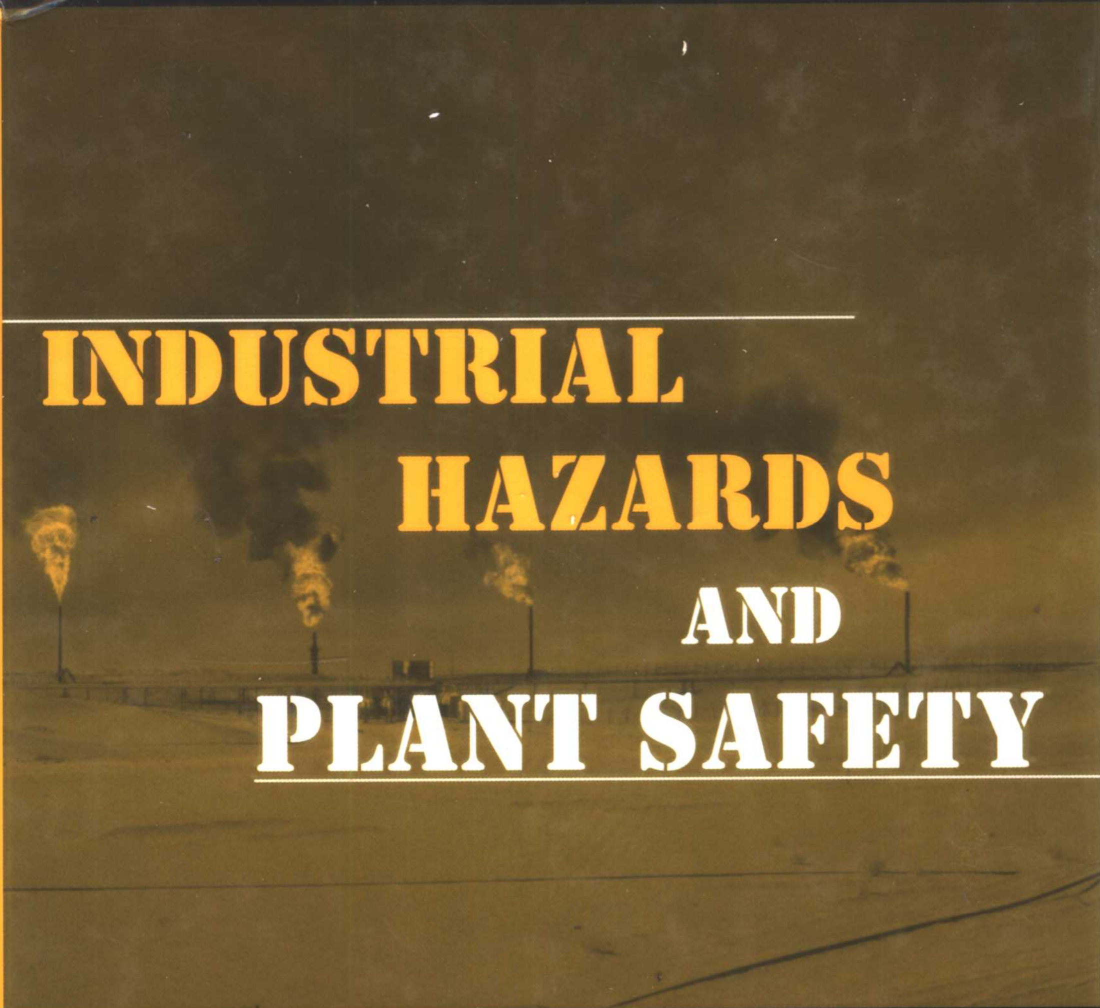

INDUSTRIAL HAZARDS AND PLANT SAFETY

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PREFACE

Almost all activities carry with them some risk to life, limb, property and the environment. In considering whether to carry them out, we implicitly weigh the risks, a concept that compares the likelihood of undesirable outcomes and their consequences, against their benefits. With technological development, risks have escalated to such an extent that the consequences of accidents are sometimes large enough to dominate the design and operation of certain enterprises, such as those in the aerospace and nuclear industries. Prevention and mitigation of such accidents has also had major impact on the process industries for over a century, e.g., through codes to prevent failures of pressures vessels, but it is only recently that this body of knowledge has been assembled in coherent form. Perhaps the most important contribution in this direction is a work of great scholarship by the late Frank Lees, titled *Loss Prevention in the Process Industries* (2nd Edition, Butterworth, 1996). While this is undoubtedly the definitive reference in the field, for some time there has been a need for texts that are more approachable and pedagogically oriented. This book is an attempt to address these issues. Rather than covering all aspects of industrial hazards and plant safety, it focuses on developing an understanding of the risks associated with accidental events that impact design and operation in the process industries. In particular, it emphasizes transport processes in such problems, which is aligned with my own research interests. The following paragraphs outline how this book came about.

On a morning in March 1988, Werner Haefeli, of Hoffmann-La Roche, together with colleagues from Ciba-Geigy and Sandoz, approached me after a lecture I had just presented at the Swiss Federal Institute of Technology (ETH) in Zurich. They wanted to interact regarding some experiments and analyses arising out of the AIChE Design Institute for Emergency Relief Systems (DIERS), in which their companies were participating. The problems seemed interesting, and I got involved in their work. One thing led to another, and I ended up spending an extended sabbatical during 1990 and 1991 at the ETH, and consulted with several European companies on a wide range of chemical plant safety problems. In particular, work with the various Montedison (Italy) companies, such as Himont, Montefluos, Farmitalia, and Montedipe, introduced me to many different safety issues, including heavy gas and aerosol dispersion, containment of emergency relief streams, early detection of runaway reactions, suppression of explosions, and so on. In dealing with some of these problems, I collaborated on occasion with the people at Ciba-Geigy. This left me with great respect for the safety technology they had developed, in particular with regard to explosions, which I have drawn on extensively in this book. At the same time, I worked at a more strategic level with companies such as det Norske-Veritas, and the UKEA, who were developing their plant safety programs, and considering acquisitions to establish their market positions. While all this was far removed from my usual research activities in multiphase systems and turbulence, I found the activities very stimulating and continued to interact with various European companies, such as the

Ciba-Geigy, Hoffmann-La Roche, Shell, Enichem, Snamprogetti, etc., even after I returned from my sabbatical in Switzerland to research and teaching in Santa Barbara.

During my 1990-91 sabbatical, I was invited by the Swiss Institute of Engineers and Architects to present a series of 1 1/2-hour lectures on industrial hazards and plant safety. Hoffmann-La Roche hosted these lectures, and they were widely attended by a cross section of engineers from the Swiss chemical industry, as well as from various governmental and regulatory bodies. Each lecture was followed by about a half a day of discussions, and I can safely say that I learned more from the participants than they learned from me. This book, then, is a direct outgrowth of the lectures I presented a decade ago. It still retains some of this flavor. Much of the material, however, has been presented every year in a senior-level course to undergraduates at UC Santa Barbara, and this has led to some rounding out of the more idiosyncratic edges that remained from the original lecture series.

The book starts with several case studies of accidents, from which I have tried to draw out significant plant safety issues. This is followed by a discussion of hazard evaluation methods, some of which originated in the chemical industry, such as HAZOP, and others that have been taken from the nuclear and aerospace industries. This is more or less the order in which I presented the lectures in Switzerland originally, the rationale being that such methods can be used to develop the scenarios needed for the later chapters. I then move on to discussing emergency relief and treatment of the relief streams, as these measures are of central importance in mitigating risks arising from a variety of accidents. Explosions are dealt with next, and I draw on my interactions with Ciba-Geigy and, as mentioned earlier, in particular, the pioneering work of Dieter Bartknecht. The rest of the book deals with the behavior of accidental releases, first with regard to dispersion and then with regard to fires and vapor cloud explosions. The consequences of releases in terms of injuries and property damages are treated rather cursorily, though the use of probits is introduced, and consequences of heat radiation and pressure waves are considered qualitatively.

The choice of topics is somewhat oriented towards what students need to see in a chemical engineering curriculum, although the book is also aimed at the practicing engineer— having, as mentioned, been developed from a series of lectures for such an audience. I have tried to emphasize, where possible, fundamental aspects and mechanisms related to phenomena, and, even when presenting empirical correlations, tried to present a rationale for the form of parameterization adopted. Problem sets are presented at the end of each chapter to aid in use of the book for teaching. The problems in many cases are quite open-ended and require some research, as well as standard computational packages such as *Mathematica*. The level, however, is such that seniors should have no real difficulty in tackling them.

It remains for me to acknowledge the many people who have contributed to this book: first and foremost, Werner Haefeli and his many colleagues at Hoffmann-La Roche, Ciba-Geigy, Sandoz and Lonza, for developing my interest in the subject and persuading me to turn the lectures I presented in Switzerland into a book; and second, Geoff Hewitt, the Editor of the Taylor and Francis series of which this book is a part, as well as my co-principal investigator in several research projects, for continuing to take an interest in the project and prodding me at strategic moments to "close the deal". Luigi Chiechi of Montedison was an able mentor from whom I

learned much, Arne Ronold and Terje Sondvendt of det Norske-Veritas, Franco Prandini of Himont, Stephen Richardson and Graham Saville of Imperial College, Paolo Andreussi of the University of Pisa, Simberto Senni and his colleagues at Snamprogetti, Rene Reijnhart of the Technical University of Delft, and George Yadigaroglu, my gracious host and continuing collaborator at the Swiss Federal Institute of Technology all contributed much to this project. Finally, Jim Huff, formerly of Monsanto, Stan Grossel, formerly of Hoffmann-La Roche (U.S.), Hal Kemp, and my colleague, Theo Theofanous, helped considerably in developing the senior course taught at UC Santa Barbara.

Needless to say, the faults in this book are all my own, and, while I have tried to ensure that the information contained here is correct, there are undoubtedly many errors. A book of this nature synthesizes much information from many sources, and, while the publishers and I have made every effort to identify each source and obtain permission to reproduce copyright material, some sources may have been overlooked. In this regard, I would like to thank Priscilla Yang of Imperial College, London, for her continuing efforts to track down the original sources and obtain their permission. My apologies to any copyright holders whose rights I may have unwittingly infringed upon.

To conclude, chemical plant safety is a living and rapidly developing subject. It is also central to the well being of the process industry. I hope this book contributes to advancing understanding and stimulating development of this important field.

Sanjoy Banerjee
Santa Barbara, CA USA
2002

CONTENTS

CHAPTER
ONE

INTRODUCTION

1.1 SCOPE OF INDUSTRIAL PLANT SAFETY

Aspects of industrial processing that may lead to injury and property loss may be considered under two broad, albeit somewhat arbitrarily-defined, categories. The first is concerned with exceptional situations that develop over relatively short time-scales and in this sense lead to "acute" problems. For the purposes of this text we will call this plant safety and understand that it encompasses design, construction and operation to reduce the likelihood of hazardous incidents, and mitigate their consequences should they still occur.

The second is concerned with more "chronic" problems that arise from routine releases through effluent streams, whether continuous or batch, and disposal of unusable by-products. We call this waste management, and exclude the technology needed to handle and minimize such problems from consideration in this book.

Plant safety even under this restrictive definition is still an extremely wide field. At one end of the spectrum it deals with cognitive processes and human behavior and at the other end with the fluid mechanics of reactive flows. In between we have issues such as: how to motivate operators to behave as if accidents were imminent when in fact they hardly ever occur, how to design a control room, how to build intrinsic safety into a process, how to control an unexpected over-pressure transient, how to calculate the consequences of a pipe failure, how to prevent explosions, and so on. Clearly in any discussion of plant safety one has to be selective, with the selection being influenced by the types of accidents and problems encountered recently in the industry.

In addition, an underlying philosophy must guide the discussion, and in this book, the philosophy is to stress the fundamental aspects of the processes involved rather than to focus on empirical formulae. Some of the phenomena are obviously so complex that they can be calculated only through correlations based on large-scale experiments. In cases where this is necessary the limitations of the correlations and the range of conditions over which they may be expected to apply have to be stated, where possible.

Turning back now to the selection of issues, valuable qualitative information may be obtained from a number of studies, such as by Planas-Cuchi et al. (1997), those by the insurance industry, and by examining some accidents such as those at Texas City (1978), San Juan Ixhuatepec (1984) and Bhopal (1984). The following sections contain brief discussions of these aspects followed by a summary of the main issues that arise.

1.2 PERSPECTIVES RELATED TO ACCIDENTS

The safety of industrial plants has become a subject of public concern because of several notable accidents, some of which are listed below; and several of which are well discussed in Willey (1999):

- the 1974 Flixborough explosion (Parker 1975) in which 28 were killed, 89 injured and severe damage caused to buildings,
- the 1975 Beek propylene release and refinery fire in which 14 were killed,
- the 1976 Seveso accident in which highly toxic substances were released to the environment causing contamination to wide areas with attendant health implications for the surrounding populace,
- the gas storage plant catastrophe near Mexico City at San Juan Ixhuatepec (1984) in which about 500 people perished and extensive damage was done,
- the Bhopal toxic gas release (1984) in which about 3400 were killed and many more injured,
- the chemical spill at Basel in 1986 which severely contaminated the Rhine,
- the gas explosions in the North Sea Occidental (Piper Alpha) platform that resulted in the loss of 167 lives and destruction of the platform, see Cullen (1990),
- the vapor cloud explosion near Ufa, Russia due to leakage from a liquified gas pipeline that was ignited by two passing trains on the TransSiberian Railway, causing thousands of deaths and injuries,
- more recently, the 1997 explosions at the HPCL refinery in Vishakapatnam in which 60 fatalities occurred (Khan and Abhasi (1999),
- the 2000 El Paso pipeline explosion near Carlsbad, New Mexico that killed 12.

In all these cases either a fire, or an explosion, or a runaway chemical reaction were involved. In addition there have been numerous releases and accidents of lesser magnitude.

This has led to a spate of legislation, for example OSHA Regulation 29CFR1910.119, the Seveso I and Seveso II Directives of the European Union (Council Directives 82/501/EC and 96/82/EC respectively). The availability of information and databases regarding accidents have also been substantially enhanced (see Kirchsteiger, 2000). To obtain a perspective of the types of accidents and the losses associated with these, consider the classical study of Doyle (1969) that identified the two major causes of losses as fires (42% frequency and 30% of financial loss) and explosions (53% frequency and 69% of loss). A decade later a similar insurance survey performed by Norstrom (1982) also highlighted the importance of fires (41% frequency and 20% of loss) and explosions (23% frequency and 66% of loss). It should be noted that "explosions" in the sense used by both Doyle (1969) and Norstrom (1982) include runaway chemical reactions. More recently, Planas-Cuchi et al. (1997) have examined the UKAEA (1994) MHIDAS database for "fires", "explosions" and "gas cloud" incidents. In broad terms, their study is in line with the earlier work of Norstrom and Doyle.

Some interesting inferences can be drawn by examining Norstrom's paper. For example, the majority of the financial loss (59.6%) is in so-called "heavy hazard" chemical industry as opposed to the "extra heavy hazard" class. The heavy hazard class includes most polymerization processes as well as solvent extraction, sulphonation, low pressure hydrogenation and other processes involving flammable or combustible materials. The extra heavy hazard class involves organic peroxides, explosives manufacture, nitrations, Grignard reactions, etc. Probably because of the precautions taken with the extra heavy hazard class, they constitute only 4.2% of the financial loss. The other major category is the manufacture of petrochemicals which constitute about 20% of the financial loss. The frequency of occurrence for the extra heavy hazard class, petrochemicals class and heavy hazard class are 4.9%, 8.9% and 32.1% respectively. In more recent times there have been several major accidents related to the petroleum and petrochemicals industry that may affect the relative importance of this class – see, for example, the table in Khan and Abbasi (1999). Nonetheless the perspective gained from Norstrom's (1982) study are still valuable.

Figure 1.1 shows the losses in the chemical industry for 1978-80 period as reported by Industrial Risk Insurers. In looking at the value of the losses according to how they contribute to the overall percentage, only 12.7% of the occurrences were for claims/settlements greater than $100,000. However these constituted 95% of the total financial loss. Figure 1.2 shows the losses sorted by the value of loss and its frequency of occurrence. Very few losses were greater than $2.5 million but these constituted 55.8% of the total value.

Without going into more detail the implications of these statistics may be summarized as:

- The greatest financial value and frequency of loss is due to explosions (including runaway reactions.)

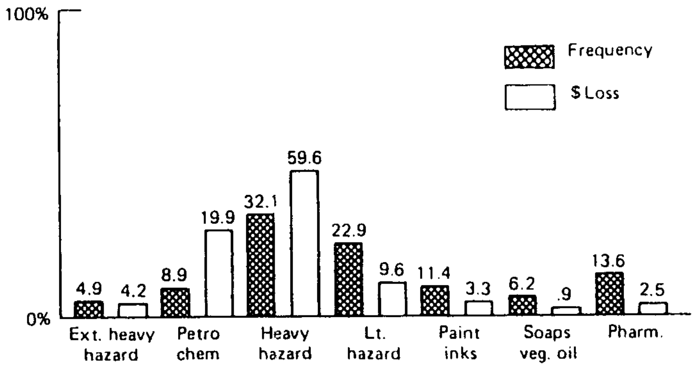

Figure 1.1. Losses in the chemical industry, IRI chemical and allied classes, 1973-1980 occupancy analysis. Frequency loss, cross-hatched bar; dollar loss, open bar (from Norstrom, 1982, courtesy of John Wiley and Sons, Inc)

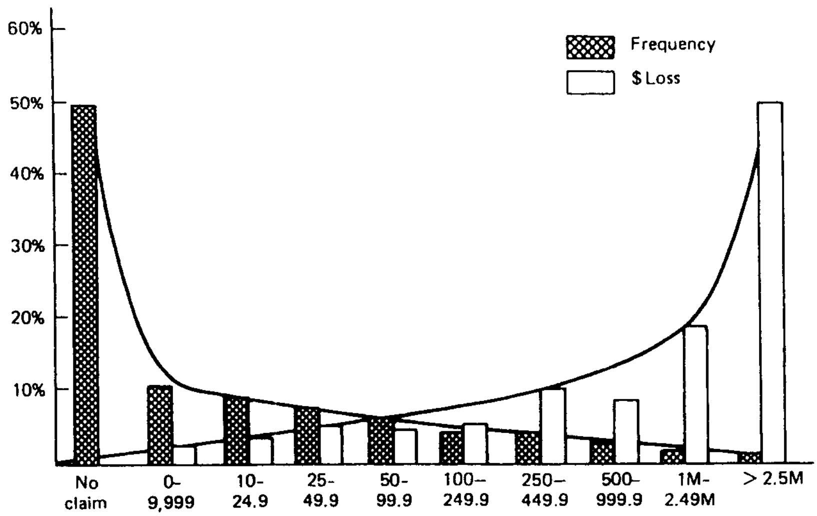

Figure 1.2. Losses in the chemical industry, IRI chemical and allied classes, 1978-1980 size of loss analysis. Frequency loss, cross-hatched bar; dollar loss, open bar (from Norstrom, 1982, courtesy of John Wiley and Sons, Inc).

- From the insurance viewpoint, most of the large losses occur very infrequently and cannot be accurately predicted from the experience of a single firm. To quote from Norstrom, "Clearly, major losses in the chemical industry can be characterized as having relatively low frequency but enormous dollar loss potential associated with them."

A Japanese study by Uehara and Hasegawa (1986) provide additional insights. They examined some 1270 incidents at factories between 1968 and 1980 focussing on fires and explosions. They found, particularly for the petrochemical industries, that death-related accidents were often a result either of fires and/or explosions initiated by leaks of flammable liquids with low flash points from reaction systems or initiated in the reaction equipment itself. They suggest that the direct causes may have been closely related to abnormalities in the reaction processes. Furthermore, these accidents were primarily responsible for the losses that were greater than 1 billion yen (~ $10 million). Some other interesting results were:

- a large number of accidents occurred during maintenance (about one-quarter of the total for petroleum refineries),

- about half the accidents in petroleum refineries were primarily caused by human error, e.g. improper management, improper inspection, misoperation, etc. Also, the number of accidents neither correlates with the largest losses nor with fatalities. For example petroleum refineries had the largest number of accidents but most of them were quite small. On the other hand the major disasters arose in the petrochemical industry, primarily due to "abnormality or misoperation in the reaction process" to quote Uehara and Hasegawa (1986).

More recent studies corroborate these conclusions, but also highlight the importance of decomposition reactions, e.g. Ho et al. (1998).

1.3 TRANSPORTATION ACCIDENTS

The U.S. Department of Transportation maintains a Hazardous Materials Information System which is a valuable data source for incidents arising from truck, railcare and pipeline transport (TT, RC and P in the following Tables). Ormsby and Le (1988) have surveyed the data for gasoline, natural gas, liquefied petroleum gas (LPG), ammonia and chlorine. While these data exclude recent incidents such as the explosion following a leak of the El Paso Gas pipeline near Carlsbad, NM that resulted in 12 fatalities, nonetheless the main conclusions are of interest. (Natural gas is essentially methane, whereas LPG is a mixture of propane and butane). They have presented a summary of the data in the form shown in Figure 1.3 excluding natural gas transmission by pipeline. Figure 1.4 shows the data for pipeline transmission. The data are presented in so-called F-N curves, where F is the frequency of an event which results in fatalities to N or more persons. vs. N, the number of fatalities. Note that the societal risk appears higher in Europe or other countries, e.g. Mexico, than in the U.S. but account is not taken of recent accidents such as the US El Paso pipeline-related explosion. For example, fatalities/(10^9 tonne-miles) are 5.9, 4.8 and 0.34 in Mexico, Europe and U.S. respectively for LPG. The European statistics are somewhat skewed by the Los Alfreques, Spain accident on July 11, 1978 in which 215 persons

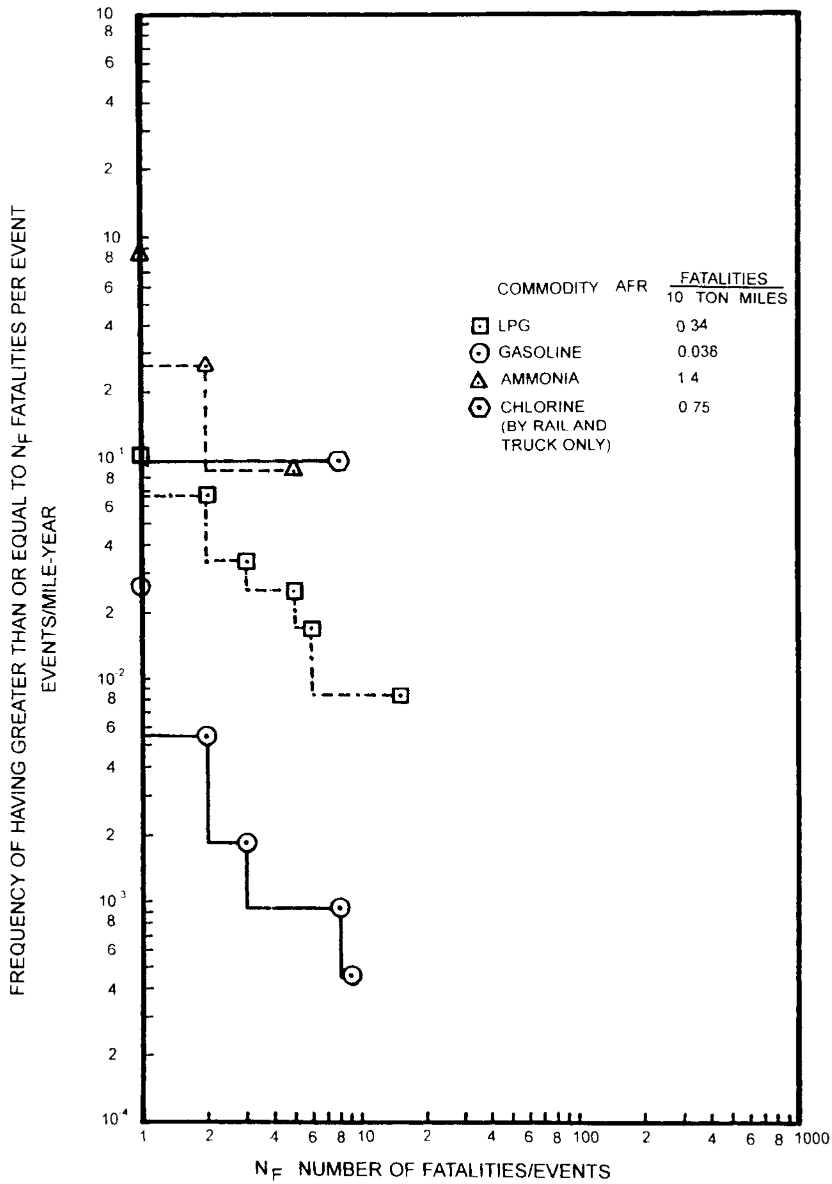

Figure 1.3. Actual societal risk curves for hazardous materials, shipments in the U.S., all modes of transportation, 1978-1985 (from Ormsby and Le, 1988, courtesy of IChemE).

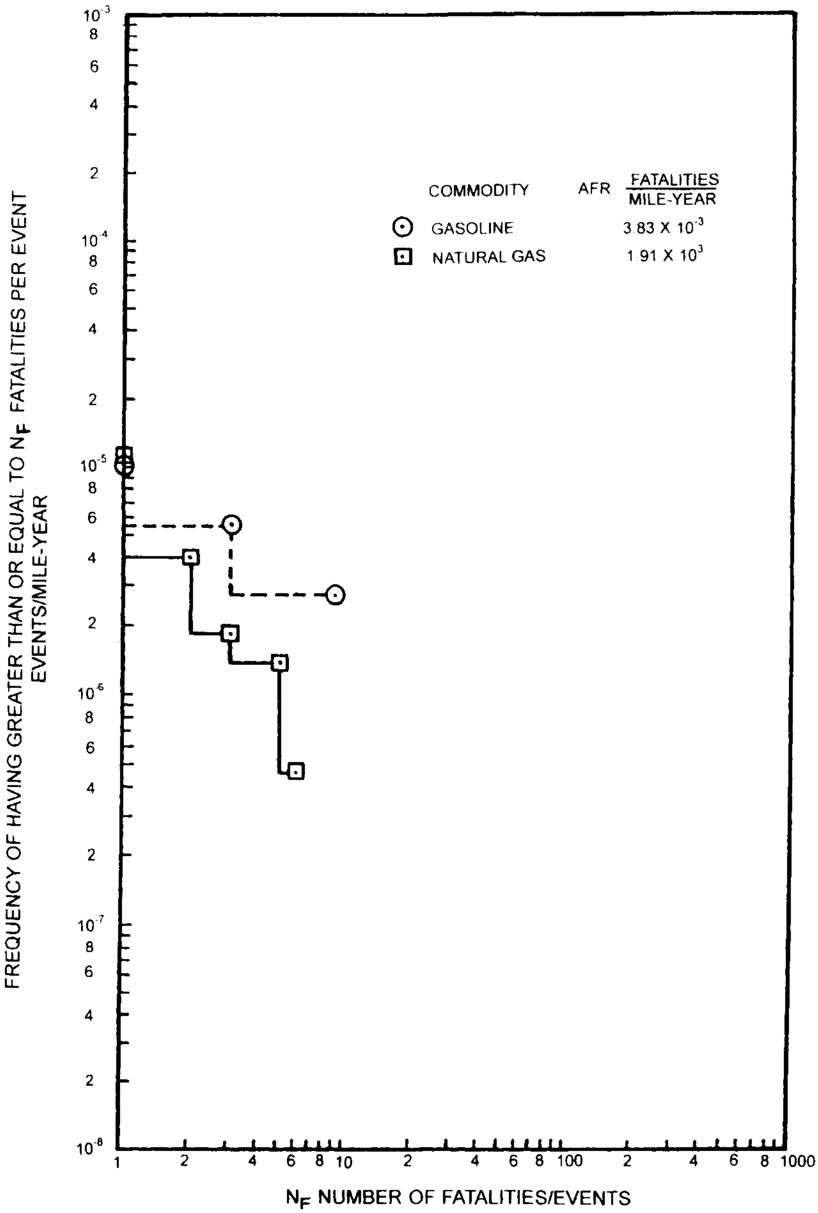

Figure 1.4. Actual societal risk curves for gasoline and natural gas pipeline transmission in the U.S. (from Ormsby and Le, 1988, courtesy of IChemE).