Methods for Assessing and Reducing Injury from Chemical Accidents
Edited by Philippe Bourdeau and Gareth Green

17 *The Nature of Chemical Hazards, their Accident Potential and Consequences*

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17.1 INTRODUCTION

Large-scale accidents due to the reactivity or toxicity of manufactured products have been happening for a long time: the first recognized dust explosion, in a flour mill, occurred in 1785 (Bartknecht, 1984); documented case histories are available for most of this century (Lees, 1980). Their frequency and severity have tended to increase in the post-Second World War period with the spectacular expansion of the chemical/petrochemical industries, punctuated by some notorious disasters; yet earlier ones (e.g. ammonium nitrate explosions) were no less devastating. Recent statistics would indicate a slow improvement due to greater awareness (Bhola, 1985; Uehara and Hasegawa, 1986), likely to be offset by further expansion and geographical diversification in the coming decades, to meet the impact on world demand of further products diversification, population growth and improving standards of living.

Although the range and ubiquity of chemical hazards are unparalleled in other sectors, disclosure of their potential to cause extended harm and regulatory tools were slow in coming (ACMH, 1976, 1979, 1984; following Flixborough). This is also due to chemistry being long established as an immensely complex panoramic field which defies description and ordering. The term 'major hazards' was coined to designate the most ominous cases, featuring large quantities of flammable/explosible substances (fuels, feedstocks, industrial gases), large quantities of toxic, unstable or very reactive substances (feedstocks and process intermediates) and far smaller quantities of acutely toxic and persistent chemicals, as such or as by-products of an unwanted/uncontrolled reaction, that last category being more debatable. Those headings transcribe the normal accident categories: fire, explosion (unconfined/confined) and toxic release; and they also guide research efforts. The present chapter will attempt to give an overview of all aspects, not limited to toxics which are only part of the problem.

Each accident is a unique, often bizarre, event, albeit with repetitive patterns but great 'variability' in terms of cause/consequences ratio. Hazards quantification alone (exemplified in the Seveso Directive, 1982) is but an alarm signal for further examination and action to be taken. Estimates of consequences for that accident potential necessarily involve its context – population density, neighbouring hazardous items, topography/meteorology, etc. – as well as an appreciation of the likelihood of occurrence (which may or not lead to full risk quantification). The aim of this chapter is to recall, however briefly, that

(a) sophisticated methodologies, often in-house, are available to guarantee plant safety at all stages of planning, construction/commissioning, operation, stand-by/maintenance, etc., and concrete safety precepts are listed in Varadarajan (this volume, Chapter 16) or, for processes, in Kletz (1984);
(b) although the fine details of an accident and of its consequences generally cannot be predicted, but only reconstituted, reasonably realistic quantitative or probabilistic estimates can be made for diverse postulated cases (see, e.g. COVO, 1982; Lannoy, 1984), on which to found better the decision-making/regulatory process, siting and emergency planning;
(c) apart from process monitoring, plants and storage facilities are (or can be) fitted out with mitigation devices, to lessen the extent or escalation of abnormal/hazardous situations, on- and off-site. They are no substitute for emergency preparedness and less readily applicable to transportation and pipelines.

There is a proviso: methodologies to assess or regulate the 'chemical risks' are still being elaborated and also reflect national attitudes (Ottway and Peltu, 1985). Recommendations in the matter would be of interim, non-consensual nature at this stage. Equally, this introductory chapter (as indeed most 'loss prevention' work) places emphasis on sudden, acute industrial/transportation accidents, the classic major hazards aspects. Other equally important aspects – industrial epidemiology, medical follow-up, food chain contamination, reclamation, etc. – are addressed in subsequent chapters.

17.2 THE SCALE OF THE PROBLEM

Major hazards do not merely result from the infinite diversity of substances at hand (counts range from half a million to several million) or insufficient knowledge of properties (like stability, toxicity, etc.) or agglomeration in large quantities. What is less perceived is that huge flows of fuels and chemicals are the life-blood in the tissue of industrial society, with as much capillary and ubiquitous end-distribution as for water or electricity: practically no location, population group or activity is entirely immune.

Some overall production, consumption and trade figures are recalled in Tables 17.1 to 17.11 (Eurostat, 1985; CEFIC, 1985) to illustrate the scale of

Table 17.1 Per capita energy consumption (rounded, in te oil eqivalent, with 1 kWh = 0.086 kg o.e.)

Location	Total in Te oil eq	Electric energy share			
		In Te oil eq.	Total (10^3 kWh)	Industry (10^3 kWh)	Other uses (10^3 kWh)
CND	6.9	1.1	12.9	5.7	7.2
*E.10	3.25	0.36	4.2	2	2.2
JPN	2.6	0.38	4.4	2	2.4
USA	6.7	0.80	9.3	3.5	5.8
USSR	4	0.37	4.3	3	1.3

*E.10 = European Community prior to the accession of Spain and Portugal.

Table 17.2 Internal energy consumption (in M.te oil equivalent, rounded)

Location	Coal and brown coal	Oil	Gas	Nuclear	Primary electricity	Total
CND	23	73	46	9	19	170
*E.10	216	430	158	64	14	882
JPN	64	181	24	28	8	305
USA	362	660	430	75	28	1555
USSR	333	361	359	25	12	1090

*E.10 = European Community prior to the accession of Spain and Portugal.

Table 17.3 Share of primary energy source in energy consumption (per cent)

Location	Coal and brown coal	Oil	Gas	Nuclear	Primary electricity	Oil and gas
CND	13	43	27	5	11	70
*E.10	24	49	18	7	1.5	67
JPN	21	59	8	9	2.6	67
USA	23	42	28	4.8	1.8	70
USSR	30	33	33	2.2	1.1	66

*E10 = European Community prior to the accession of Spain and Portugal.

these activities in industrialized countries. Soon enough comparable ones will come to light in most of the world (with increased motorization and use of plastics, fibres, fertilizers and pesticides) and some productions (ethylene, methanol, ammonia) may well migrate altogether to oil- and gas-rich areas, boosting shipping of those basic chemicals towards far-away downstream

Table 17.4 Bulk production figures for certain chemicals, 1982–1983 (in M.te, rounded)

Location	Sulphuric acid	Chlorine	Nitrogenous fertilizers	Phosphate fertilizers	Potash fertilizers	Plastics
CND	3.1	1.2	1.9	0.6	5.4	0.8
*E10	17.8	5.8	8.0	3.6	4.2	17.9
JPN	6.5	3.5	1.1	0.6	–	6.4
USA	29.3	8.3	9.0	7.3	1.7	17.4
USSR	23.8	—	11.5	6.6	8.1	3.3

*E10 European community prior to the accession of Spain and Portugal.

Table 17.5 European consumption of olefins and aromatics, 1984 (in M.te, rounded)

Country/group	Ethylene	Propylene	Butadiene	Benzene
*E. 10	10.4	6.5	—	4.9
W Europe	12.5	7.2	1.2	5.2

*E.10 European community prior to the accession of Spain and Portugal.

Table 17.6 Ethylene derivatives, 1984 (in per cent of consumption, rounded)

Polyethylene	Dichloroethane Vinyl chloride	Ethylene oxide	Ethylbenzene Styrene	Others
52	19	11	7.5	10.5

Table 17.7 Propylene derivatives, 1984 (in per cent of consumption, rounded)

Polypropylene	Acrylonitrile	Cumene	Propylene oxide	Others
33	16	9	11	31

users. Relocation will be further encouraged by specific trends in present traditional areas: high labour costs, population decline, saturation of markets, several environmental/land use constraints, sea-front operations. The globalization of the sector and its continuing growth will also globalize the hazards into areas which were long immune and perhaps societies not structured at this time to handle disasters (be it, in emergencies, lack of ready access, poor

Table 17.8 European chlorine trade, 1984. (in 10^3 te, rounded)

Country	Consumption	Imports	Exports
Belgium	541	29	44.5
Germany	3425	69	60
France	1483	80	7.2
Italy	922	0.5	45.6
Netherlands and Denmark	545	25.5	29
UK	993	10	3.7
E.C.	7908	214	190

communications, lack of disaster services and much else), or simply to 'regulate in depth' those bewilderingly complex technical and societal issues which affluent societies are only beginning to perceive and tackle.

Reasons for the post-war mutation of an already mature industry have been surveyed (Taylor, 1977; Shell, 1983) and may be recalled briefly. A common index is oil production, which roughly doubled every decade, now temporarily flattening with the economic crisis and a modicum of conservation measures; the expansion of natural gas, while more recent, is no less spectacular, defying difficult locations (North Sea, Siberia). Proven recoverable reserves are at least equivalent and, as a secular trend, one may even expect a steady 'penetration' of gas, displacing other vectors in the energy mix (Marchetti, 1977). Safety problems would mutate accordingly.

Much of this was driven, as might be expected, by the energy demand: onslaught of mass motorization, substitution of coal in electricity production and domestic heating, in sum the 'supply-side' availability of a cheap, efficient, abundant liquid fuel. Economies of scale and longer sea-routes amplified capacities and hazards accordingly. Crude carriers jumped from 10–20 kte in the 1950s to, typically, 0.3–0.5 M.te in the 1970s, and refineries or integrated complexes presently handle tens of M.te per year. Limits to growth and gigantism have been perceived and there is now a modest reversal, driven by

Table 17.9 LPG flows in W. Germany (Hartwig, 1984)

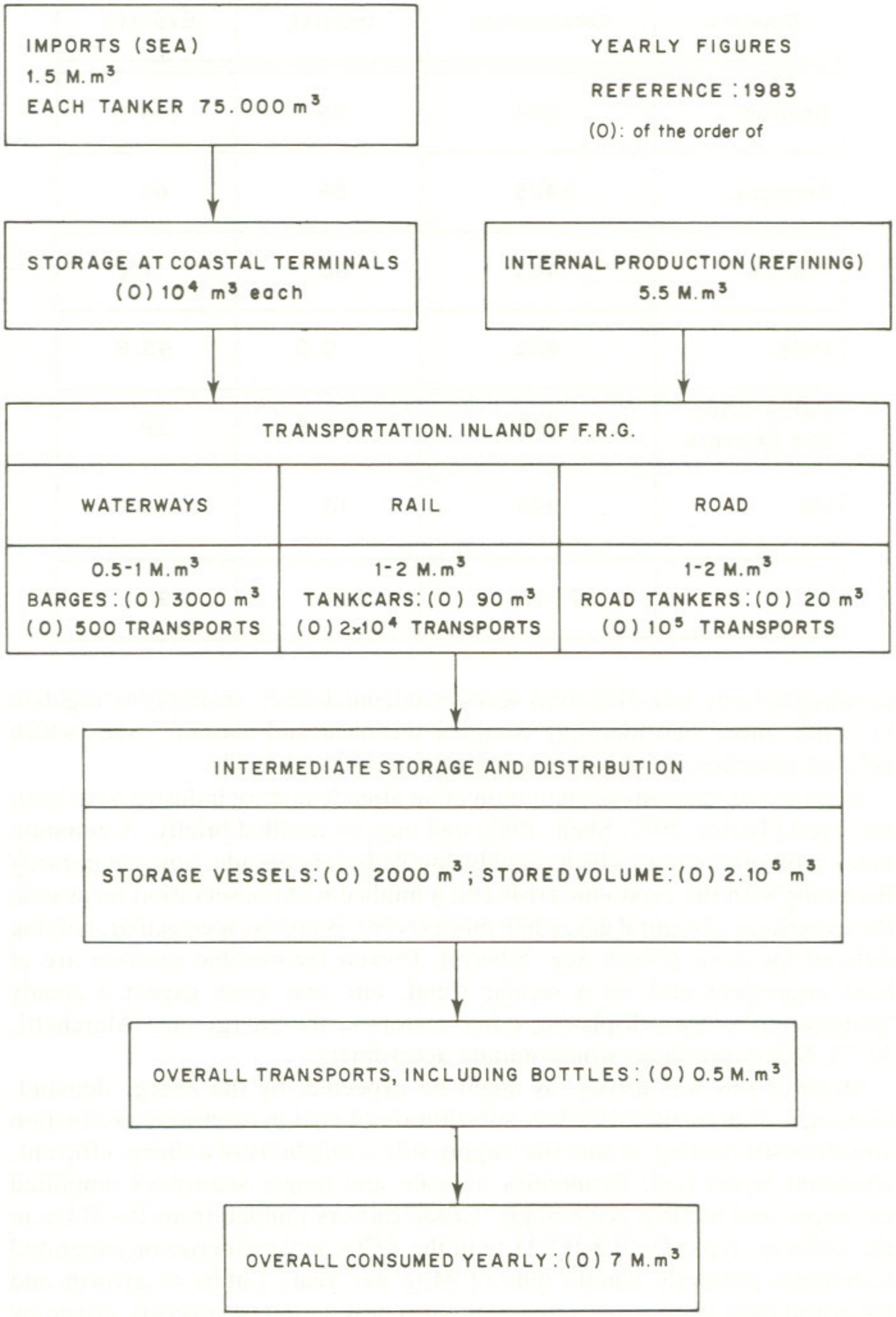


Table 17.10 Chlorine yearly flows in W. Germany, in M. te (Hartwig, 1984)

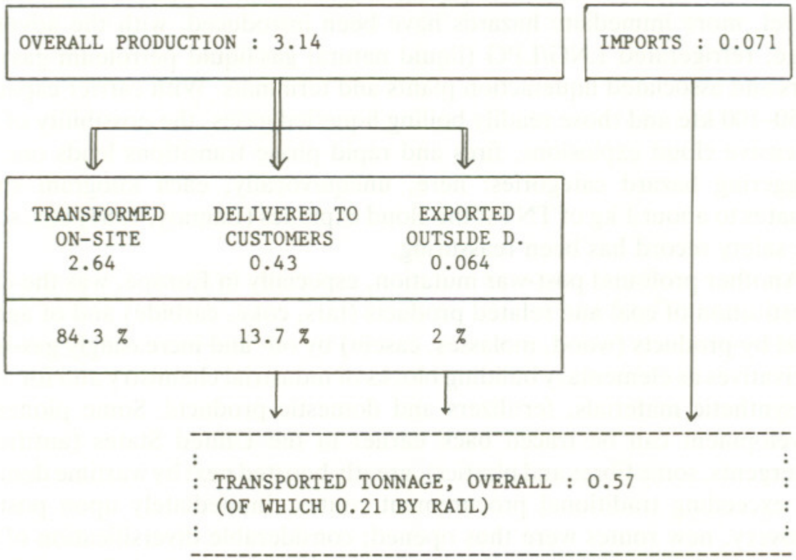
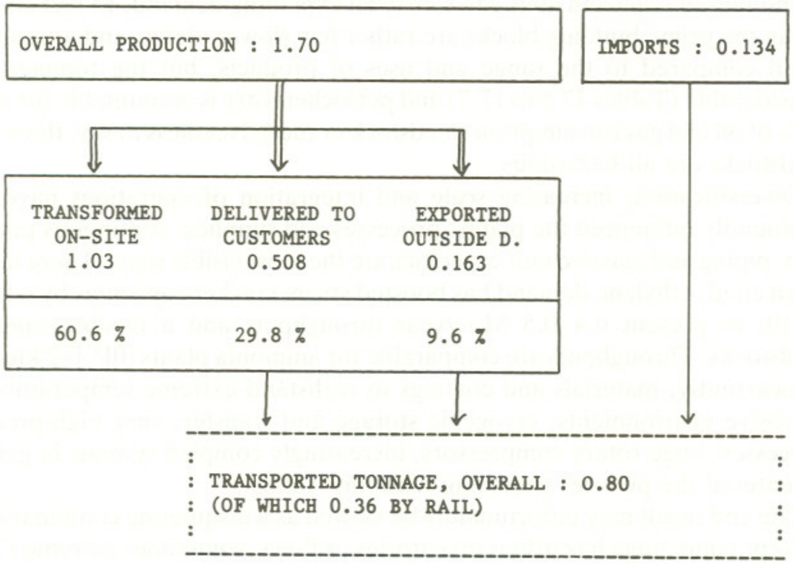


Table 17.11 Ammonia yearly flows in W. Germany, in M. te (Hartwig, 1984)



the difficulty of insuring against and compensating for supertanker accidents and spills, the convenience of piping and relocation of primary processing. Novel, more immediate hazards have been introduced, with the advent of large, refrigerated LNG/LPG (liquid natural gas/liquid petroleum gas) carriers and associated liquefaction plants and terminals. With carrier capacities of 50–100 kte and those readily boiling liquefied gases, the possibility of very extensive cloud explosions, fires and rapid phase transitions leads one into staggering hazard categories: here, unequivocally, each kilogram spilled equates to about 1 kg of TNT if the cloud explodes (Lannoy, 1984) but, so far, the safety record has been reassuring.

Another profound post-war mutation, especially in Europe, was the entire substitution of coal and related products (tars, coke, carbide) and of agricultural by-products (wood, molasses, casein) by oil- and increasingly gas-based derivatives as elementary building blocks of industrial chemistry and for a host of synthetic materials, fertilizers and domestic products. Some pioneering development can be traced back earlier in the United States (antifreeze, detergents, some fibres and plastics), greatly boosted next by wartime demands far exceeding traditional procurement routes. Immediately upon post-war recovery, new routes were thus opened; considerable diversification of products, rapid expansion (e.g. of polymers production) resulted. Several factors concurred: cheapness and convenience of oil; profitable downstream processing of refining by-products; cost advantage, convenience in end-manufacturing, superior or innovative qualities of those many synthetics; economies of scale and ability to satisfy an exploding demand. In fact and still today the prime building blocks are rather few (lower olefins and aromatics), when compared to the range and uses of products, but the tonnages are considerable (Tables 17.5 to 17.7) and petrochemistry is accountable for about 10% of oil and gas consumption (feedstock or fuel). Needless to say, those bulk feedstocks are all hazardous.

Diversification, increasing scale and integration of operations have also profoundly influenced the plants, processes and supplies: continuous production, piping and massive unit capacities are the most visible signs. There too, as often cited, ethylene demand has boosted steam cracker capacities by a factor > 10, to present 0.4–0.5 M.te/year throughputs and a flexible range of feedstocks. Throughputs are comparable for ammonia plants [0]* 1–2 kte/day. Concurrently, materials and coatings to withstand extreme temperatures or corrosive environments, cryogenic storage and transfer, very high-pressure processes, huge rotary compressors, increasingly complex systems in general all entered the picture, stretching feasibility limits.

The end result may unfortunately be viewed as a disquieting combination to be kept tame: huge hazardous inventories or flows, sometimes extreme (T, P)

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* Of the order of

Table 17.12 Boiling point and typical storage (pressure bars, b) of common chemicals

Paraffins	Methane	Ethane	Propane	Butane	Pentane	
B.P.°C	−164	−88.6	−42	−0.5	36.1	
Storage	F.R.	F.R.	8–10 b	3–4 b	A	
Olefins	Ethylene	Propylene	1-Butene	2-Butene (cis)	1-Pentene	
B.P.°C	−103.7	−47.4	−6.3	3.7	29.9	
Storage	80 b	11 b	2.5–3 b	1.8 b	0.7 b	
Industrial	Hydrogen	Oxygen	Nitrogen	Chlorine	Ammonia	Acetylene
B.P.°C	−259.1	−209.8	−218.4	−34.6	−33.3	−84
Storage	F.R.	F.R.	F.R.	8–9 b	10–12 b	P (cylinders) A (in solution)
Others	Vinyl chloride	Ethylene chloride	Ethylene oxide	1–2 Butadiene	Benzene	Acrylonitrile
B.P.°C	−13.4	83.5	13.5	10.85	80.1	77
Storage	3.4 b	A	1.5 b	—	A	A

F.R. = fully refrigerated.
P = liquefied under pressure.
A = ambient storage.

operating conditions, reacting streams, dangerous intermediates and much else.

The diversity is of course too great to give precise ranges but, indicatively:

1. For plants, temperatures commonly reach 350 °C in crude distillation and 900 °C in vapocrackers, down to −50 °C (LPG) and below −160 °C (LNG) with cryogens. Pressures may range anywhere from 5 to 100 bar, peaking at 20–25 bar (hydrogenation), but some processes go far higher (300 bar for NH_3, 2–3 kbar with LD (low density) polyethylene). Heat inputs, in spite of heat exchange, are huge and refineries are meteorological heat islands.

   Some processes are ticklish: high temperature continuous oxidation (nylon), working close to the flammable range (ethylene oxide), danger of instability, runaway, spurious catalysis, etc., or, generally speaking, complex continuous processes stretch monitoring demands. Alternative routes, reduction of (T,P) operating conditions, reduction of batch sizes and transient inventories – all may well be advocated (Kletz, 1984) but are not always feasible or economically competitive. Plants also store, transitorily or in vessels and warehouses, large quantities of hazardous feedstocks and intermediates to offset cyclic and production variations. This equates to [0] 2 days' consumption with ethylene, [0] a few weeks in other instances and, mandatorily, 3 months for oil. Nasty intermediates (methyl isocyanate, phosgene) are encountered in the 1 to 20 te bracket. Apart from that, there is visibly intensive on-site piping of all those hazardous liquids and liquefied/pressurized gases, with considerable mass-rates and complicated routings.

2. Liquefied storage conditions are less extreme (Table 17.12) but then capacities are considerable. The familiar spheres in the landscape may typically contain 1000 to 7000 m^3 of NH_3, [0] 3000 m^3 of propylene or vinyl chloride and 500–1000 m^3 of Cl_2. Common fuels are stored in even larger quantities, [0] $10^4 m^3$ for gasoline in tankfarms. Storage *per se* is perhaps not the prime safety issue (apart from cases of embrittlement, stress corrosion with NH_3) but rather that the substance is fast transferred to and from storage via large lines and couplings and complex ancillary equipment, or piped from buffer storage between different sections of a plant or towards more remote users. There, human error looms large: broken couplings and transfer lines, overflow, inadvertent mixing, ingress of water, inadequate purging/inerting/cleaning, stuck valves, forgotten slip-discs and so forth. Hence too the vivid interest of case histories, just as for plants (Section 17.4).
3. Transportation, in all its modes, is a different issue, since in the end input–output and mass conservation imply that the huge primary flows of Tables 17.9 to 17.11 will be further parcelled down the line in endless ramifications (as indeed is shown in Table 17.9).

   Shipping, already referred to, is not restricted to crude or LNG/LPG, but includes a variety of other, more flexible vessels (for products, chemicals, lubeoil, etc.). One may expect a considerable evolution, with relocation and probable massive bulk shipping of primary processing feedstocks (ethylene, methanol, NH_3) from gas-rich areas, which will diversify the tanker and terminal hazards. Capacities are smaller once on shore: [0] a few thousand m^3 with barges, [0] 50–100 m^3 for rail tankers (US Jumbo tankcars apart) and [0] 20 m^3 for road tankers, but there the diversity and frequency are extreme and transiting in the close proximity of dense settlements is almost guaranteed: over 200 people were killed at the Los Alfaques campsite by the crashing and fireballing of an ordinary 22 te propylene tanker (Hymes, 1985). There are specific problems with trains of mixed chemical and fuel tankers, because of contagion if derailed, in marshalling yards too.

One should not infer from all this the apocalyptic impression that the industry is 'unsafe at any speed'. Safety is a constant, essential component of design and management of operations, but it has its cost and, in a period of economic slump, restructuring operations, capacity cuts and increased competition, there is lingering suspicion that its quality suffers too. Recent 'series of incidents', end-1986, are a warning as well as an indication of widespread substandard practices regarding maintenance and updating.

17.3 SALIENT ASPECTS OF CHEMICAL ACCIDENTS

The chemical/petrochemical sector is extremely diversified. Unsurprisingly, incidents of all types are relatively frequent and varied, but a few prime reasons and patterns can be highlighted in simple terms.

17.3.1 Containment

Almost invariably (as opposed to the multiple barriers of nuclear facilities), hazardous substances are 'single-contained' and only a vessel shell or pipe wall or flanged gasket separates them from the immediate environment. Any breach of containment integrity will thus result in release and spreading (perhaps mitigated in fixed installations by catchment bunds or separation walls or water curtains). The same holds for many relief devices (valves, rupture discs), which are not necessarily ducted to a dump tank or flare: especially if pressure-driven and in elevation, there may be a tendency to rely on rapid spontaneous dilution and entrainment.

As aggravating circumstances, internal pressure and elevated temperature are often at play in processes and many substances are corrosive or unstable, brittle failures of vessels and pipes have occurred and loss of containment cannot be ruled out. Prime fuels and chemicals are stored or transported in bulk, as liquefied pressurized gas (LPG, Cl_2, NH_3) or fully refrigerated cryogens (LNG). In the first case the release is pressure-driven and generates a flashing jet, in the second a spreading and fast evaporating pool, either one resulting in the swift build-up of a large hazardous cloud.

Growing concern over 'major hazards' may well lead to greater stringency of certification and licensing, but containment practices themselves can hardly change fundamentally, for inescapable reasons of tradition, cost and competitiveness, so that containment failures are bound to reoccur.

17.3.2 Negative Buoyancy

In recent years, most attention has been devoted to dense gas clouds, because of the alarming frequency of UVCEs (unconfined vapour cloud explosions) at ground level. Not all chemical clouds are denser than air – releases may be hot or in elevation – but the vast majority of bulk flammables and toxics will generate dense clouds because of density, cold storage, flashing, aerosols component, etc. The behaviour differs markedly from classic atmospheric dispersion, since the contaminant will slump and spread at ground level, as a 'superstable' shallow layer of a few metres depth, gravity-driven at first and tending to follow the path of least resistance (around obstacles, down slopes and channels). This blanket effect augments the danger, on-site or near ruptured carriers/pipelines: a flammable cloud will readily find an igniter (furnace, motor, static sometimes) after a short travel; a toxic one will carry its threat over appreciable distances (some kilometres) before diluting to harmless levels. Spreading is swift (clouds run faster than men) and escape or evacuation not always feasible.

17.3.3 Divergence

Many reactions of industrial interest are exothermic and that heat must be removed from the reacting stream/batch. The reactors then also have a marked positive temperature coefficient (from Arrhenius' law), so that an upset, a loss of cooling, a 'hot spot' from poor stirring/inadvertent mixing, etc., boost the reaction rate and may trigger secondary reaction peaks. With positive temperature feedback, the process is self-reinforcing and the divergence exponential, in first approximation, till the system bursts or vents or turns around by reagent exhaustion. A divergence may also be initiated by traces of catalytic impurities, or occur in solid/powder form substances (spontaneous ignition/decomposition), or unstable ones (thermal explosion).

Propensity to 'runaway' is characteristic of many processes or substances and not easily countered, other than by strict process monitoring and provision for relief venting (Section 17.9). In general, the failure of (smaller) batch reactors, a classic case, remains far below disaster level and does not necessarily result in toxic release either, but there are also total surprises with poorly known substances and some major catastrophies on record (nitro compounds – Seveso, Bhopal, etc.).

17.3.4 Domino Effect

Sometimes chemical complexes are gutted by a single UVCE (Flixborough), or many people are injured by one toxic release; often too a perhaps lesser incident escalates, propagating through the plant or storage or tankfarm, with multiple chain consequences. The vector will often be fire, blast, missiles and fireballs, or any combination of these. The speed of propagation varies from case to case but, although evolving over hours, sometimes days, escalation proves difficult to stop, as vividly illustrated at Mexico City, Priolo, Naples, etc., in recent years (Pietersen, 1985; Manuele, 1986).

In established chemical complexes, this is hardly surprising: expansion, diversification, integrated cycles have led to gradual build-up and site congestion, with by now inadequate respect distances and thick forests of pipes, columns and tanks confined in a limited area. However, the danger of escalation or multiple consequences is equally present with rail tanker trains of chemicals and fuels, berthing sea tankers, loading/unloading of road tankers, warehouses of mixed goods, and so on.

17.3.5 BLEVE and Fireballing

With tanks of flammables, an insidious self-escalation is a BLEVE (boiling liquid expanding vapour explosion) followed by aerial fireball formation. Strictly speaking the acronym BLEVE may describe the bursting of any vessel containing a liquid of well above atmospheric vapour pressure; common usage restricts it to the ductile rupture, under the influence of fire, of a fuel/liquefied gas tank. Contents are released explosively, a rich burning cloud uplifting and consuming itself as a glowing spheroid/mushroom in a matter of seconds ([0] 10–30) with an intense radiant heat pulse. Smaller fireballs, say from bottled gas or smaller road tankers, remain at ground level. There was an untold number of BLEVEs and fireballs at the PEMEX (Mexico City) LPG complex, including four 1500 m^3 spheres (Pietersen, 1985).

Uplifted fireballs, from rail tankcars or storage spheres, can indeed be huge (one to several hundred metres diameter), yet not far from ground and they project downwards, umbrella-like, a scorching heat flux which can cause severe burns (skin and retina) and ignite other materials. Accompanying the BLEVE vessel failure, large tank fragments are projected, dished ends 'frisbee', tubular end-sections 'rocket' over sizeable distances, [0] several hundred metres, and further destruction and escalation result.

In emergencies and until recently, that scenario was insufficiently recognized. In fact, in a fire any storage vessel, however humble, is a BLEVE candidate and records show that not only spectators but transporters, intervention teams, even firemen do not always anticipate sudden fireballing and get caught.

17.3.6 Toxic Clouds and Fumes

Accidents resulting in a significant toxic release only represent [0] one-third of classic case histories, even though there is a greater variety of potential candidates than for flammables and they are more systematically listed. Nor is it always simple accidental release from storage or transportation: runaways, venting, fires in fertilizer stockpiles/mixed warehouses, the combustion of synthetic household materials, waste dumps, etc. – all may generate noxious clouds and some substances (e.g. acrylonitrile) are both flammable and toxic. Nor is the release always accidental, especially at night . . .

The issue is more complex than previous ones and not only because of diversity or longer-term effects. Assuredly, the 'harmful potential' of a large, drifting cloud (of, say, Cl_2 or NH_3) is huge, dilution is slow, danger can be carried large distances 'beyond the fence'. Yet, trivially, that potential is only realized if, because of prevailing wind and topography, human targets and living creatures are in its path and sufficiently long exposed or close to the source to be affected (or in rarer instances if lasting contamination results).

Table 17.13 Some historical chlorine accidents

Location	Year	Source	Scenario	Area	Quantity (Te)	Fatalities	Casualties	Evacuees
St Auban FR	1926	Storage	Tank burst	Urban	25	19	—	—
Zarnesti RO	1939	Storage	Tank burst	Factory	24	60	—	—
Rauma SU	1947	Storage	Overfilling/burst	Factory	30	19	—	—
Wilsum Ger.	1952	Storage	Tank failed	Factory	15	15	—	—
Los Angeles Cal. US	1976	Cylinders (14)	Fire	Urban	—	—	72	2000
Baton Rouge La. US	1976	Storage	Explosion	Factory	90	—	—	10000
Youngston Fla. US	1978	Rail tanker	Accident/puncture	—	25	8	138	—
Mississauga Ont. CND	1979	Rail tanker	Fire + puncture	Urban	70	—	—	250000
San Juan, Puerto Rico	1981	Water treatment	Valve corrosion	Urban	2	—	2000	—
Cerritos (Potosi) Mex.	1981	Rail tankers	Brake failure	Semi-urban	90 – 150	28	1000	> 5000

First World War data

Location	Year	Source	Scenario	Area	Quantity (Te)	Fatalities	Casualties	
Yper	1915	Cylinders	6 km line release	Trenches	168	5000	15000	No masks
Total WW1	1915 1918	Chlorine + phosgene	—	—	32000	36600	100000?	Masks (probably)

Table 17.14 Some historical ammonia accidents

Location	Year	Source	Scenario	Area	Quantity (Te)	Fatalities	Casualties	Evacuees
Lievin FR	1968	Road tanker	Tank failed	Urban	19	6	15	—
Crete Nebr. US	1969	Rail tanker	Collision	Urban	90	8	35	—
Blair Nebr. US	1970	Storage	Overflow 2,5 Hr	Rural	160	—	—	(3 km cloud)
Potchefstroom SAfr.	1973	Storage	Embrittlement/ rupture	Urban	38	18	65	—
Houston Tex. US	1976	Road tanker	Collision	Highway/urban	19	5	150	(Local)
Deer Park Tex. US	1976	Road tanker	Skid/crash	Highway	19	6	200	—
Cartagena, Columbia	1976	Fertilizer plant	Explosion	Urban	—	21	30	—
Cuernevaca Mex.	1977	Pipeline	Failure	Urban	—	2	90	—
Pensacola Fla. US	1977	Rail tankers (2)	Derailed	Urban	—	2	46	1000
Crestview Fla. US	1979	Rail tankers (10)	Derailed	Urban	—	—	14	5000
Los Pajaritos, Mex.	1984	Pipeline	Failure	Urban (slum)	—	4	46	—

Table 17.15 Some major releases of other toxics

Location	Year	Material	Source	Scenario	Area	Quantity (Te)	Fatalities	Casualties
Hamburg Ger.	1928	Phosgene	Storage	Cover lost	Urban	11	10	> 200
Poza Rica Mex.	1950	SH_2	Factory	—	Factory	—	22	320
Baltimore Md. US	1978	SO_2	—	15 km drift	Urban	—	—	100
Chicago Ill. US	1978	SH_2	Tanker	—	Terminal	—	8	29
Memphis, Tenn. US	1979	Parathion	Storage	Release after explosion/fire	Factory	—	(2000 evacuees)	150
London, UK	1980	Cyanide	—	Release after explosion/fire	Factory	—	(4000 evacuees)	—
Fort Knox, Kent. US	1980	V.C.M.	Rail tankcar	Puncture	—		(7000 evacuees)	several
Fitchburg, Mass. US	1982	V.C.M.	—	Release after explosion	Factory		(3000 evacuees)	9
Livingston, La. US	1982	Vinyl Chloride tetra-ethyl	Rail tankcar	Puncture	—	—	(3000 evacuees)	—
Bhopal, India	1984	Methyl-isocyanate	Storage	Runaway	Urban/ factory	20/30	2000	20,000 +

Table 17.16 Risk of tranportation, per tonne, Rijnmond area (Technica, 1985)

Substance	Mode	Probability of N or more fatalities per tonne transported $N=1$	$N=10$	$N=100$	$N=1000$	$N=10\,000$
Chlorine	Rail	3.4×10^{-9}	2.7×10^{-9}	1.2×10^{-9}	10^{-10}	—
	Pipeline	5.6×10^{-9}	1.7×10^{-9}	1.1×10^{-10}	—	—
Ammonia	Seaborne	6.8×10^{-9}	1.6×10^{-9}	2.3×10^{-10}	3.2×10^{-11}	4.5×10^{-13}
	Waterways	1.6×10^{-8}	5.8×10^{-9}	4.2×10^{-10}	—	—
	Rail	2.2×10^{-9}	3.7×10^{-10}	4.5×10^{-13}	—	—
	Road	3.1×10^{-10}	3.4×10^{-12}	—	—	—

Consequences may thus depend far more on the vagaries of meteorological conditions, intermittency, location and surrounding population density than (as one might expect off-hand) on the absolute magnitude of the release: in contrast to most cases of Tables 17.13 to 17.15, some very large spillages in open country (90 te of Cl_2, Baton Rouge 1977; 160 te of NH_3, Blair 1970) caused no harm nor (with evacuation of a quarter of a million persons) did the notorious Mississauga 1979 chlorine derailment.

In factories, small and sometimes protracted toxic releases are not infrequent but toxic alarms are mitigated by staff preparedness, the availability of respirators and shelters and, if need be, in-house confinement or evacuation of surrounding populations; multiple fatalities on record were rather due to sudden, acute events (vessel failure, runaway, explosion). There are more potential problems with transportation in bulk (multiple rail tankcars, barges on inland waterways, pipelines sometimes), since the accident can happen anywhere along the route. Accident frequencies are rather low in Europe, as shown in Table 17.16 for the comparative risks of modes of transportation of Cl_2 and NH_3 in the Rhine estuary, specific of course to that huge chemicals concentration.

Classic 'loss prevention' pays less attention to accidental releases of small quantities of vary acute toxics, with long-lasting or long-delayed effects. Actually, it would take an unusual dispersive mechanism (e.g. an explosive runaway followed by air-borne contamination or seepage) to pollute a substantial area or stretch of surface water and cases of very acute lasting contamination are few (Table 17.17, for dioxin), but the risk cannot be excluded. There are constant multifarious hazards to aquifers/waterways, land, food chains, etc., stemming from the indiscriminate dumping or accidental seepage of standard noxious chemicals and wastes, or from overkill in the use of fertilizers and pesticides, which are the object of other sets of research and regulation (e.g. in Winteringham, 1984; SGOMSEC 2, 1985).

Only predominant mechanisms have been evoked here (Sections 17.3.1 to 17.3.6). This brief survey readily shows that for acute accidents intervention,

Table 17.17 Recorded accidents involving TCDD

Identification	Lugwigshafen D	Duphar NL	Bolsover UK	Seveso I
Quantity (kg)	< 1 kg	0.01–0.3	–	2
Fatalities	–	4 (delayed)	–	–
Casualties	55	50	80	250+
Area affected	building	building	factory site	up to 7 km

Note: There were about 20 recorded instances of severe occupational exposure (1949–76) at the time of Seveso.

medical preparedness and first aid should anticipate not only toxic harm but also almost invariably multiple fatalities and injuries from severe burns and fire engulfment, blast and body impact, projectiles, collapse of structures, and so on. Much the same holds for emergency preparedness, as there is far more public concern over toxic clouds (or food/water poisoning) than over catastrophic fires and explosions, an underestimated off-site risk.

17.4 LEARNING FROM ACCIDENTS

Over 200 major chemical incidents were recorded in 1984, including Mexico City and Bhopal but excluding many unknown or lesser ones, near-misses, etc. (*Loss Prevention Bulletin*, 1984). Can beneficial lessons be learned from such a toll in one year?

Chronological listings and more explicit case histories are widely available (e.g. Gugan, 1979; Lees, 1980; COVO, 1982) and sundry examples are given in topical monographs (e.g. Baker *et al.*, 1983; Field, 1982). Regular reporting is ensured by specialized publications (*Lloyd's Weekly*, *Loss Prevention Bulletin*, etc.) and accident data banks (FACTS at TNO, Netherlands; MHIDAS at UKAEA) have been or are being set up by professional risk analysts. Information thus available originates from multiple sources (enquiries, insurers, media) and often proves uneven or patchy, also because of *sub judice* confidentiality. The reporting generally concentrates on the broad features of the happening and the immediate losses incurred: fatalities, casualties, cost, perhaps nearby damages. A few extreme instances are given Tables 17.13 to 17.15 for toxics, in the 'disaster' category. One prime interest of such listings and banks is statistical. Examples are given Tables 17.18 and 17.19, derived from FACTS for the period 1969–84 (Bhola, 1985). They relate to: fatal/physical injury; fire/explosion; flammable/explosible release of > 1 te; any toxic release. More elaborate correlations over approximately 3000 reported cases (1976–86) in the Rijnmond area (Rotterdam) rest on plant incidents 'that could be or could become observable outside of the fence' (Blokker and Goos,

Table 17.18 Categories of substances involved in major accidents, in %, referring to 235 cases of the FACTS database (Bhola, 1985)

Gases and liquefied gases	Flammable liquids	Flammable and reactive solids	Peroxides	Toxic chemicals	Corrosive chemicals
26	25	6	1	37	5

Note: 50% of accidents analysed were in process operations,
13% in storage and 12% in transportation.

Table 17.19 Causes of major accidents (in per cent) referring to 216 cases of the FACTS database (Bhola, 1985)

DESIGN AND MANUFACTURE: 15.5%	
– design faults	1%
– incorrect materials	8.5%
– faulty construction/assembly	6%
OPERATIONAL FAILURES: 49%	
– process failure: overpressure, overfill, loss of vacuum	26%
– runaway, instability, thermal shock	7.5%
– alarms/protections malfunction, maintenance/electrical fault	9.5%
– incorrect procedures, or operating conditions	6%
HUMAN FACTORS: 32%	
covering: inadequate training/communication, operator error/lack of supervision, stress, etc.	
EXTERNAL AGGRESSIONS: 3.5%	
covering: natural hazards (earthquakes, flood, storm, lightning), aircraft crash, sabotage/vandalism, etc.	

1986); correspondingly, actual and potential (more unfavourable conditions) hazards to surroundings were ranked 0 to 5 (for health and material damage) but with only a few minor cases on actual record. From either study it emerges for instance that human error was a contributory factor in approximately one-third of the cases, a standard figure. Other sub-classifications such as substances and masses released, types of plants and components where failures occurred may help in devising more realistic accident scenarios in risk assessment.

To draw universally valid conclusions from such statistical studies would be

Table 17.20 Information to be supplied to the Commission by the Member-States pursuant to Art. 11 of the Directive. Each item is to be responded to

I. General data

Date and time of the major accident; country/administrative region; address; type of industrial activity ——.

II. Type of major accident

Explosion ——; fire ——; emission of dangerous substance ——; substance(s) emitted ——.
Description of the circumstances of the major accident; emergency measures taken.
Causes of the major accident: known ——; not known ——; to be supplied later ——.

III. Nature and extent of the damage
a) within the establishment: ——
casualties (killed, injured, poisoned); persons exposed; material damage.
b) outside the establishment: ——

casualties —— (killed, injured, poisoned); persons exposed ——;
material damage ——; damage to the environment ——;
the danger is still present ——, no longer exists ——.

IV. Medium and long-term measures, particularly those aimed at preventing the recurrence of similar major accidents (to be submitted as the information becomes available).

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risky. Data selection criteria and lower limits, if specified, may differ and, more important, factual conditions and practices may also vary between countries or geographical areas: serious rail transportation accidents appear at first sight more frequent in the USA (possibly reflecting greater media coverage). Another drawback for present purposes is that emergency response, medical aspects, follow-up, etc., are excluded from standard accident banks and not explicit either in the mandatory accident reporting of the Seveso Directive (Table 17.20).

Well-documented accident records would be invaluable for the statistical validation of predictive 'consequences models' (e.g. cloud drift, travel of missiles, radiative damage from fireballs). Most examples for this pertain to flammables (Holden and Reeves, 1985; Pietersen, 1985; Davenport, 1986). Toxic releases are less exploitable; excepting the extensive studies of TCDD contamination distribution at Seveso, the more likely and large ones (Cl_2, NH_3) only indicate maximum cloud extent from burnt grass, photographic records, odour perceived, etc., in accident listings; small releases of acute toxics or with longer lasting effects are often missing. Similarly, well-documented case studies and derived recommendations, film/video records of accident evolution and countermeasures are of obvious help in the design and layout of plants and mitigation devices, or in the training of operators and intervention teams (e.g. the hazard workshop/video training modules of I. Chem. E.). All this is in the hope that lessons need not be relearned, nor accident scenarios repeated, yet they are.

Accident statistics, especially fatalities, have long supplied a basis for comparing the liability of disparate industrial sectors, a safety or human-cost index relating to occupational, non-occupational or societal categories. Well-rehearsed figures indicate that:

1. For professional exposure, the fatal accident rate (FAR, per 10^8 working hours = 10^3 working lives) is [0] 4 to 5 overall and [0] 2 to 3 for major incidents, compared to figures appreciably larger in, say, mining or building and orders of magnitude larger for industrial epidemiology. Those values may differ appreciably according to company or country and be thrown out of kilter by a single disaster.
2. The corresponding individual risk figure (occupational fatality) is [0] 10^{-4} per year. For the public at large, mortality statistics categories – poisoning, fire, explosion, etc. – are generally too broad and quantify the diffuse risk from chemicals and fuels, rather than the risk from major incidents (Grist, 1978). For the latter a plausible figure is [0] 10^{-7} to 10^{-6} per year, far below ordinary causes, rising to [0] 10^{-5} to 10^{-4} per year in the close vicinity of plants, storage facilities or transportation links (Canvey, 1978).
3. The risk of multiple fatalities is often transcribed into risk contours (on a map) or *f–N* graphs (probability of *N* or more fatalities per year v. *N*). Such presentations allow a comparison of unrelated hazard categories, man-made and natural (e.g. WASH.1400, 1974; Royal Society, 1981) and the latter turn out to be far greater. In the method of quantified risk assessment (QRA) the graphs refer to given items (storage facilities, plants) or situations (siting, mode of transportation) in their population context, as a guide to decision making.

   Similar arguments of comparative acceptability and residual risk have fuelled the nuclear debate for two decades (Farmer, 1967) and that precedent shows that public opinion is hardly swayed by them at all, but magnifies instead the threat of isolated disasters remembered, or subconscious fears (cancer, the bomb, chemical warfare . . .).

17.5 THE QUANTIFICATION OF MAJOR HAZARDS

The standard definitions

Hazard = the potential to cause harm (to people, property, the environment), whether that potential is realized or not and
Risk = the likelihood of that potential, or of certain consequences, being realized in a given time-span

Table 17.21 Notifiable inventory thresholds, non-isolated storage (first revision proposed figures in brackets)

Flammable gases	Highly flammable liquids	Flammable liquids	Liquid oxygen	Hydrogen	Acetylene	Ethylene oxide	Propylene oxide	Acrylonitrile	
200 t	50,000 t	200 t	(2000) t	50 t	50 t	50 t	50 t	200 t	
Nitroglycerine	Cellulose nitrate	Ammonium nitrate	Hydrazine nitrate	Trinitrobenzene	Trinitrotoluene 2, 4, 6	Mercury fulminate	Picric acid	Sodium picramate	Sodium chlorate
10 t	100 t	5000 t (2500) t	50 t	50 t	50 t	10 t	50 t	50 t	250 t
Chlorine	Bromine	Phosgene	Sulfur dioxide	Nitrogen oxides	Hydrogen sulfide	Hydrogen cyanide	Methyl isocyanate	Formaldehyde	Ammonia
50 t (10) t	500 t	20 t (1) t	1000 t (500) t	50 t	50 t	20 t	1 t (150) kg	50 t	500 t
Sodium selenite	Aldicarbe	Parathion	Hydrogen phosphide	Arsenic hydride	Selenium hexafluoride	Hydrogen selenide	N.Chloroformyl morphine	Chloromethyl. methylether	2, 3, 7, 8 T.C.D.D.
100 kg	100 kg	100 kg	100 kg	10 kg	10 kg	10 kg	1 kg	1 kg	1 kg

Flammable gases : boiling point < 20°C at atmospheric
Highly flammable liquids : boiling point > 20°C at atmospheric; flash point < 21°C
Flammable liquids : flash point < 55°C

are complementary, but not truly separable. Risk has been extensively debated in recent years (nuclear, primarily) but what precisely would be an acceptable residual risk level remains unclear, except in extreme cases where the chance of occurrence or recurrence is vanishingly small or the cost of removing it altogether absurdly elevated. Limits of cost or feasibility are merely embodied in blanket prescriptions, e.g. 'as low as reasonably achievable (or practicable)'. Conversely, what constitutes a major hazard is defined tautologically, by stating that it could cause a major accident (in terms of fatalities, injuries, material or lasting environmental damage), but here too, few venture to go further and define acceptance levels.

Limited historical experience shows that, on average, chemical accidents are short-ranged and the possibility of extended-scale disasters rather remote. However, the particular consideration of those which might cause extensive losses and claims, or endanger populations 'outside of the fence', has focussed attention on the low probability, high consequences end of the spectrum, not necessarily apprehended in standard regulations. Emphasis is often placed on acute events, of rapid evolution and difficult mitigation, with transient exposure of the targets. Only to give an idea, 10 to 20 on-site fatalities or 20 to 30 million dollars' damage already connote a very large chemical accident, or disaster (Manuele, 1986).

The aim of hazards quantification is regulatory: to establish thresholds above which the actual or future hazard is ascertained and registered. In that first approach, also in view of the number of cases, no great sophistication is needed and those thresholds are related to levels of damage by simple, mechanistic 'effects models'. While this is straightforward scaling for combustive phenomena (explosions, radiative fires) and unstable substances, finding equivalences is more difficult for toxics or above all environmental damage. (What is the likely cost of reclamation?)

The simplest concept here is the one of danger radius, or threatened area, disregarding location or probability of occurrence. This happens to be the foundation of the Seveso Directive: its threshold values originate in a – not recent – study, postulating that a major hazard could seriously endanger an area – not further specified – of 1 km^2, either short term (explosion, fireball, drifting toxic cloud) or longer term (unacceptable contamination over one year). In short, this corresponds to 2 te equivalent TNT for explosions, to concentrations greater than twice the short-term exposure limit (STEL) for toxic clouds and to a contamination level (mg/m^2), $C_L = LD_{50}$ (dermal) or $C_L = 2LD_{50}$ (oral) in mg/kg for acute and persistent toxics (Consult-Eur and Harwell, 1978). Salient figures are reported in Tables 17.21 and 17.22; they will undergo periodic revisions, and they reflect an uneasy consensus. Note that a distinction is made between isolated and multiple storage in notification obligations, in an attempt to account for the 'domino effect'.

For toxics, the Directive *de facto* introduces two groups: a limited number of

Table 17.22 Sensitive inventories and notifiable inventories, isolated storage (figures in tonne – first revision proposed figures in brackets)

Product	Flammable gases	Highly flammable liquids	Liquid oxygen	Acrylonitrile	Ammonium nitrate	Sodium chlorate	Chlorine	Sulphur dioxide	Sulphur trioxide	Ammonia
Art. 3 Art. 4	50	10.000	200	350	500 (250)	25	10	20	(15)	60
Art. 5	300	100.000	2.000	5.000	5.000 (2.500)	250	200 (50)	500	(50)	600

Articles 3 and 4 of the Directive: Member States ensure that the *manufacturer* has examined major accident risks involved, informed on-site staff and trained on-site intervention team(s).

Article 5 of the Directive: Notification becomes mandatory, covering several aspects. In short:

- product(s), process, quantities, possible undesirable effects
- siting, on-site staff, plant prevention and mitigation devices
- on-site emergency planning, interfacing with off-site emergency planning

Further obligations, placed on the national authorities, are:

- information of off-site people potentially threatened
- verification/inspections and the setting up of an off-site emergency plan

Accidents must be reported to the appropriate national authorities and subsequently C.E.C.

bulk toxics in te quantities (Cl_2, NH_3, etc.) and an extensive mixed bag of other toxics, carcinogens, mutagens, teratogens, etc., in far smaller quantities, [0] kg, not fully reported here. With a few possible long-lasting exceptions, say TCDD, the second listing has been endlessly criticized for including many substances which would require long-lasting (occupational?) exposure, or an unusual receptor density to cause sudden catastrophic harm.

The second distinction made (Table 17.22) between notifiable and sensitive inventories (which are lower or referred to simpler criteria) is practical: in the second case the onus is on the manufacturer alone to set up in-house intervention measures; in the first one obligations are wider ranging, including off-site emergency planning and information of the public. This too illustrates the questionable mental separation of accidents into site-circumscribed ones, an occupational risk, and those reaching 'beyond the fence', endangering the public. A more serious drawback is that the Directive actually only deals with fixed installations, leaving the issue of transportation fairly blurred.

Such an approach to hazards quantification, also perhaps introduced outside of the EC, can only be viewed as a first systematic attempt at grappling with an extremely complex issue. The next, obvious and contentious step is case-by-case consequences assessment, for which there is no agreed methodology at this stage and where consideration of a range of scenarios, environmental conditions (meteorological, population density), effects and vulnerability, etc., can also lead to wide compounded error margins, or pile up pessimistic assumptions leading to worst outcomes, or simply prove a costly and time-consuming exercise much resisted by the industry.

There is, however, a simple reason why hazards quantification based on crude danger–distance or danger–area estimates works approximately: with acute, short time-scale events relevant distances L (say, the danger/vulnerability distance) generally scale as the cube-root of the mass M (the hazardous tonnage) or of the energy release E, a slow dependency. For instance, crude modelling (not substantiated here) thus yields the following merely indicative danger radii (Vilain, 1986):

L (metre) $\sim 100\sqrt[3]{M}$ (tonne) for severe structural damage and probable fatality, from hydrocarbon–air cloud explosion.
L (metre) $\sim 65\sqrt[3]{M}$ (tonne) for aerial fireballs.
L (metre) $\sim 110\sqrt[3]{M}$ (tonne) or $250\sqrt[3]{M}$ (tonne), respectively for Pasquill categories D and F, for chlorine puff dispersion down to 100 ppm (serious discomfort).

This is also why chemical accidents prove generally to be circumscribed and predictions are not very sensitive to the fine details of a scenario.

17.6 THE QUANTIFICATION OF EFFECTS

Estimates of the direct effects of incidents have long backed safety prescriptions (e.g. for the spaced storage of explosives or flammables, to prevent escalation). However simplified, quantitative predictions are then needed and the increasing attention paid to chemical hazards and accident scenarios has resulted in a proliferation of sub-models, backed by a growing body of experimental validations. In that respect, however, the extensive information appearing in the recent loss prevention literature is often topical, but a few national guidelines attempt a complete coverage (*Yellow Book*, 1980) and some pilot PRA studies supply useful descriptions of their set of underlying physical models (COVO, 1982; Technica, 1985, for toxics).

In making quantitative predictions the simplifying postulate is that accidents are not quantum jumps but can be described step-wise. The scenario is thus separated into successive stages, each with its characteristic phenomenology which can be sub-modelled appropriately. For instance a flammable cloud explosion would entail successive consideration of: confinement failure (vessel, pipe); gradual spillage and evaporation of contents; cloud formation and spreading; ignition and in-cloud flame propagation; blast generation and propagation in air; targets loading and response; resulting damage at a distance. A similar separation applies to toxic releases, terminating in targets exposure, dose and damage estimates (Figure 17.1). Each step naturally calls for specific methodologies and the time-scales also differ, [0] minutes for spillage, cloud travel or fires, [0] seconds for explosive phenomena, blast and missiles travel. A further distinction is sometimes made between ‘effects models’ for the prediction of physical effects and material damages and ‘vulnerability models’ incorporating the impact on man and the environment (Table 17.23), but their early steps and sub-models are similar.

Consider these early steps or frames of the film first (e.g. release, spreading, combustion, etc.). Their sub-modelling rests on well-established physics, a deterministic approach, and focuses on the prediction of a limited number of salient parameters, given certain initial and boundary conditions. Examples are, not limitatively: the mass rate of a spillage, for given driving pressure and breach size; the radial growth of a cryogenic liquid pool and its vapour evolution, over a given substrate at some higher temperature; the advection, dilution and growth of a dense gas cloud, its time-dependent isoconcentration contours [e.g. LFL (lower flammability limit), LC_{05}], given boundary values for the windspeed, stability, ground roughness, etc.; the amplitude and shape of a blast wave at cloud edge, given values of the reactivity (or flame speed) and the cloud shape (hemisphere, pancake . . .); the characteristic dimensions and emissive power of a pool fire or lifted fireball, for a given fuel type and pool size or BLEVE mass; and so on. In general those sub-models will yield straightforward cause–consequences relationships, albeit adjusted to experimental observations or presumed to represent ensemble-averaged values when

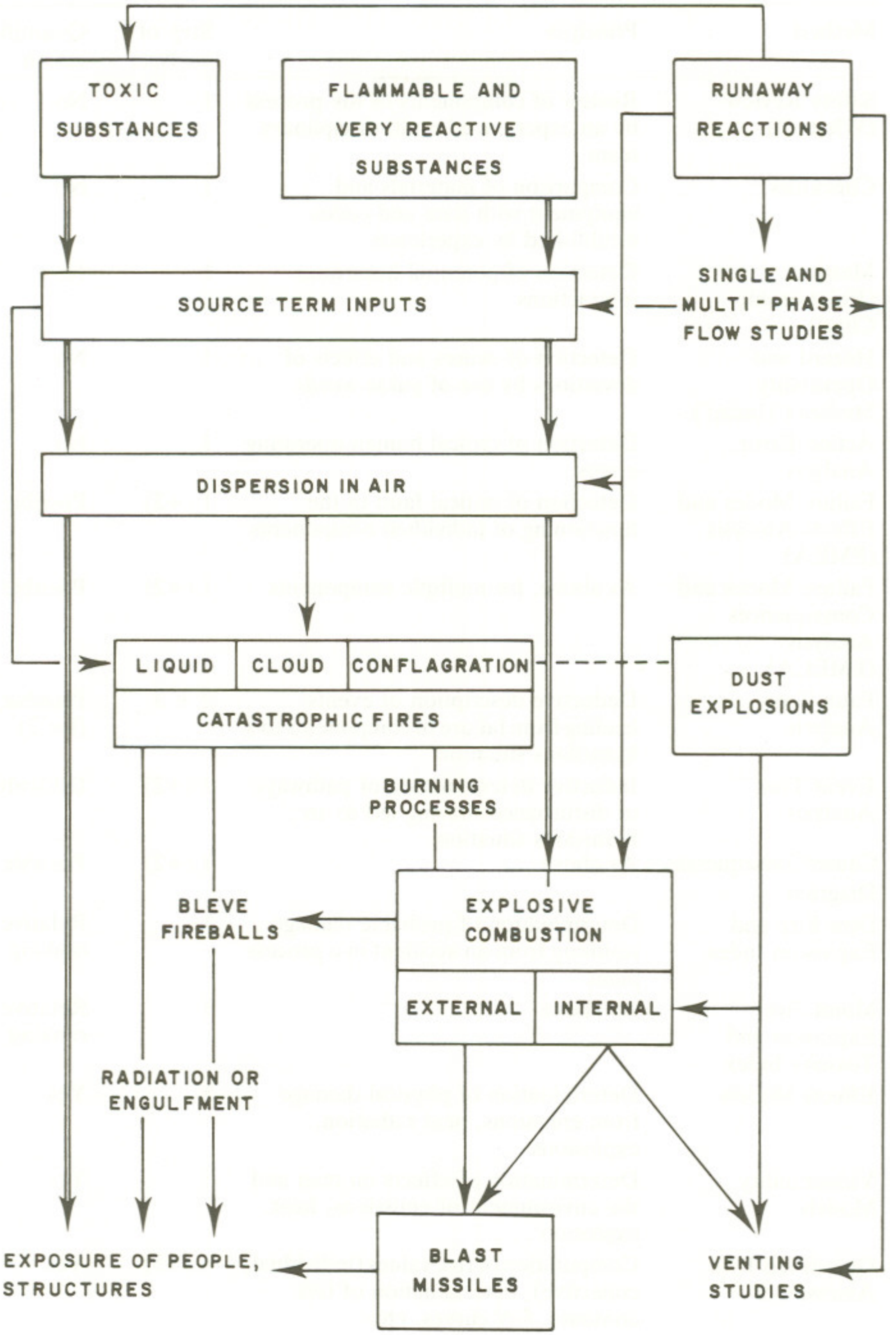

Figure 17.1 Principal phenomenologies and modelling in major hazards research

Table 17.23 Some methods available for risk assessment (CEFIC)

Method	Principle	Step of analysis	Quantification
Safety Review (What if?)	Review of components of the process by an experienced multi-disciplinary team	1	No
Checklists	Comparison of materials and equipment with data and codes established by experience	1	No
Matrices (Relationship Chart)	Detection of potential hazardous interactions	1	No
Hazard and Operability Studies ('Hazop')	Detection of causes and effects of deviations by use of guide words	1	No
Action Error Analysis	Detection of critical human operating errors	1	No
Failure Modes and Effects Analysis (FMEA)	Detection of critical fault in the functioning of individual components	1 (+2)	Possible
Failure Modes and Consequences Analysis (FMECA)	As above, for multiple components	1 (+2)	Possible
Fault Tree Analysis	Deductive description of events leading from failure of components to a hazardous situation	2 + 3	Possible (for 2)
Event Tree Analysis	Inductive determination of pathways of disturbances having led to an hazardous situation	1 (+2)	Difficult
Cause/Consequence Diagram	As above	1 (+2)	Possible
Dow Fire and Explosion Index	Determination of probable damage resulting from an accident in a process plant	3	Relative ranking
Mond Fire, Explosion and Toxicity Index	As above	3	Relative ranking
Effects Models	Determination of physical damage from emissions, heat radiation, explosions . . .	3	Yes
Vulnerability Models	Determination of effects on man and the environment of emissions, heat, explosion . . .	3	Yes
Quantified Risk Assessment	Computation of risk values (individual, collective), determination of risk contours, *f–N* curves, etc.	4 (+5)	Yes

The classification is based on the following steps: (1) hazard identification; (2) event likelihood; (3) evaluation of consequences; (4) estimate of risks; (5) assessment. Also see Parry, 1986, for a survey of methods.

dealing with certain stochastic phenomena (turbulent flows, dispersion or combustion), which actually suffer from considerable 'variability' in repeated runs. Particular sub-models, already referred to under Section 17.4, are simple empirical correlations or statistical distributions (e.g. for the size and travel of fragments/missiles), without further elucidations.

The advantage of those specific sub-models is that they can be tested directly against appropriate experimental data, as to validity and accuracy, or perhaps adjusted accordingly. Much such recent research has been devoted to dense gas dispersion at short range (e.g. in 'Battelle', 1979, 1982, 1984; 'Sheffield', 1984, 1986 and many others), and is now turning to the 'source term' (release phenomenology) and combustion aspects. The seemingly mechanistic approach should not mislead: the absolute accuracy of most sub-models is poor ([0] × 2 or so for radiant phenomena, [0] × 5 for much of dense gas dispersion or fast deflagration in non-ideal conditions) nor can limited data-sets presently indicate preferred ones of more general validity. Apart from topical monographs, few overviews of those diverse methods are available (Von Karman, 1982, 1983; Vilain, 1986).

One tendency in recent years has been towards increased sophistication, e.g. 2-D/3-D finite elements/finite differences codes incorporating turbulent diffusion or combustion subroutines for the description of dense gas dispersion or cloud combustion. Because of computing power and cost limitations, the grids are often too coarse (e.g. to describe far-field toxic dispersion) and too few cases can be explored parametrically. This is why simpler sub-models (box models for dispersion, 1-D/2-D geometries for explosion/flames) remain so widely used in risk assessment: their foundations are dubious, but they yield reasonable first-order estimates for practical purposes, limitative to one or few successive steps being tackled. Otherwise, difficulties of interfacing and compounding error margins soon arise and full modelling of most complex scenarios remains arduous at best.

17.7 THE QUANTIFICATION OF CONSEQUENCES

Coming to the end of the concatenation, material damage can also be estimated, in diverse ways. Blast damage estimates to plant items, storage vessels, structures (permanent deformation, rupture, collapse) are amenable to structural mechanics and related codes (see e.g. Baker *et al.*, 1983 for simple methods). Conversely, a careful post-accident mapping of damages to revelatory items (broken windows/walls, buckled tanks, bent posts) allows rough determinations of the explosion epicentre and strength (Gugan, 1979). Based on statistics, war records and testing, many simple correlations are indeed available, either v. scaled distance, or as damage probability (per cent of samples) v. loading diagrams, for side-on ΔP_m and by categories of structural items (*Yellow Book*, 1980); those correlations often imply a TNT equivalent and may disregard the – all important – shape of the deflagrative pressure pulse. Radiative damage is less univocal: fire tends to keep on and propagate and this is why estimates often refer to ignition thresholds, v. incident flux q or deposited energy Q (per unit area) or in q–Q diagrams. Data are available for a variety of household and garment materials, plastics, wood, grass, etc. (Glasstone and Dolan, 1977; Baker *et al.*, 1983).

Vulnerability models try, in similar fashion, to quantify harm to human targets (injuries, burns, toxic effects). Animals, crops and the environment in general seldom appear in standard risk assessments at this stage and it may be conjectured that priority was first given to an overwhelming number of awkward sites near population centres.

For injuries and burns, the damage can again be expressed by quantitative correlations or as probability (per cent chance) v. a causative factor. Examples are: body (abdomen) penetration by glass fragments and projectiles; non-penetrating head injuries; whole-body displacement and impact; eardrum or lung rupture; first-to-third-degree skin burns; retina burn, etc., for which simple methods, of military origin mostly, are available (Baker *et al.*, 1983). Fatalities from exposure to radiant heat are sometimes estimated by the probit equation (Eisenberg *et al.*, 1975):

$$Y\ (\text{Probit}) = -14.9 - 2.56 \ln 10^{-4}\, I^{4/3}\, t$$

I = incident flux (W/m^2) t = exposure, seconds
which is based on bomb data (Hiroshima) and has not been updated. Otherwise, a comprehensive treatment of radiative damages is given in SRD reviews (Hymes, 1983, 1985).

Toxicity is much more difficult to treat, because of the diversity of substances and modalities of causing harm: by inhalation or skin contact or ingestion, instantaneously or with delayed effects, etc., and this is not altogether separable from either the likely state of the substance (gas, flashing/boiling liquid particulate) or the vector, the dispersive energy driving it into contact with its targets (driving internal pressure of a storage vessel or runaway batch; flashing jet or boiling pool; entrainment by a venting fluid; wind advection) or the plausible duration of exposure. For such reasons, the grouping of substances into two classes – most bulk toxics, lethal upon inhalation of [0] gram quantities; and acute toxics, lethal upon body intake of [0] milligram quantities – places perhaps unrealistic emphasis on the latter (Table 17.21; Marshall, 1982). So do LC_{50}/LD_{50} values without consideration of spreading and exposure mechanisms, pathways and persistence. It has often been argued that acute toxics in limited quantities (say, [0] kg), with the possible exception of dioxin and other catastrophic runaway products, constitute a different class of hazards, subject to different safety precautions altogether (ACMH, 1984).

In most risk assessments, the emphasis is on a limited group of bulk toxics

Table 17.24 Some toxic criteria (COVO, 1982)

Effect	Time	Concentration (ppm)
	Toxic criteria for chlorine	
Odour detectable by most people	Any	1.0
Negligible effects – mild irritation	Any	<3.0
Serious distress – strong irritation	Any	5–20
Lethal	a few breaths	1000
	<15 min	>75
	30–60 min	40–60
	60–90 min	35–51
	Toxic criteria for ammonia	
Odour detectable by most people	Any	25
Negligible effects – mild irritation	Any	<100
Serious distress – strong irritation	Any	300–500
Lethal	a few breaths	>5000
	<15 min	2000–5000
	30–60 min	>1700
	Toxic criteria for hydrogen sulphide	
Odour detectable by most people	Any	0.1–0.4
Safe for 8-hour exposure	8 hours	10
Maximum that can be inhaled without serious consequences	60 min	200
Lethal	rapidly	>900
	<30 min	600–800

present in tonne quantities and capable upon release of generating a cloud of appreciable dimensions, drifting 'beyond the fence' and rendering speedy escape/evacuation difficult. Those gases are not necessarily denser than air and the inventories of Table 17.21 and 17.22 are not an index of likely relative stored quantities. Most emphasis, traditionally, is placed on chlorine and ammonia: far larger quantities are present and their toxicity data treated more confidently than for the rest.

Table 17.25 Some probit constants for chlorine

n	a	b	Units of C, T	Source
2.75	− 17.1	1.69	ppm, min	Eisenberg, 75 US Coast Guard
2.75	− 11.4	0.82	ppm, min	COVO, revised
2	− 16.9	1.90	ppm, min	MIT
2.75	− 5.3	0.5	ppm, min	Rijnmond, 85

Note: The probit equation is assumed of the form
$\mathrm{Pr} = a + b \ln (C^n t)$

Simplified treatments refer to scaled concentration thresholds (Table 17. 24) or non-linear toxic load limits. An example for chlorine is (Pape and Nussey, 1985):

$$C^{1.67} \times t > 2.10^4 \quad \text{for significant exposure}$$

C = concentration, ppm; t = exposure, minutes.

Those limits are easily slotted into dispersion calculations and mitigating factors (escape, being indoors) can also be incorporated. However, increasing use is also made of probit equations at the tail-end of probabilistic risk assessments. Current probit equations are recalled in Table 17.25 and 17.26, for Cl_2 and NH_3, with no preference at this stage. The comparatively small numerical differences of coefficients and exponent values lead, however, to a considerable spread of estimated damage probabilities (e.g. in Technica, 1985). Another source of uncertainty, with non-linear dose–damage relationships, is the intermittency or fluctuating character of cloud concentrations; approximate methods have been proposed (Griffiths and Hegson, 1984) but the effect is difficult to quantify and currently is being researched.

17.8 THE QUANTIFICATION OF RISKS

Reliability analysis and probabilistic risk assessment were first applied extensively in the aerospace and nuclear sectors (WASH.1400, 1974). In the latter case the fundamental problem was then to assess the comparative acceptability of the large-scale introduction of replicated nuclear plants of one given type (LWR, light water reactor). A few comparable scoping studies have been performed for the chemical sector (on the acceptability of LPG for motor transportation, on Cl_2 and NH_3 transportation), but the assessments there generally refer to given items (a production unit, a storage facility, a pipeline) of which there is of course an infinite variety.

Table 17.26 Some probit constants for ammonia

n	a	b	Units of C, T	Source
2.75	− 30.57	1.385	ppm, min	Eisenberg, 75
2.75	− 7.41	2.205	g/m^3, min	Canvey I, 78
2.75	1.14	0.782	g/m^3, min	Canvey II, 78
2	− 35.9	1.91	ppm, min	COVO, 80
2	− 31.8	1.90	ppm, min	MIT
2	− 9.82	0.71	ppm, min	Rijnmond, 85

Note: The probit equation is assumed of the form
$\mathrm{Pr} = a + b \ln (C^n t)$

The concept of risk is indeed probabilistic and, briefly put, its quantification may involve two different sets of probability (or frequency) values:

1. Reliability values, of failure/malfunction of individual components, or of so-called 'contributory events' leading successively or jointly to the hazardous outcome, the first step of the accident proper. Those probabilities may be assigned discrete values (from failure rate statistics) or treated as distributions (e.g. log-normal) and, combining, one thus arrives at the yearly probability of occurrence of selected 'top events'. Human error, erroneous operator actions mostly, can be incorporated (Bellamy *et al.*, 1986) but that development is more recent.
2. Branching values, at all nodes of the event tree, fanning out from a given initiating event to describe step by step the set of its possible outcomes and their relative likelihood. Those probabilities may also reflect options (the breach is above/below vessel liquid level, the cloud ignites or not), or factual data (windspeed/direction frequencies, failure/damage probabilities), combined with such factors as population distribution, day/night, indoors/outdoors and the intervention or not of mitigating actions, emergency procedures or evacuation. Consequences can be calculated in parallel by appropriate modelling of the steps involved along the event tree (the concept is illustrated in ultra-simplistic manner in Figure 17.1). Summing up, results can be presented as risk contours on a map or as cumulative frequency *f–N* curves, of which detailed examples are given in earlier pilot studies (COVO, 1982, for storage facilities).

Tools, dedicated computer packages, are now available and being perfected to perform those quantified risk analyses (QRA), which are somewhat the province of specialized organizations and consultancies. Although QRA is enforced in some European countries for regulatory purposes, there is far from universal acceptance and industrial concern has been expressed repeatedly, especially when applying the methodology to 'off-site' risks in the public

Table 17.27 Some probabilities of initiating events (Lannoy, 1984)

STORAGE VESSEL LEAKAGE, per year

Type	Atmospheric storage	Double-wall cryogenic storage	Pressurized storage
Significant leak	10^{-4}	2×10^{-5}	10^{-5}
Major leak	6×10^{-6}	10^{-6} (both envelopes)	10^{-6}

PIPELINE LEAKAGE, per km per year (significant to major)

Liquid hydrocarbon	Liquefied gas	Gas, cross-country	Gas plant, per year
5.5×10^{-4}	3.7×10^{-4}	3.7×10^{-4}	1.6×10^{-4}

TRANSPORTATION OF HAZARDOUS SUBSTANCES, accident per km per year

Road, standard	Road, highway	Railroad, average	Cross-country	Switchyard, siding
1.6×10^{-7}	0.6×10^{-7}	1.3×10^{-7}	0.7×10^{-7}	2.3×10^{-7}

SHIPPING OF HAZARDOUS SUBSTANCES, accident per km per year

Location	Coastline	Waterways	Harbours, per year
Global average	1.8×10^{-7}	2.9×10^{-6}	7.8×10^{-4}
Hydrocarbons, liquefied gases	1.3×10^{-7}	2.7×10^{-6}	7.8×10^{-4}
Chemicals, explosive substances	1.9×10^{-6}	1.1×10^{-5}	1.4×10^{-3}

domain. Whatever the real reasons, it is undeniable that for complex installations QRA exercises can be expensive and time consuming and their interpretation calls for a great deal of expert judgement if one is to avoid simplistic go/no-go decisions. There are indeed no universally agreed 'acceptable risk' levels or boundaries for chemical hazards, although some have been proposed from time to time for individual or societal risk (e.g. in Fearnehough, 1984, for pipelines, or Helsby and White, 1984, for individual plants). Nor, finally, should ready quantification obscure the fact that predictive models subtending the exercise or probability assignments may err greatly and that allowance should be made for substantial error bands. Table 17.27 shows probabilities of initiating events.

17.9 THE MITIGATION OF CONSEQUENCES

Prevention, avoiding hazardous situations, malfunctions and incidents, is of course the prime approach to safety, resting on: awareness of the hazards; proper layout, design, construction and operation; scheduled inspection/maintenance; operators' certification and supervision; monitoring and availability of prompt intervention teams. There is no substitute for high standards of plant design and management, enforced by appropriate authorities but, equally, safe practices are less easily transferred than technologies (Jourdan, 1985).

However, chemical accidents do occur and will occur again, and various quite simple schemes have been devised to impede or limit their spread or escalation. They include:

- passive built-in devices, intervening automatically: pressure-relief valves, bursting discs and panels, flame barriers/quenchers;
- remote-controlled devices, actuated by alarm signals or upon detection of anomalous conditions: trips, dump-valves, vents/flares, injectors of quenching/inerting substances, emergency coolers;
- a variety of external devices, active or passive, not directly tied to the process: catchment bunds and dump tanks; blast-resistant walls, bunkers and gas-tight shelters; lances, sprays and water curtains. For those, a degree of on-site human intervention or participation is often presumed (spraying water/foam, putting on protective clothing/respirators, taking shelter).

The diversity of the schemes listed should not delude us: the diversity of anomalous situations to cope with is equally great and each one calls for some appropriate solution, tailored to the anticipated problem, its severity and (especially) time-scale, which much limits choices and sometimes feasibility. Perusal of case histories shows that the acute phase of some accidents can be too rapid or the extent of the energy release, of the travel of projectiles, etc., too large to allow remedy and this restricts mitigation to the earlier steps of the chain of events, simply trying to avoid a worse outcome. One may also note that, compared to the 'defence in depth' and wealth of safety devices and redundancies of nuclear facilities, many chemical items would appear unsophisticated or less protected (e.g. smaller batch reactors for fine chemicals or discontinuous manufacturing).

Two schemes of broader validity have been extensively investigated and developed:

1. Venting, fast relieving the internal anomalous overpressure in a vessel, a duct, a building to avert its catastrophic failure. Quite often large-area, fast-acting devices are needed to cope with rapid rise-times and large mass-rates. Extreme examples are the venting of runaway batch reactors, or the relief of internal gas or dust explosions (e.g. in factory halls, or grain silos).

   Much attention has been devoted to that aspect of runaways, particularly vent sizing to exhaust promptly the generally multiphase reacting contents ('Chester', 1979, 1984, for a survey of methods). More recently, results and methodologies of the extensive DIERS (Design Institute for Emergency Relief Systems) programme have been released and are implemented on a part users' club, part commercial basis (Swift, 1985; Moronha, 1986).

   Simple methodologies are also available for gas and dust explosion relief in normal vessel configurations. Based on laboratory-scale testing in standard apparatus and grouping of substances in a few reactivity classes, simple scaling is applied to estimate vent areas; it is generally based on the Bartknecht 'cube-root law' and other correlations. Convenient vent sizing homographs are widely available, sometimes enshrined in national regulations (Bartknecht, 1981; Field, 1982; Lunn, 1984; for overviews). Discrepancies arise in elongated configurations or in the presence of repeated obstacles and constrictions, because of flame acceleration effects.
2. Water or steam curtains, which force-dilute flammable or toxic clouds, hopefully below LFL or harmful concentrations. They are simply ramps of spraying nozzles/ejectors, which can be disposed around potential 'sources' (storage vessels, catchment bunds) or across the presumed path of a spreading cloud. Portable devices are also available (peacock-tail sprays). The principle is that a high velocity spray entrains air with a large volumetric ratio ([0] 10^3), which suffices to dilute a crossing plume, essentially by increasing its depth. Dilution factors of [0] 3 to 4 are achieved in the near-field, as well as partial containment, for classic dense gases ('Manchester', 1981; 'Utrecht', 1984). Much less is known of the effect of curtains on reacting or soluble gases and aerosols (NH_3, phosgene).

Little of the foregoing readily applies to mobile items, rail tankcars and road tankers, which have very limited relief devices or monitoring instrumentation; or to innumerable smaller storages of gasoline, kerosene, LPG, etc., in filling/refilling stations; or to pipelines in open country. In such cases, mitigation is often conditional upon the swift arrival on the spot of intervention teams, mobile units, etc., and on implementing emergency measures such as limiting access and removing people. However, when dealing with transportation or pipeline accidents, which can occur almost anywhere and develop rather swiftly, emergency preparedness and timely intervention become problematic and records often illustrate the (lucky or fatal) importance of location and density of surrounding targets.

Another problem is that an endless variety of hazardous substances are constantly on the move, requiring proper identification and knowledge of emergency procedures, if accidentally released. To assist intervention and first-aid teams, there have been introduced (on a non-compulsory basis . . .) easily recognizable transport documents (TREMCARDS, in Europe), data banks, answering services and mutual-aid networks (CHEMTREC, CHEMNET, in the USA). Rapid further developments should be expected, with the improvement of communication networks, the advent of cellular telephones, or the possible storage of extensive chemical/medical information on CD–ROMS (compact disc–read only memories) for portable use, yet with all attendant problems of international standardization and cross-border communication.

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