SAFETY IN THE PROCESS INDUSTRIES

Ralph King

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Foreword

I am delighted to have been asked by Ralph King to write the foreword to his excellent book. Although I do not necessarily share all his expressed views I do wholeheartedly support the substance contained therein, which is not only readable but is packed full of vital information and learning experience. If it receives the attention it deserves it will, in my opinion, help to make the process industry both a healthier and safer place to work in and a better neighbour.

As a practising safety officer in the process industry I welcome this book and wish it had been available when I began my safety career; it will join a select few in my bookcase.

Bill Sampson
The Dow Chemical Company, King's Lynn, Norfolk

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Preface

It may seem presumptuous for one writer to attempt to cover all the hazards of the process industries, with their many different technologies. Yet when considering the causes of past accidents, most appear to be well within the understanding of anyone with a broad technical background. The single writer has at least one advantage over a panel of authors in that he or she can present the subject as a logical whole and in a consistent style.

The book is written in a sincere attempt to help all those involved in the management, development, planning, design, construction, operation, inspection and maintenance of process plant, as well as safety professionals. It is hoped that it will also be read by insurers, lawyers, MPs, local councillors, civil servants, journalists and producers of TV programmes concerned with process hazards and disasters.

We humans have developed a love–hatred relationship with our process industries. We depend on them for cheap, standard and usually stable (sometimes too stable!) bulk products which supply much of the material needs of our bourgeoning population. Yet many fear and curse the process industries because of their potential for death, destruction and pollution caused by the escape of flammable, toxic or otherwise harmful chemicals and intermediates used in them. Escapes may be sudden and massive, causing such disasters as Flixborough, Seveso, Bhopal and the poisoning of the Rhine, or they may be small but persistent, leading to disease and premature death. The dangers are liable to increase when the industries and their technologies cross national frontiers and especially when they are set up in Third World countries which lack the resources, trained personnel and infrastructure needed to control them. Here situations which are seldom found in more industrialised countries, except in war-time, are common.

The hazard potential in many process industries is like a time-bomb. This potential is inescapable, although it can sometimes be reduced by minimising the quantities of harmful substances present or using less dangerous ones. The main hazards with which we have to deal are the several different ways in which harmful substances can escape. That is what this book is about.

Safety in the process industries depends first, on ensuring high integrity in the plant as designed and built; second, in maintaining that integrity throughout its working life in the face of wear and corrosion; third, in operating it skilfully and safely to avoid conditions which increase the likelihood of releasing harmful substances; and fourth, in thoroughly checking all modifications for unsuspected hazards which they may introduce.

Past disasters have engendered much of today's concern over safety within our process industries and the monitoring of their hazards. The numbers and total (inflation adjusted) value of very large losses worldwide in the hydrocarbon processing and chemical industries more than quadrupled between the first and last of three consecutive ten-year periods ending in 1987, according to Marsh and McLennan's eleventh 30-year survey (summarised in Appendix E). However, much has been and is being done. Safety and safety training are high on the priorities of professional groups on both sides of the Atlantic and in international organisations such as the International Labour Office. Legislation in European countries arising from EEC directives (e.g. the UK CIMAH and COSHH Regulations) is having a marked effect in raising standards. Penalties for infringements have become tougher. The number of conferences held annually on some aspect of health and safety in the process industries has increased several times during the last 15 years. Many excellent training films and other material now available are referred to here in Appendix M.

In many ways it was the indelible memory of the Flixborough disaster of 1974 and of my involvement in the subsequent investigations that spurred me to write this book. Yet memory, like a *jinnee*, is a provoking companion, constantly trying to throw its owner off-balance. I was fortunate in having Don Goodsell, formerly Butterworth's commissioning editor, as a guide, philosopher and friend. Having commissioned me to write the book, Don often had to wrestle with the *jinnee* and replace it in its bottle before I could complete the manuscript on an even keel. While writing it, many fresh hazards have come to light and aspects of which I was at first only dimly aware were thrust upon me. As a result, the book has grown considerably beyond its intended size.

Besides Don, the generous financial help of the Colt Foundation was vital. I am also indebted to many people and organisations for providing source materials and allowing me to make full use of them, and for reading parts of the manuscript, correcting errors and making suggestions. Only the following to whom I owe a special debt are listed here, although they are in no way responsible for my own opinions expressed in the book or for its shortcomings:

- Bill Sampson, safety officer of Dow Chemical Company Limited, King's Lynn, and The Dow Chemical Company itself;
- Professor Trevor Kletz, formerly safety advisor to ICI's petrochemical division;
- Glynne Evans, senior engineering inspector and pressure vessel expert in the UK Health and Safety Executive, Bootle, and many others in HSE;
- Dr Barry Turner, author of the book *Man-made Disasters* and head of the Sociology Department of Exeter University;

- Laurie Flynn, producer of the *World in Action* television documentary on the Bhopal disaster, and Granada Television who made it;
- Professor Frank Lees, author of *Loss Prevention in the Process Industries* and Professor of Plant Engineering in the Department of Chemical Engineering, Loughborough University;
- David Brown and other former and present officials of the International Labour Office, Geneva;
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- Dr Doran, manager of the Explosion Hazards Team of ICI Chemicals and Polymers, Northwich;
- Mr G. C. Wilkinson, formerly chief inspector of aircraft accidents in the Department of Transport;
- Arthur Robertson and Joyce Hainsworth, directors of Furmanite Engineering Limited of Kendal, Cumbria;
- David Gee and Steve Rabson, former and present national health and safety officers of the General Municipal, Boilermakers and Allied Trades Union, Claygate, Surrey;
- Mr J. Clifton, head of the Major Hazards Group of the Safety and Reliability Directorate of the UKAEA, Warrington;
- Peter Syrett, mechanical engineer of Howard Humphreys and Sons, Consulting Engineers, Leatherhead;
- Ken Palmer, consultant to Sedgwick International Ltd, insurance brokers, London;
- David Lewis, consultant and explosion expert, Liverpool;
- Antony Cuming, safety specialist of Atkins Research and Development, Epsom;
- The Institution of Chemical Engineers and Brian Hancock, head of its health and safety group, Rugby;
- The Chemical Industries Association and the Society of Chemical Industry, London;
- Past and present editors of *Process Engineering* and *The Engineer*, London.

I must apologise to and thank many other helpers and organisations whose names are not included in this list. Sources of illustrations and quotations reproduced here (with permission) are acknowledged elsewhere in the text.

Errata

Page 62 In Figure 4.1, the reactors should be labelled

1, 2, 3, *4* (R252*4*), *5* (R252*5*), 6.

Page 69 In line 3, 'R4' should read 'R5'.

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Appendices

Introduction

Most human activities carry special risks. Steel erectors and roof workers are most at risk of falling while machine operatives are more at risk of lacerations. The risk profiles of particular industries change with time as certain hazards (such as boiler explosions) are conquered and new ones (such as gamma-rays) appear.

The main hazards of the process industries arise from the escape of process materials which may be inherently dangerous (e.g. flammable or toxic) and/or present at high pressure and high or low temperatures. Large and sudden escapes may cause explosions, toxic clouds and pollution whose effects extend far beyond the works perimeter. Such major accidents include the explosion of liquefied petroleum gas in Mexico City in 1984 which resulted in 650 deaths and several thousand injuries, followed two weeks later by the release of toxic methyl isocyanate gas in Bhopal, India, which caused over 2000 deaths and over 200 000 injuries. These have rightly attracted world attention. Small and persistent escapes may lead to chronic ill-health and environmental pollution. Their insidious effects which have taken longer to arouse the public have contributed to the present prominence of 'green' issues.

Hazards differ widely between processes. Their magnitude depends mainly on the process materials and their quantity. The probability of an accident depends more on the process conditions and their complexity.

To prevent repetition of past disasters, correct diagnosis and exposure of the relevant hazards is essential. The lessons then need to be incorporated in the training of managers and staff who may be faced with these hazards, in company rules, in codes of practice and sometimes in legislation. Diagnosis is often difficult and controversial and one seldom knows whether it is quite correct or complete. It first requires all known and possibly relevant facts to be disclosed, related and assessed. To do this a broad scientific and technical background is more important than a legal one. As Sir Geoffrey De Havilland and P.B.Walker pointed out after the early Comet disasters[1], most accidents in the technical sphere are caused by combinations of (relatively straightforward) hazards. Unfortunately, the legal and political connotations of many accident inquiries may put investigators under pressure to give undue attention to explanations which would exonerate parties whom they represent. Yet even the most objective investigation may succeed only in identifying several possible causes, each of which must be treated to minimise the probability of future failures.

The process industries

I cannot better the definition issued by the journal *Process Engineering*[2]:

> The process industries are . . . involved in changing by chemical, physical or other means raw materials into intermediate or end products. They include gas, oil, metals, minerals, chemicals, pharmaceuticals, fibres, textiles, food, drinks, leather, paper, rubbers and plastics. In addition the important service areas of energy, water, plant contracting and construction are included.

From this we can visualise the process industries as an intermediate stage in the transformation of raw materials of every kind – animal, vegetable or mineral – into materials and finished goods. The process industries convert these diversified raw materials into standardised bulk products. Some are sold direct to the customer (e.g. motor fuel), some merely packaged before sale (e.g. milk and lubricating oil), and some (e.g. wood-pulp and polyethylene) supplied to factories which make finished products.

Clear dividing lines cannot always be drawn between process industries and those which precede or follow them. Those preceding include mineral dressing at mines, water treatment (e.g. for injection into oil wells to assist recovery) and milk pasteurisation and cereal treatment at the farm. Those following include thermal and mechanical forming and cooking processes such as the casting and cold drawing of metals, the spinning and weaving of fibres, the moulding of plastics and the baking of bread. Many typical hazards of the process industries discussed here are found again in the industries which precede or follow them. This book is also addressed to those working in them.

The process industries account for about a tenth of the working populations of many industrialised countries. Those so-classified in the UK are listed in Appendix A with the numbers of employees. Of these about 30% work in oil, gas and chemicals.

Chemical hazards

Today there is widespread concern over the hazards of chemicals, not only to those who work with them but also to the environment and the general public. However well-designed a plant may be, it is very difficult to entirely prevent some dangerous materials from escaping. The longevity and concentration in nature of chemicals such as chlorinated biphenyls and chlorofluorocarbons, whose hazards only became apparent after they had been in production for many years, has heightened this awareness. One major problem in dealing with hazardous chemicals is that there are so many of them. There are now about *five million* chemicals listed in *American Chemical Abstracts*, and over 100 000 compounds in NIOSH's *Registry of Toxic Effects of Chemical Substances*[3].

Apart from the general problems of manufacture, special ones arise in bulk transport by road, rail and water, and when pregnant women are employed in manufacture and packing[4]. Much new legislation has followed this public concern. If its results are often disappointing, this is largely because of the wide gaps in understanding and experience between the legislators and those most at risk[5].

Many readers will surely be familiar with the *Handbook of Reactive Chemical Hazards* by Bretherick[6], which covers some 7000 chemicals, and *Dangerous Properties of Industrial Materials* edited by Sax[7] which refers to more than 19 000 such materials. A useful classification of hazardous chemicals for quick reference is that published by the National Fire Protection Association of America[8] (Appendix B). This provides a numerical rating of 0 to 4 for three regular hazards of every chemical – health, flammability and reactivity.

All those using, handling or making chemicals should have full information, which the supplier should provide, about their properties and possible hazards. Material safety data sheets (MSDS) giving this information should be brought to the special attention of persons and departments in need of it (e.g. fire, safety, medical, operations, maintenance, cleaning and transport). An EC directive and MSDS form, whose draft headings (June 1990) are given in Appendix C, is expected to be issued in 1991. Compliance with the directive will be judged on whether the user has sufficient information to work safely rather than on the provision of lists of specific data. An MSDS form issued by OSHA[9] for use in ship repairing, shipbuilding and shipbreaking is also shown in Appendix C. MSDSs for a wide range of chemicals are available from the on-line data base OHS.MS produced by Occupational Health Services Inc. [M.12].

In considering chemical hazards, we must think not only of chemicals in their restrictive sense but of all materials which may display hazards designated as chemical. They can include soils, minerals, metals, mineral waters, gases, food, drink, fuels, building materials, pharmaceuticals, photographic materials, textiles, fertilisers, pesticides, herbicides and lubricants. Each is composed of one or more of the 92-plus chemical elements and may well have hazards resulting from its composition.

Safety and technical competence

Safety in the process industries cannot be treated as a separate subject like design, production or maintenance, but is inextricably interwoven into these and other activities. It depends on both the technical competence and safety awareness of all staff and employees.

At least one company tries to solve this problem by assigning its key production and maintenance personnel for periods, usually of several months, during the early part of their careers, to work in the safety or loss-prevention department under a permanent safety manager. This gives them a new outlook and philosophy on safety which they do not easily lose when they return to face the myriad pressures of production. Furthermore, they are aware that their superiors in the management structure share their experience and outlook. It is hardly surprising that this company has an exceptional safety record.

Of the various specialists involved, the process engineer occupies a central position. While not always recognised in terms of his authority, he should by education and experience be able to appreciate, on the one hand, the chemistry of the process and the materials processed, and on the other, the factors involved in the mechanical design and construction, and in the materials of construction used. He should be thoroughly familiar with hazards inherent in the process and should be aware of those arising from the detailed engineering and other areas outside his direct concern.

About this book

Although many specialised books and papers have been written about specific facets of hazard control in the process industries, only a few have attempted to cover the whole field. One (published in the UK) is Lees's *Loss Prevention in the Process Industries*[10] which was written mainly as a reference book for students. It has a very comprehensive bibliography and gives quite a detailed mathematical treatment of reliability theory, gas dispersion and some protective systems. While it does not define the process industries, it is clearly slanted to the oil, gas, petrochemical and heavy chemical industries. Another is *Safety and Accident Prevention in Chemical Operations*[11], with chapters by 28 specialists, edited by Fawcett and Wood and published in the USA. I have drawn extensively on both books and refer to them frequently. Like them, this book does not attempt to cover the special hazards of nuclear energy, biochemical engineering or offshore oil and gas production.

Having spent about a third of my working life in several different countries, I have tried to write from an international viewpoint. I have also tried to adopt a multi-disciplinary approach while using a minimum of mathematics. To avoid repetition, each subject is treated as far as possible in a single appropriate place, with extensive cross-references to other chapters, sections and subsections. Here square brackets [ ] are used for '(see) chapter, section, appendix, etc.'.

The 23 chapters of this book fall loosely into four parts.

Part I, 'Setting the stage', includes the first five chapters. These deal with history (mainly recent), the legal background and five major accidents, their causes and lessons.

Part II, 'Hazards – chemical, mechanical and physical', comprises the next eight chapters. Five of these deal with the toxic, reactive, explosive, flammable and corrosive hazards of process materials.

Part III, 'Hazard control in design and maintenance', consists of the next five chapters. These include discussions of modern ideas about reliability, active and passive protection, control instruments and permit-to-work systems.

Part IV, 'Management, production and related topics', comprises the last five chapters and includes training, personal protection and hazards which arise in the transfer of modern technologies.

The book has several appendices, one of which, Appendix M, lists sources of help and information, particularly for safety training. A glossary of abbreviations used is given at the end of the book.

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Chapter 1

From past to present

History has several lessons for us about the hazards of the modern process industries. One is the toxicity of many useful metals and other substances won from deposits in the earth's crust. Although the dangers of extracting and using lead have been known from the earliest times, these seem later to have been forgotten. A second lesson, then, is that past lessons are sometimes forgotten after a lapse of a few years, when history has an unfortunate habit of repeating itself.

A third lesson is that there is often a time-lag between the initial manufacture of hazardous substances and general appreciation of the dangers. Today we are all aware of the hazards of asbestos, CFC refrigerants and aerosols, chlorinated hydrocarbon insecticides, benzene and the bulk storage of ammonium nitrate. Only recently all were considered to be safe and needing no special precautions. Similar time-lags occurred a few decades ago before the hazards of yellow phosphorus (matches) and benzidine (dyestuffs) were appreciated.

A fourth lesson is that it is usually the lowest and least articulate strata in society who bear the brunt of industry's hazards.

A fifth lesson is that the capacities of process plants and the magnitude of major losses involving them have increased continuously *and are still increasing*. Related to this and to the high capital : worker ratio of these plants is the high ratio of capital loss : human fatalities in most major fires and explosions. This does not, however, apply to poisoning and pollution incidents which spread well beyond the works boundary (cf. Seveso and Bhopal).

The recent world record of large losses in the process industries, especially oil and chemicals, is truly alarming and gives us no grounds for complacency. The numbers of losses in excess of $10 million (adjusted to 1988 values), and their total value, have increased greatly in each successive decade since 1958, particularly in the second decade as the following figures show[1]:

Period	Number of losses over $10 million at 1986 values	Total ($10 million)
1958–1967	13	442
1968–1977	33	1438
1978–1987	58	2086

Having persisted for so long, it would be very surprising if these themes did not continue into the future. If history teaches us nothing else, it should warn us to be sceptical of claims that the use of some new material in an industrial process is entirely safe. Usually only time will tell.

This chapter falls into seven largely unrelated sections each forming a brief historical sketch. (The reader can skip any of these without losing the thread of the argument.)

1.1 Origins of process hazards

Several typical hazards of the process industries have a very long history. This is because a number of the 92-plus chemical elements (particularly metals and semi-metals) of which all matter is compounded are poisonous, and are naturally concentrated here and there on and below the earth's surface.

As human prowess developed, the mastery of fire, and through it the invention of smelting to obtain bronzes and other metals, released fumes which affected the health of the craftsmen. Another early 'industrial' hazard was the making of flint tools, where abundant archaeological evidence of silicosis has been found.

As human occupations became more specialised, it was clear that some were more dangerous and less healthy than others. Thus Hephaistos, the Greek god of fire and patron of smiths and craftsmen, was lame and of unkempt appearance, while Vulcan, the Roman god of metal workers and fire, was also ugly and misshapen. It is now thought that the lameness of the smith-gods was the result of arsenic poisoning, since many of the ores from which copper and bronze articles were made contained arsenic, which improved the hardness of the resulting articles.

From the earliest times, there has been a strong prejudice among the articulate elite against such craftsmen. Socrates was reported to have passed the following judgement:

> What are called the mechanical arts, carry a social stigma and are rightly dishonoured in our cities. For these arts damage the bodies of those who work at them or who have charge of them, by compelling the workers to a sedentary indoor life, and in some cases spending the whole day by the fire. This physical degeneration results in degeneration of the soul as well.

The social cleavage illustrated by such attitudes to industrial hazards has persisted through human history. Despite the recent elimination of many of these hazards, our social and economic structure and the mental habits that go with it are slow to adjust to the possibilities of a golden age, free from occupational hazards and excessive working hours, in which all can enjoy our common heritage of knowledge, invention and accumulated technical progress. It is tragic, as the British miners' strike of 1984/1985 showed, that working people still feel compelled to fight for the right to continued employment in an occupation notorious for accidents and disease.

In more recent times, some occupational diseases were so common as to have acquired well-known names, such as those quoted by Hunter[2]:

> Brassfounders' ague, copper fever, foundry fever, iron puddlers' cataract, mule-spinners' cancer, nickel refiners' itch, silo-workers' asthma, weavers' deafness and zinc oxide chills.

1.2 Toxic hazards of ancient metals[2]

Several of these hazards have persisted to the present day, although their forms have changed. To say that any metal is poisonous is an over-simplification. Metals usually occur combined in nature and few are found in their free state. While several inorganic compounds of a metal display the same characteristic toxic features, the degree of toxicity of such compounds depends on their solubility in water and body fluids, as well as on the ionic and complex state of the metal. Insoluble elements and compounds are seldom toxic in themselves. The first lead ore worked at Broken Hill in Australia was the relatively soluble cerussite, $PbCO_3$, the dust of which caused much disease among the miners. Fortunately this was soon worked out, and the ore subsequently mined was galena, PbS, which is very insoluble, and has caused few cases of lead poisoning.

Besides the toxic inorganic compounds whose effects are typical of the metal present, there are many man-made organo-metallic compounds, which have different and more acute toxic effects. An example is the volatile tetraethyllead, used as a petrol additive, which produces cerebral symptoms. Nickel carbonyl, used in the purification of nickel, is another example. Even metals which exhibit no marked toxicity in their inorganic compounds, such as tin, can form highly toxic organo-metallic ones (tetramethyltin).

The hazards of two metals used since antiquity, lead and mercury, are next considered. They are discussed again [23] in the context of technology transfer to developing countries.

1.2.1 Lead

The symptoms of inorganic lead poisoning – constipation, colic, pallor and ocular disturbances – were recognised by Roman and earlier physicians. The symptoms of poisoning by organo-lead compounds include insomnia, hallucinations and mania. Lead ores have been smelted since early Egyptian times. Being soft, dense, easily worked and fairly resistant to corrosion, lead was long the favourite metal for water pipes, roof covering and small shot. With the invention of printing, it became the principal metal used for casting type. White lead (a basic carbonate) and red lead (an oxide) were long used as paint pigments and ingredients of glass and pottery glazes. The smelting of lead ores (Figure 1.1) and the manufacture and use of lead compounds increased greatly during the Industrial Revolution, together with an increase in death and injury among workers exposed to them.

Figure 1.1 Sixteenth century furnaces for smelting lead ore

The health hazards to lead workers featured in Victorian factory legislation and it was eventually recognised by Sir Thomas Legge that:

> Practically all industrial lead poisoning is due to the inhalation of dust and fume; and if you stop their inhalation, you will stop the poisoning.

Although the conditions in established lead processes improved considerably after this, newer large-scale uses of lead, first, the manufacture of lead-acid car batteries, and second, the manufacture and use of volatile organo-lead compounds for incorporation into petrol to improve its performance, brought further hazards. Several multiple fatalities occurred during the cleaning of large tanks which had contained leaded petrol. The worst happened at Abadan refinery during World War II while I was working there. There were then about 200 cases of lead poisoning with 40 deaths among Indian and Iranian workers.

As the hazards of lead are better appreciated today, its use has declined. One special hazard in its production is that many lead ores also contain arsenic, which is even more toxic [23.3.2].

1.2.2 Mercury

Mercury, the only liquid metal, is highly toxic and has an appreciable vapour pressure at room temperatures. Symptoms of poisoning from mercury vapour are salivation and tenderness of the gums, followed in chronic cases by a tremor. Another symptom is *erethism*, a condition in which the victim becomes both timid and quarrelsome (Figure 1.2), easily upset and embarrassed, and neglects his or her work and family. Merely to be in an unventilated room where mercury is present and exposed to the atmosphere can, in time, lead to mercury poisoning.

Figure 1.2 The Mad Hatter, drawn by Tenniel

Mercury occurs as its sulphide in the ore cinnabar, which has been mined in Spain since at least 415 BC, and mercury poisoning has long been prevalent among workers employed in such mines and reduction plants.

Mercury has long been used as such in the manufacture of thermometers and barometers, and more recently in the electrical industry for contact breakers, rectifiers and direct current meters. New compounds of mercury have been invented and commercialised, including mercury fulminate, used in detonators, and organo-mercury compounds used as antiseptics, seed disinfectants, fungicides and weedkillers. Mercury is used as cathode and solvent for metallic sodium in the Castner–Kelner process for the production of chlorine and caustic soda. This process has now been largely replaced by others which are free of the mercury hazard. In most of its industrial applications there are well-authenticated cases of poisoning by exposure to mercury vapour, or dusts containing its compounds. Mercury poisoning has been notorious in the felt-hat industry for centuries, where mercuric nitrate was used to treat rabbit and other furs to aid felting.

An infamous case of mass poisoning from organo-mercury compounds occurred among the fishermen and their families living along the shores of Minamata Bay in the south of Japan in the 1950s. This was ultimately traced to the discharge of spent mercury-containing catalyst into the bay from a nearby chemical factory which made vinyl chloride monomer. Organo-mercury compounds settled in the silt of the bay and were ingested by fish which were caught, sold and eaten by the local inhabitants and their cats. By July 1961 there had been 81 victims, of whom 35 died. The symptoms included numbness in the extremities, slurred speech, unsteady gait, deafness and disturbed vision. The mud of the bay remained loaded with mercury compounds for many years afterwards.

1.3 Changing attitudes to health and safety in chemical education

The last fifty years have shown great changes in attitudes to chemical safety in schools and colleges. This is clear from my own education in the 1930s. The first hazardous chemical to which I was exposed was mercury. This was in our school chemistry laboratory-cum-classroom (1932–1936). Our chemistry master, a middle-aged bachelor, had studied under Rutherford and had a penchant for research. For this he needed copious supplies of mercury, which he purified in his spare time in the school laboratory. Although I did not recognise his symptoms at the time, in retrospect the tremor of his hands, his high-pitched nervous twittering laugh, general shyness and odd mannerisms were typical of *erethism*. Globules of mercury, which was used for many juvenile pranks, were scattered on the laboratory benches and floor. Perhaps the fact that the laboratory was underheated saved me from serious mercurial poisoning.

At college (1936–1940), I was exposed to blue asbestos, from which we made mats for filter crucibles used in inorganic analysis, hydrogen sulphide, benzene, which was used as a common laboratory reagent and solvent, and again mercury, of which I used several kilograms for a research project. My most serious exposure was probably to a complex mixture of polynuclear aromatic compounds containing sulphur, which I was asked to prepare for a professor during a long vacation by bubbling acetylene through molten sulphur. The professor contracted cancer from his researches and died in middle age a few years later.

Chemical research was then held up to students as a vocation, demanding sacrifice of time and, where necessary, of health, in order to advance the frontiers of knowledge in the service of mankind. Madame Curie was quoted as a noble and inspiring example, whose work somehow justified the cancer which finally killed her. Other scientists such as J. B. S. Haldane and Dr C. H. Barlow who carried out dangerous and often painful experiments on their own bodies were also regarded as heroes.

It was only later that I realised that such sacrifices can only be justified if they improve the health of others. Often the reverse has been the case. A survey by Li *et al.*[15] of causes of death in members of the American Chemical Society between 1943 and 1967 showed that deaths from cancer of the pancreas and malignant lymphomas were significantly higher than among the general population. Scientists have tended to regard working conditions which they readily tolerate as quite good enough for their laboratory assistants. This is but a short step to expecting the same acceptance from industrial workers and the general public.

In spite of many exposures to harmful chemicals throughout my training and subsequent career, I am fortunate to be alive and in excellent health and still a keen squash player in my seventies. As most of my former colleagues are dead, I must be the exception which proves the rule!

The situation in schools today is very different to that in the 1930s. Safety policy has been greatly tightened over the past 20 years and most heads of science take their safety responsibilities very seriously indeed. A chemistry teacher was recently prosecuted and fined £500 for failing to take adequate safety precautions. The Association for Science Education has a Laboratory Safeguards Committee and its journal *Education in Science* carries regular updates on potential hazards. Local education authorities publish safety guidelines and individual schools are often required to have such guides to suit their particular situations. As examples of the changing situation, traditional asbestos bench mats were phased out during the 70s, and the safe handling of chemicals and manipulation of apparatus is one of the features of pupils' practical chemistry work which is assessed for the new GCSE examination.

1.4 Insurance losses in the US chemical industry

This section is based on a survey of 1028 accidents in the US chemical industry over the three-year period 1978–1980, given by Norstrom of Industrial Risk Insurers in Fawcett and Woods's book[3]. These resulted in insurance losses of $152 million, exclusive of deductibles and self-retention by the insured. Only one catastrophic loss of over $20 million was included, and no vapour cloud explosions. The period appears to have been one in which chemical plant losses were relatively light, considering that the loss from a single incident, the Flixborough disaster in the UK in 1974 [4], was reported at about $100 million. The survey did not include losses by those major international companies which carry their own insurance.

The following general conclusions were drawn from the survey:

1. The most frequent and severe losses in the chemical industry are caused by fire and explosion.
2. Explosion causes more severe losses than fire.
3. The main causes of explosion losses are accidental and uncontrolled chemical reactions.
4. Most explosion losses occur in enclosed process buildings and involve batch reactions.
5. Rupture of vessels, pipes and equipment contribute greatly to the magnitude of fire and explosion losses.
6. Most fire losses result from the release of flammable gases and liquids.
7. Lack of sprinklers and water spray was a major contributory factor in 38% of fire losses.

While only 12.7% of the individual losses exceeded $100 000, these together accounted for nearly 95% of the total monetary value of all claims. The following details therefore apply mainly to losses greater than $100 000, which are referred to subsequently as 'large losses'.

Figure 1.3 shows the percentages of the numbers and total value of large losses grouped by cause (explosion, fire, windstorm and all other). Over 50% of the losses and over 70% of their total value were caused by explosions, with fire accounting for 33% of the losses and 20% of their total value. Windstorm and other causes accounted, however, for a higher proportion of minor losses.

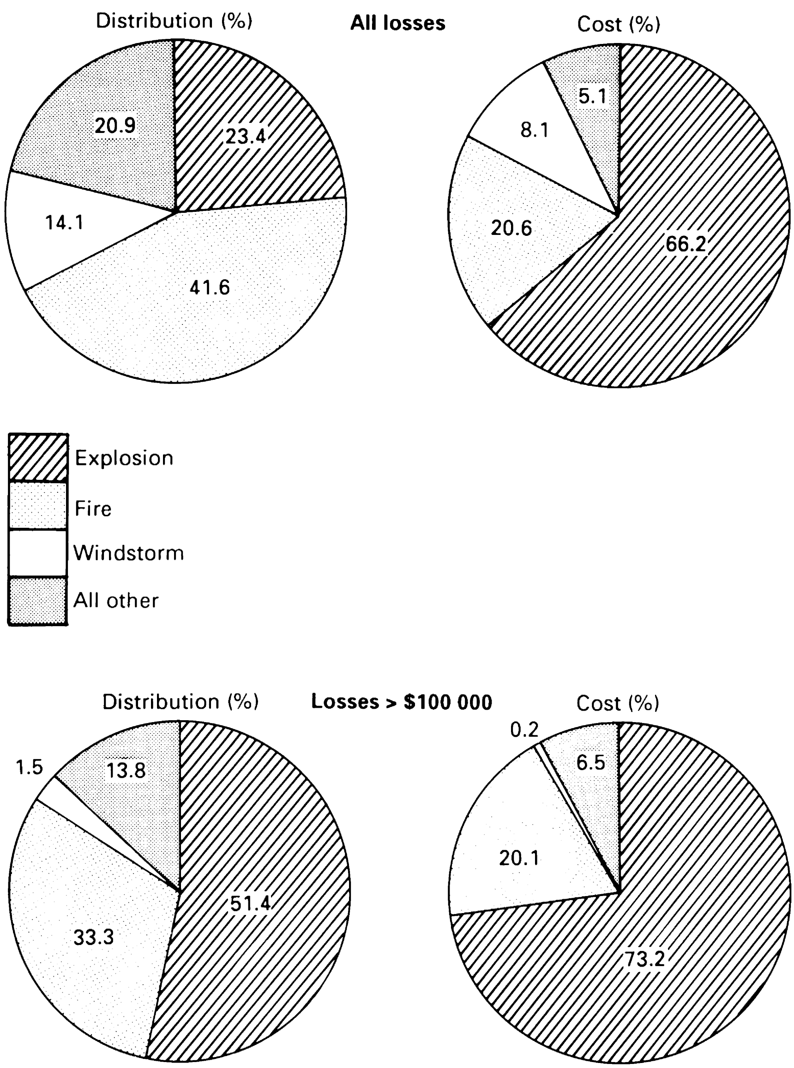

Figure 1.3 Peril analysis of US chemical losses, 1978–1980 (data from reference 3)

Table 1.1 Occupancy analysis of US chemical losses 1978–1980

Occupancy class	*Frequency (%)*	*Percent of total $ loss*
Extra-heavy hazard. Organic peroxide and explosive manufacture, nitrations and other very hazardous processes	4.9	4.2
Petrochemicals. Processes using hydrocarbon feedstock, mainly olefin plants	8.9	10.9
Heavy hazard. Polymerisation, solvent extraction, sulphonation, hydrogenation and processes involving flammable and combustibles	32.1	59.6
Light hazard. Mainly inorganics	22.9	9.6
Paint, dyestuffs, inks	11.4	3.3
Soaps and vegetable oils	6.2	0.9
Pharmaceuticals and fine chemicals	13.6	2.5

Table 1.1 gives the 'occupancy' analysis of losses, i.e. according to the branch of the industry where they occurred.

The preponderance of losses in the 'heavy hazard' class which in the UK are for the most part regarded as petrochemicals should be noted. The small dollar losses of the last two categories may have been partly exaggerated by the high 'self-retention' of risks which is common in these industries.

Figure 1.4 shows the percentage frequencies of large fire and explosion losses by location.

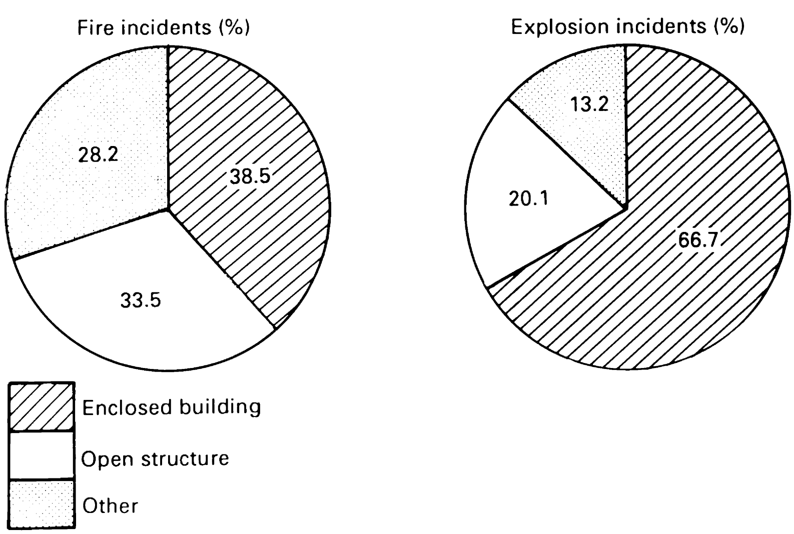

Figure 1.4 Location analysis of large fire and explosion losses (data from reference 3)

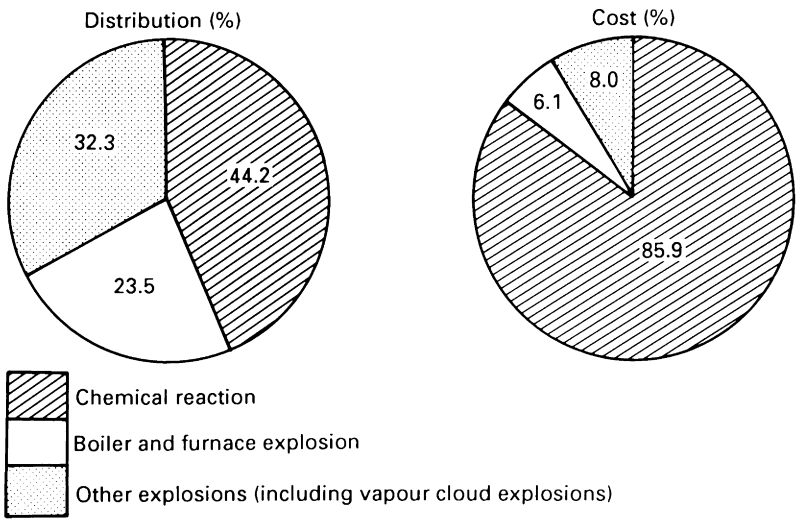

Figure 1.5 Analysis of large explosion losses by cause (data from reference 3)

1.4.1 Explosion losses

Because of the importance of explosions as a cause of loss, these are further analysed. Figure 1.5 gives a percentage breakdown of the numbers and total value of large explosion losses by cause (chemical reaction, boiler and furnace explosions, and other causes). Table 1.2 gives an analysis of those large losses caused by chemical reactions.

Table 1.3 analyses explosion losses by the type of process where they occurred.

Table 1.2 Analysis of chemical reaction losses

Cause	*Frequency (%)*
Accidental reaction[a]	33.3
Uncontrolled reaction[b]	40.0
Decomposition of unstable materials	13.3
Other causes	13.4

[a] Due to accidental contact of material(s).
[b] Intended reactions which become uncontrollable.

Table 1.3 Analysis of explosion losses by type of process

Type of process	*Frequency (%)*
Batch reaction	60.0
Continuous reaction	13.6
Recovery unit	6.6
Evaporation unit	6.6
Other	13.2

1.4.2 Large fire losses

These are analysed by cause in Table 1.4.

Table 1.4 Analysis of large fire losses by cause

Cause	*Frequency (%)*
Release or overflow of flammable liquids/gases	28.5
Overheating	24.3
Failure of pipe or fitting	14.3
Static electricity or spark	9.5
Electrical or mechanical breakdown	9.4
All other	14.0

1.5 Recent UK experience

Here we consider, first the general safety record of the 'mainstream' process industries in the UK (listed with their employment statistics in Appendix A), and second, some special features of accidents in the chemical sector. Both are based on information published by HSE[4,5].

1.5.1 Safety record for 'mainstream' process industries

Incidence rates for fatal plus major injuries in the various sectors of these industries are given in Table 1.5 for the years 1981–1983/1984, based on the 1968 standard industrial classification (SIC) which was still in use by HSE.

The industries listed in Table 1.5 are in two groups:

1. The 'chemical sector' as recognised by the Factory Inspectorate[5]. Employment figures (1984) for this sector are included in Table 1.5.
2. Other 'mainstream' process industries listed in Appendix A which are not included in the chemical sector. These include most of the food, drink and tobacco processing industries, most of the metal-producing industries, and paper and board. Most involve chemical reactions of some kind.

The fatal and major accident incidence rates of most industries listed in Table 1.5 are higher than the average (87.8) for all UK manufacturing industries in those years. The safest, with average incidence rates below 50 per 100 000 employees, were toilet preparations and tobacco, which involve little or no chemical reactions and only moderate temperatures. The more dangerous, with average incidence rates above 150, were lubricating oils and greases, dyestuffs and pigments, vegetable and animal oils and fats, coke ovens and manufactured fuel, iron and steel general, other base metals and paper and board.

The hazards of coke ovens, etc. and the metallurgical industries are well known and include those of high-temperature operations, dust, solids handling, and gassing from carbon monoxide.

Table 1.5 Fatal and major injury incidence rates for UK process industries

SIC Order	*Description MLH*[b]	*Employment in 1984* ($\times 10^3$)	*Fatal and major injury incidence rates*			
Chemical sector[c]			1981	1982	1983	1984
IV	262 Mineral oil refining	18.2	125.0	189.6	117.6	82.4
IV	263 Lubricating oils and greases	4.9	158.7	180.3	137.0	204.1
V	271 General chemicals	111.5	95.2	120.6	138.8	131.8
V	272 Pharmaceuticals	73.8	70.8	69.2	43.5	58.3
V	273 Toilet preparations	20.6	28.8	20.1	39.0	34.0
V	274 Paint	25.0	58.8	51.5	67.5	64.0
V	275 Soaps and detergents	16.7	67.5	93.2	89.8	119.8
V	276 Synthetic resins, plastics materials and synthetic rubber	42.6	75.9	96.4	135.2	105.6
V	277 Dyestuffs and pigments	8.7	150.8	181.8	269.7	264.4
V	278 Fertilizers	7.8	74.8	50.5	125.0	128.2
V	279 Other chemical industries[d]	53.3	54.9	47.9	75.5	80.7
	Total Order V chemicals	360.0				
XIII	411 Man-made fibres	15.1	49.9	63.1	118.4	92.7
	Total chemical sector A	398.2				

Other mainstream process industries		1981	1982	1983
III	211 Grain milling	93.4	100.6	123.6
III	212 Bread and flour confectionery	74.5	78.6	81.9
III	213 Biscuits	29.9	54.7	29.6
III	214 Bacon curing, meat and fish products	98.0	104.7	116.8
III	216 Sugar	104.2	146.1	163.0
III	217 Cocoa, chocolate and sugar confectionery	48.2	45.3	63.2
III	218 Fruit and vegetable products	65.5	74.7	97.5
III	219 Animal and poultry foods	128.1	149.6	157.0
III	221 Vegetable and animal oils and fats	164.2	133.3	213.3
III	229 Food industries n.e.s.	90.4	86.2	84.5
III	232 Soft drinks	56.6	116.1	107.9
III	239 Other drink industries	74.4	65.5	15.2
III	240 Tobacco	54.0	49.6	44.6
IV	261 Coke ovens and manufactured fuel	228.1	280.0	267.9
VI	311 Iron and steel general	243.2	218.8	211.2
VI	321 Aluminium and aluminium alloys	100.0	114.0	132.3
VI	322 Copper, brass and other copper alloys	88.8	111.1	170.9
VI	323 Other base metals	159.0	158.4	200.0
XVIII	481 Paper and board	142.0	167.4	206.2

[a] Per 100 000
[b] Minimum list headings
[c] As listed in Table 13 of Report by HM Chief Factory Inspector, 1985[5]
[d] Comprising polishes, adhesives, etc., explosives and fireworks, pesticides, etc., printing ink, surgical bandages, etc., photographic chemical materials

1.5.2 Special features of accidents in the chemical sector

An analysis of the more serious accidents in this sector made by the Chemical National Industry Group (NIG) of the HSE in 1983[5] is summarised in Table 1.6. This showed that 65% of these accidents were process related.

Table 1.6 Main types of incidents in the chemical industry in 1983

Incident type	*Number*	*%*
Release of chemicals (including 97 toxic, 51 corrosive, 45 flammable, 23 hot and six other materials)	222	34.5
Machinery incidents	77	12.0
Process-related fires and explosions	66	10.3
Falls from a height	56	8.7
Falls at same level and striking against objects	39	6.1
Pressure system and other equipment failures (where main risk was not from chemicals released)	24	3.7
Hit by falling objects	23	3.6
Failure or overturning of lifting equipment	22	3.4
Struck or trapped by vehicle	15	2.3
Affected by chemicals during work (e.g. by decanting, charging, etc. without significant escape or spill)	13	2.0
Run-away exothermic reactions (with no major release of chemicals)	9	1.4
Manual handling and strains	8	1.2
Non-process-related fires and explosions	7	1.1
Confined space incidents – people overcome	5	0.8
Electric short circuits	5	0.8
Not elsewhere classified	52	8.1
Total	643	100.0

This study also brought out the following significant points:

- Of the 222 releases of chemicals which occurred, 127 (57%) affected people directly or indirectly; 92 (41%) occurred during normal process operation with no immediate direct involvement of workpeople; 64 (30%) happened during repair, maintenance or cleaning operations.
- Sixty-two of the 643 incidents (9.6%) involved personnel other than those employed by the factory occupier, i.e. contractors, visitors, etc.
- Forty-nine cases of acute ill health were recorded in the year, mostly associated with the release of chemicals or confined-space incidents.
- Thirty pipework failures occurred in addition to 37 incidents involving flexible hoses or insecure temporary joints.
- Seventeen of the 643 incidents involved clear failures of permit-to-work procedures.
- Seventeen incidents involved tanker vehicles or tank containers.

1.5.3 Further features of accidents in the chemical sector

The findings of the above survey were confirmed by a more extensive three-year survey reported by Robinson of the Chemical NIG[6], which revealed several additional points including the following:

1. *Releases*. 55% of chemical releases affected personnel; 15% of chemical releases involved failure of flexible hoses or insecure joints between flexible hoses and fixed connections; 35% of releases of flammable materials ignited.
2. *Substances involved in incidents*. One or more chemicals were involved in about 50% of the incidents; 184 different substances were involved, of which 108 were only involved once.The numbers of incidents involving the same substance more than ten times are given in Table 1.7.

Table 1.7 Number of times the same chemical was involved 1983–1985

Times	*Chemical*	*Times*	*Chemical*
52	Unspecified hydrocarbons	16	Hydrogen chloride
45	Sulphuric acid	14	Hydrochloric acid
38	Hot water or steam	13	Petrol
35	Chlorine	12	Phosgene
32	Caustic soda or potash	12	Xylene/toluene
28	Explosives or pyrotechnics	11	Nitrous fumes
28	Ammonia	10	Hydrogen sulphide
20	Vinyl chloride		

3. *Maintenance-related incidents*. 30% of reported incidents were maintenance based. Of these, 65% involved injury, over 50% involved release of harmful substances and over 25% involved maintenance of pipes, pumps and valves. In 75% of cases investigated, management failed to take all reasonable precautions, particularly over permit-to-work systems and the provision of adequate protective equipment. Mineral oil refining and the dyestuffs and pigments industries had considerably higher incidence rates than other chemical industries.
4. *Accidents involving permits-to-work*. 8% occurred where no permit existed; 55% involved inadequate permits; 37% occurred when permits were not followed by employees.
5. *Injuries from machines*. Machinery accidents, although less frequent than in other industries, were noticeably concentrated in the pharmaceutical and plastics sectors.

1.6 Vapour cloud explosions (VCEs) and other major world losses in the hydrocarbon-chemical industries

The incidents discussed here are summarised in Appendix D, based on a paper[7] by Davenport of Industrial Risk Insurers, and in Appendix E, based on annual reviews of large property losses in the hydrocarbon-chemical industries published by Marsh and McLennan[1, 1a]. Most of the incidents are of the types discussed in section 10.5.

Appendix D[7] lists 25 VCEs, each causing a property loss in excess of $10 million, between 1950 and 1983, during which a total of 69 VCEs were reported, i.e. about two per year. Each of the 25 large VCEs caused an average of 4 fatalities and an average property loss of $40 million. From this it is clear that the economic incentives to reduce the incidence of VCEs are at least as strong as the need to save lives. Methods of recognising installations where VCEs are possible and of evaluating the maximum probable property damage if one occurs are described in section 12.4.

Appendix E lists 97 major world property losses (including VCEs, and each in excess of $10 million at 1988 values) in the oil, natural gas and chemical industries from 1963 to 1988, excluding those in communist countries. The loss figures relate only to property damage, debris removal and cleanup. Claims for business interruption, employee injuries and liability are excluded. While most of these losses involved fires and explosions, some other incidents involving collapse, pressure rupture, implosion, flooding and windstorms are included. Offshore accidents involving gas/oil production and ships at sea are excluded and no information is given about about human casualties. Bhopal [5.4], in which 2500 people died, is not included since the property damage in that incident was comparatively light.

1.6.1 Analysis of large losses

The twelfth edition[1a] of Marsh and McLennan's annual review analyses the 150 largest losses since 1959. The number and total magnitude of the losses during each consecutive five-year period are shown in Figure 1.6. The progressive increases are due partly to the availability of more complete loss data in recent years but more to the dramatic increase in the size of process units. Thus the capacity of single-train ethylene plants has risen from 20 000 t/a to 700 000 t/a. More congested plant layouts resulting from efforts to minimise energy needs, piping and instrumentation have also increased the magnitude of individual losses.

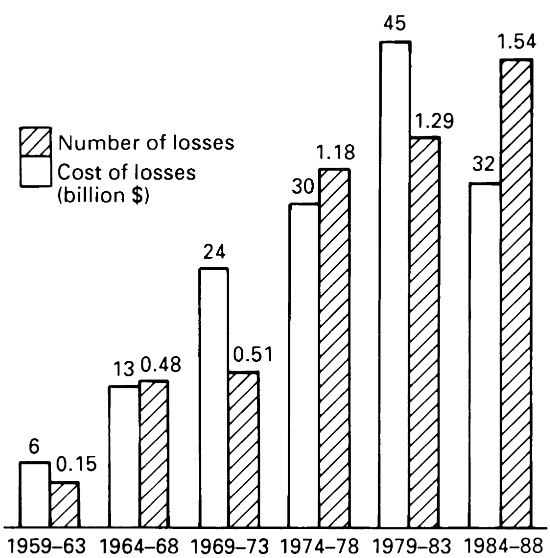

Figure 1.6 Number and total magnitude of large losses, 1959–1988 (data from reference 1a)

The distribution of loss and average value of losses over $10 million at 1988 values for various types of complex are shown in Figure 1.7. Most of such losses occurred in oil refineries while the highest average losses occurred in natural gas processing plants.

The primary causes of loss, broken down into seven headings, are shown in Figure 1.8. Mechanical failure of equipment was the most frequent of these causes. Many of these failures resulted from metal corrosion, erosion, embrittlement and/or fatigue. Most of these could have been avoided by proper inspection and maintenance. The next most frequent cause was stated to be operational errors made on the spur of the moment. Most of these could have been avoided by providing more thorough written operating procedures and guidance and more careful selection and training of operators themselves.

The relative frequency of involvement of eleven different types of equipment in origin of loss is shown in Figure 1.9. Piping systems, which include hose, tubing, flanges, gauges, strainers and expansion joints, were the most frequent origin of loss. The low frequency of losses originating at pumps and compressors was unexpected.

An analysis of whether the loss occurred while the installation was in normal operation or not showed that 24 per cent of the losses occurred during start-up, shutdown, during maintenance or while the plant was idle. In some cases operators had become aware of trouble (leaks etc.) while the plant was running and were in the process of shutting it down when the loss occurred.

Table 1.8 shows the frequency and average cost of four types of large losses.

The most devastating losses involved the delayed ignition of vapour clouds of accidentally released materials. Vapour clouds often cover a large area before igniting, thus causing widespread fires and blast damage. They also cause flying missiles which cause fires and damage remote from the point of vapour release. The miscellaneous type included a wind-storm, rupture of a steam pipe and a tank collapse.

Figure 1.10 shows the frequency of different types of loss for different types of complex. Here there is a marked contrast between oil refineries and chemical plants: 75% of losses in chemical plants were initiated by explosions and 8% by fires, compared with 13% by explosions and 52% by fires in refineries.

Attempts to classify losses by source of ignition proved of limited value since in most cases the source of ignition remained unknown.

Most of the installations where these losses occurred can truly be called 'self-destructing'. By this I mean that unless they are maintained in a high state of integrity, even minor failures can quickly escalate into catastrophes.

When a plant is operating unprofitably in a period of depressed markets and high oil prices, like a redundant ship it can barely be sold for its scrap value. There is a strong temptation to skimp on maintenance and run it on a shoestring, until times improve or it goes up in smoke. The conscious decision to close it down may be more difficult to take both politically and economically. Hard times are also dangerous times. New safety legislation and increased insurance premiums may have little effect on this situation.

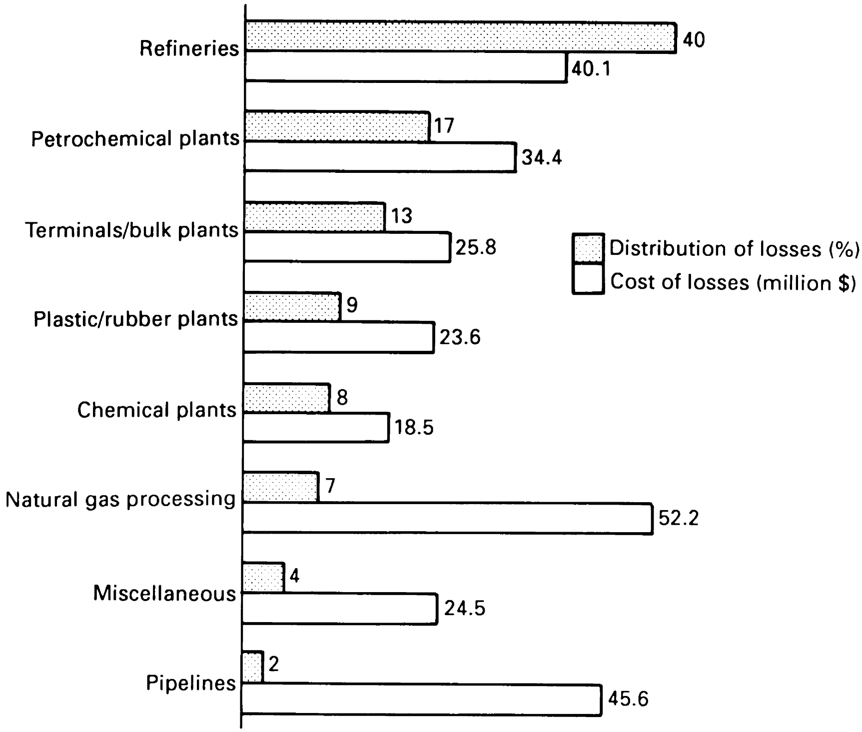

Figure 1.7 Distribution and average cost of large losses by type of complex (data from reference 1a)

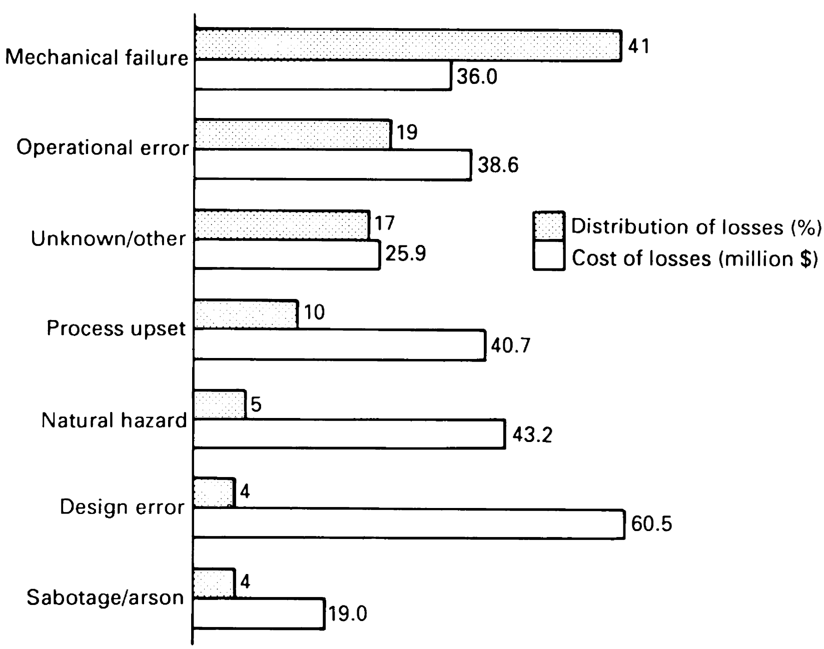

Figure 1.8 Primary causes of large losses (data from reference 1a)