.6 happening, the probability of failure of the total system by this route can be calculated.

	Probability of failure $\times 10^3$
Steam trap	1
Flow control valve	0.1
Level control, sub-system	0.5
High level shut-down, sub-system	0.04

The probabilities are added for OR gates, and multiplied for AND gates; so the probability of flooding the vaporiser is given by:

$$(1 + 0.1 + 0.5)10^{-3} \times 0.04 \times 10^{-3} = 0.06 \times 10^{-6}$$

The data on probabilities given in this example are for illustration only, and do not represent actual data for these components. Some quantitive data on the reliability of instruments and control systems is given by Lees (1976). Examples of the application of quantitive hazard analysis techniques in chemical plant design are given by Wells (1996) and Prugh (1980). Much of the work on the development of hazard analysis techniques, and the reliability of equipment, has been done in connection with the development of the nuclear energy programmes in the USA (USAEC, 1975) and the UK.

The Centre for Chemical Process Safety of the American Institute of Chemical Engineers has published a comprehensive and authoritative guide to quantitative risk analysis, AIChemE (2001).

Several other texts are available on the application of risk analysis techniques in the chemical process industries; see AIChemE (2000), Frank and Whittle (2001) and Kletz (1999b).

### 9.7. ACCEPTABLE RISK AND SAFETY PRIORITIES

If the consequences of an incident can be predicted quantitatively (property loss and the possible number of fatalities), then a quantitive assessment can be made of the risk.

$$\frac{\text{Quantitive assessment}}{\text{of risk}} = \left\{ \begin{array}{l} \text{Frequency of} \\ \text{incident} \end{array} \right\} \times \left\{ \begin{array}{l} \text{loss per} \\ \text{incident} \end{array} \right\}$$

If the loss can be measured in money, the cash value of the risk can be compared with the cost of safety equipment or design changes to reduce the risk. In this way, decisions on safety can be made in the same way as other design decisions: to give the best return of the money invested.

Hazards invariably endanger life as well as property, and any attempt to make cost comparisons will be difficult and controversial. It can be argued that no risk to life should be accepted. However, resources are always limited and some way of establishing safety priorities is needed.

One approach is to compare the risks, calculated from a hazard analysis, with risks that are generally considered acceptable; such as, the average risks in the particular industry, and the kind of risks that people accept voluntarily. One measure of the risk to life is the "Fatal Accident Frequency Rate" (FAFR), defined as the number of deaths per 10<sup>8</sup> working hours. This is equivalent to the number of deaths in a group of 1000 men over their working lives. The FAFR can be calculated from statistical data for various industries and activities; some of the published values are shown in Tables 9.8 and 9.9. Table 9.8 shows the relative position of the chemical industry compared with other industries; Table 9.9 gives values for some of the risks that people accept voluntarily.

Table 9.8. FAFR for some industries for the period 1978–90

Industry	FAFR
Chemical industry UK manufacturing Deep sea fishing	1.2 1.2 4.2

Table 9.9. FAFR for some non-industrial activities

Activity	FAFR
Staying at home	3
Travelling by rail	5
Travelling by bus	3
Travelling by car	57
Travelling by air	240
Travelling by motor cycle	660
Rock climbing	4000

Source: Brown (2004).

In the chemical process industries it is generally accepted that risks with an FAFR greater than 0.4 (one-tenth of the average for the industry) should be eliminated as a matter of priority, the elimination of lesser risks depending on the resources available; see Kletz (1977a). This criterion is for risks to employees; for risks to the general public (undertaken involuntarily) a lower criterion must be used. The level of risk to which the public outside the factory gate should be exposed by the operations will always be a matter of debate and controversy. Kletz (1977b) suggests that a hazard can be considered acceptable if the average risk is less than one in 10 million, per person, per year. This is equivalent to a FAFR of 0.001; about the same as deaths from the bites of venomous creatures in the UK, or the chance of being struck by lightning.

For further reading on the subject of acceptable risk and risk management, see Cox and Tait (1998).

### 9.8. SAFETY CHECK LISTS

Check lists are useful aids to memory. A check list that has been drawn up by experienced engineers can be a useful guide for the less experienced. However, too great a reliance should never be put on the use of check lists, to the exclusion of all other considerations and techniques. No check list can be completely comprehensive, covering all the factors to be considered for any particular process or operation.

A short safety check list, covering the main items which should be considered in process design, is given below.

More detailed check lists are given by Carson and Mumford (1988) and Wells (1980). Balemans (1974) gives a comprehensive list of guidelines for the safe design of chemical plant, drawn up in the form of a check list. A loss prevention check list is included in the Dow Fire and Explosion Index Hazard Classification Guide, Dow (1987).

### Design safety check list

#### Materials

- (a) flash-point
- (b) flammability range
- (c) autoignition temperature
- (d) composition
- (e) stability (shock sensitive?)
- (f) toxicity, TLV
- (g) corrosion
- (h) physical properties (unusual?)
- (i) heat of combustion/reaction

#### **Process**

- 1. Reactors
  - (a) exothermic—heat of reaction
  - (b) temperature control—emergency systems
  - (c) side reactions—dangerous?
  - (d) effect of contamination
  - (e) effect of unusual concentrations (including catalyst)
  - (f) corrosion
- 2. Pressure systems
  - (a) need?
  - (b) design to current codes (BS 5500)
  - (c) materials of construction—adequate?
  - (d) pressure relief—adequate?
  - (e) safe venting systems
  - (f) flame arresters

#### Control systems

- (a) fail safe
- (b) back-up power supplies
- (c) high/low alarms and trips on critical variables
  - (i) temperature
  - (ii) pressure
  - (iii) flow
  - (iv) level
  - (v) composition
- (d) back-up/duplicate systems on critical variables
- (e) remote operation of valves
- (f) block valves on critical lines
- (g) excess-flow valves
- (h) interlock systems to prevent mis-operation
- (i) automatic shut-down systems

#### Storages

- (a) limit quantity
- (b) inert purging/blanketing
- (c) floating roof tanks
- (d) dykeing
- (e) loading/unloading facilities safety
- (f) earthing
- (g) ignition sources—vehicles

#### General

- (a) inert purging systems needed
- (b) compliance with electrical codes
- (c) adequate lighting
- (d) lightning protection
- (e) sewers and drains adequate, flame traps
- (f) dust-explosion hazards
- (g) build-up of dangerous impurities purges
- (h) plant layout
  - (i) separation of units
  - (ii) access
  - (iii) siting of control rooms and offices
  - (iv) services
- (i) safety showers, eye baths

#### Fire protection

- (a) emergency water supplies
- (b) fire mains and hydrants
- (c) foam systems
- (d) sprinklers and deluge systems
- (e) insulation and protection of structures
- (f) access to buildings
- (g) fire-fighting equipment

The check list is intended to promote thought; to raise questions such as: is it needed, what are the alternatives, has provision been made for, check for, has it been provided?

### 9.9. MAJOR HAZARDS

A series of major accidents at manufacturing sites and storage installation has focused the attention of national governments on the need to control the planning and operation of sites where there is the potential for a major accident. That is, those sites posing a substantial threat to the employees, the public and the environment.

In the United Kingdom this is covered by the Control of Major Accident Hazards Regulations 1999 (COMAH), set up by the HSE (Health and Safety Executive) to implement the Seveso II directive of the EC (European Union): see www.hse.gov.uk. The COMAH regulations supersede the previous CIMAH (1984) regulations, set up under Seveso I.

Other countries have set up similar regulations for the control of major hazards.

The aim of the COMAH regulations is to prevent major accidents involving dangerous materials from occurring and to mitigate the effects on people and the environment.

The COMAH regulations apply to both the manufacture and storage of dangerous substances. They will, in effect, apply to any chemical manufacturing process involving flammable or toxic materials that are likely to constitute a hazard. The degree of the hazard with material storage depends on the nature of the material and the quantity stored. The regulations define the minimum storage quantities for hazardous substances above which the regulations will apply.

The regulations require industrial companies to report on the operation of dangerous installations, and on the storage of dangerous materials.

It is the duty of the company to prepare a Major Accident Prevention Policy (MAPP). This will set out the policies for ensuring the safe operation of the plant and the protection of employees and the environment. It will include details of the safety management organisation that will implement the policy.

The report should include:

- i. Identification of the hazards.
- ii. The steps taken to ensure the proper design, testing and operation of the plant.
- iii. The steps taken to prevent or minimise the consequences that would follow a major incident.
- iv. The programme for training employees and providing them with safety equipment.
- v. The preparation and procedures for updating an emergency plan covering procedures to deal with a major incident.
- vi. The procedures for informing the public living outside the site, who may be affected by a major accident, of the nature of the hazard, and what to do in the event of an accident.
- vii. Policies for liaising with the local authorities in the preparation of an off-site emergency plan.

In preparing the report for the HSE the company would usually prepare a safety case assessing the nature and degree of the hazard and the consequences of an incident. This

would include details of the measures taken to alleviate the hazard and the consequences of an accident.

The preparation of safety cases under the CIMAH regulations is covered by Lees and Ang (1989). The company is required to report any major incident to the Health and Safety Executive (HSE).

The regulations covering the control of major industrial accident hazards in the United States are discussed by Brooks *et al.* in Lees and Ang (1989). Major hazards and their management are covered by Wells (1997).

### 9.9.1. Computer software for quantitative risk analysis

The assessment of the risks and consequences involved in the planning and operation of a major plant site is a daunting task.

The methodology of the classical method of quantitative risk analysis is shown in Figure 9.7. First, the likely frequency of failure of equipment, pipe-lines, and storage vessels must be predicted; using the techniques mentioned in Section 9.6. The probable magnitude of any discharges must then be estimated, and the consequences of failure evaluated: fire, explosion or toxic fume release. Other factors, such as, site geography, weather conditions, site layout, and safety management practices, must be taken into consideration. The dispersion of gas clouds can be predicted using suitable models. This methodology enables the severity of the risks to be assessed. Limits have to be agreed on the acceptable risks; such as the permitted concentrations of toxic gases. Decisions can then be made on the siting of plant equipment (see Chapter 14), on the suitability of a site location, and on emergency planning procedures.

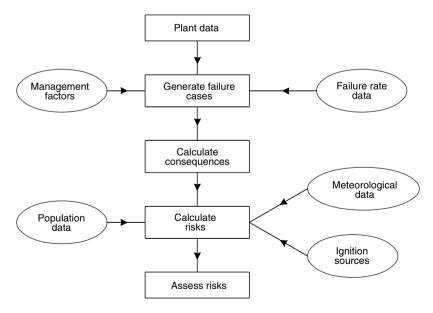


Figure 9.7. Quantitative risk assessment procedure

The comprehensive and detailed assessment of the risks required for a "safety-case" can only be satisfactorily carried out for major installations with the aid of computer software. Suites of programmes for quantitative risk analysis have been developed over the past decade by consulting firms specializing in safety and environmental protection. Typical of the software available is the SAFETI (Suite for Assessment of Flammability Explosion and Toxic Impact) suite of programs developed by DNV Technica Ltd. These programs were initially developed for the authorities in the Netherlands, as a response to the Seveso Directives of the EU (which requires the development of safety cases and hazard reviews). The programs have subsequently been developed further and extended, and are widely used in the preparation of safety cases; see Pitblado *et al.* (1990).

Computer programs can be used to investigate a range of possible scenarios for a site. But, as with all computer software used in design, they should not be used without caution and judgement. They would normally be used with the assistance and guidance of the consulting firm supplying the software. With intelligent use, guided by experience, such programs can indicate the magnitude of the likely risks at a site, and allow sound decisions to be made when licensing a process operation or granting planning permission for a new installation.

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		electrical apparatus for use in potentially explosive atmospheres (other than mining
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BS 5501:	1977-82	Electrical apparatus for potentially explosive atmospheres, 9 parts.
BS 5908:	1990	Code of practice for fire precautions in the chemical and allied industries.
BS 5958:	1991	Code of practice for the control of undesirable static electricity.
	Part 1:	General considerations.
	Part 2:	Recommendations for particular industries.
BS 2000-34	2002	Methods of test for petroleum and its products. Determination of flash point. Pensky-
		Martens closed cup method.
BS 2000-35	1993	Methods of test for petroleum and its products. Determination of open, flash and fire
		point. Pensky-Martens method.

#### 9.11. PROBLEMS

**9.1.** In the storage of flammable liquids, if the composition of the vapour–air mixture above the liquid surface falls within the flammability limits, a floating roof tank would be used or the tank blanketed with inert gas. Check if the vapour composition for liquids listed below will fall within their flammability range, at atmospheric pressure and 25°C.

- 1. Toluene
- 2. Acrylonitrile
- 3. Nitrobenzene
- 4. Acetone
- **9.2.** Estimate the Dow Fire and Explosion Index, and determine the hazard rating, for the processes listed below.

Use the process descriptions given in Appendix G and develop the designs, as needed, to estimate the index.

- 1. Ethylhexanol from propylene and synthesis gas, G.1.
- 2. Chlorobenzenes from benzene and chlorine, G.2.
- 3. Methyl ethyl ketone from 2-butanol, G.3.
- 4. Acrylonitrile from propylene and ammonia, G.4.
- 5. Aniline from nitrobenzene and hydrogen. G.8.
- **9.3.** Devise a preliminary control scheme for the sections of the nitric acid plant described in Chapter 4, flow-sheet Figure 4.2, which are listed below. Make a practice HAZOP study of each section and revise your preliminary control scheme.
  - 1. Waste heat boiler (WHB)
  - 2. Condenser
  - 3. Absorption column