7 VULNERABILITY MODELS

"The moving finger writes; and, having writ, moves on: not all your piety nor wit shall lure it back to cancel half a line, nor all your tears wash out a word of it."

Omar Khayyam

There is a sense of irreversibility in the impact of release of hazardous materials on vulnerable receptors. This has also influenced the risk perception among members of the public.

Having determined the physical effects from release events, it is important to relate the effects to final impacts on vulnerable receptors. This is the area of vulnerability analysis in hazard assessment. Although a well accepted analysis tool, the predictions can be accompanied by significant uncertainty that needs to be taken into the decision-making process. It is vital that the estimates are done with substantial knowledge of the source and circumstances under which vulnerability-models have been developed.

7.1 THE ROLE OF VULNERABILITY MODELS

In Section 5.2, we have said that there are two steps in determining consequences from hazardous incidents. These are:

- the physical effects of the event
  (gas concentrations, thermal radiation levels, explosion overpressures)
- the damage caused to the vulnerable receptor

(injury, death, level of burns, structural damage, environmental impairment)

The damage aspects are addressed by vulnerability models, using 'dose-response' relations. Dose-response data and the equivalent graphical representations show the outcomes or response of a dose on people, animals, structures or any nominated receptor. The dose can represent a quantity of a chemical exposure, an impulse from an explosion or a thermal dose. The response represents the level of injury sustained, deaths, physical damage to equipment or level of impairment. Hence the dose-response relation is a generic and common means of representing this relationship. A typical dose-response curve was seen in Chapter 5, Figure 5-2.

More generally we can use probit (probability unit) functions which represent intensity-damage relationships in an algebraic form amenable to computer implementation.

Probit functions have been developed for a wide range of vulnerability model situations. The probit variable Y is generally given as:

$$Y = k_1 + k_2 \ln(V) \tag{7.1}$$

where:

Y	= probit variable having mean of 5.0 and variance 1.0
V	= a measure of intensity of the causal factor (e.g. thermal or toxic dose)
k_1, k_2	= equation constants related to the specific event

The form of the probability P is given as:

$$P = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{Y-5} \exp\left(-\frac{1}{2}w^2\right) dw \tag{7.2}$$

Once the probit value has been calculated it is then possible to relate this to a fraction or percentage via tables, or a graph like the one shown in Figure 7-1 or a calculation such that

$$P = 0.5\left[1 + \frac{Y-5}{|Y-5|} erf\left(\frac{|Y-5|}{\sqrt{2}}\right)\right] \tag{7.3}$$

where $erf(.)$ is the error function.

From this it can be seen that a probit value of 5 translates into a fraction of 0.5. This means that 50% of the receptors will suffer the specified level of damage.

As can be seen from the probit-fraction plot, the impact from a "dose" is highly nonlinear. A simple example is the exposure of people to solar radiation where some of the population are very sensitive to low doses whilst others are very tolerant to even high doses. Hence for a given dose the use of the probit function

provides an estimate of the fraction of the exposed population affected for a specified level of intensity or dose.

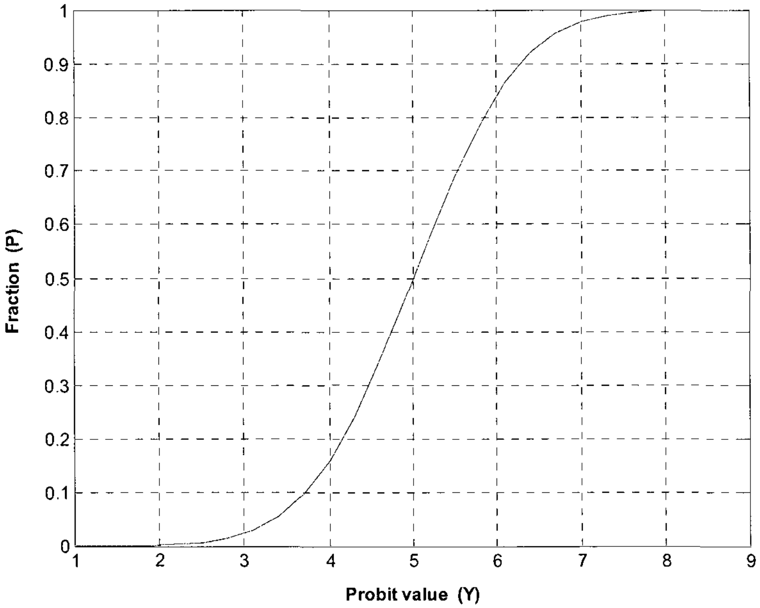

FIGURE 7-1 PROBIT VALUE VERSUS FRACTIONS

7.2 DOSE-RESPONSE MODELS FOR FIRES

Thermal radiation from fires and explosions causes a wide range of damage on people and structures. In this section impact on people is discussed whilst section 7.5 deals with structural impacts.

Table 7-1 gives an overview of general heat radiation impacts (Warren Centre 1986, Hymes et al. 1996).

TABLE 7-1 GENERAL EFFECTS OF THERMAL RADIATION

Radiation Intensity (kW/m^2)	Impact
1.2	Received from sun in summer at noon
1.6	Minimum necessary to be felt as pain
4.7	Pain in 15-20 seconds, 2nd degree burns after 30 s.
12.6	30% chance of fatality for continuous exposure Minimum level to melt plastic tubing
23.0	100% chance of fatality for continuous exposure 10% chance for instantaneous exposure
35.0	25% chance of fatality for instantaneous exposure Damage to process equipment
60.0	~100% chance of fatality for instantaneous exposure

Impacts rapidly worsen as both radiation intensity and exposure duration increase. This affects injury levels and probability of fatality. In terms of thermal radiation on people, the following impact levels are recognized (TNO 1992a, Hymes et al. 1996):

(i) First degree burns (limited to the epidermis or top layer of skin: ~0.12mm deep)
(ii) Second degree burns (penetration to the dermis or < 2mm deep)
(iii) Third degree burns (penetration into the subcutis, fat tissue)
(iv) Fatal burns

Of importance in assessing impact of thermal radiation is the wavelength. Impacts from nuclear explosions where wavelengths are in the UV-visible region (<400 nm) can be quite different from hydrocarbon fires where wavelengths are in the infra-red region (> 700 nm). This is because the higher wavelengths cause deeper skin penetration than the shorter wavelengths. Hence, the use of probit functions needs to be done carefully, recognizing the underlying assumptions and data.

Table 7-2 gives the probit equations developed by TNO in The Netherlands for impacts from hydrocarbon based fires.

TABLE 7-2 PROBIT EQUATIONS – THERMAL RADIATION IMPACTS (TNO 1992)

Radiation (t = s, q = W/m^2)			
Fatality	Y	$= -36.38 + 2.56 \ln (tq^{4/3})$	(7.4)
1st degree burns	Y	$= -39.83 + 3.0186 \ln (tq^{4/3})$	(7.5)
2nd degree burns	Y	$= -43.14 + 3.0186 \ln (tq^{4/3})$	(7.6)

Note that the intensity measure V in equation (7.1) is given by $tq^{\frac{4}{3}}$. This represents a "dose" value.

Table 7-3 gives the commonly quoted fatality probit developed by Eisenberg (CCPS 2000). The data covered exposure times between 1.43 and 45.2 seconds, and incident heat fluxes between 10 and 586 kW/m^2.

TABLE 7-3 PROBIT EQUATION - FATALITY IMPACT FROM RADIATION (CCPS 2000)

Radiation	$t = s,\ q = \dfrac{W}{m^2}$	
Fatality	$Y = -14.9 + 2.56 \ln\left(\dfrac{t.q^{\frac{4}{3}}}{10^4}\right)$	(7.7)

In both Table 7-2 and 7-3, the impacts do not normally consider the protective effects of clothing and hence they overpredict impacts where people are clothed. In the case where clothing ignites, it is often the case that 100% fatality is assumed.

Where the mitigating effect of clothing is considered, the percentage of exposed skin becomes important. This varies for the age group considered. For infants the exposed area is around 32% whilst for an adult it is around 20% (neck,

head, arms and hands). Combined with the population distribution these assumptions reduce the impact to around 15% of the unprotected impact (TNO 1992a). The type of clothing and the attenuation of thermal radiation have not been discussed, and therefore, this level of reduction cannot be applied in all situations.

EXAMPLE 7-1 FIRE RADIATION, LETHAL BURN

Fire with 10 seconds exposure and heat flux of 45 kW/m^2.
Using probit equation (7.4) for fatality:

$$\begin{aligned} Y &= -36.38 + 2.56 \ln(t.q^{4/3}) \\ &= -36.38 + 2.56 \ln(10 \times 45000^{4/3}) \qquad (7.8) \\ Y &= 6.09 \end{aligned}$$

The probit-fraction relation gives an impact of 86% fatalities. If the effect of clothing is considered (impact reduced by a factor of 0.15) then fatalities drop to 13%. The Eisenberg probit, equation (7.7) gives a probit value of 4 and thus 16% fatalities compared with 86% from the TNO probit.

7.2.1 Variability in Probit Estimates

It is useful to compare the general predictions from various probit models for thermal impact on people. Figure 7-2 shows the probit value (Y) for a range of thermal loads and the subsequent predictions for the TNO and Eisenberg models. A significant difference exists and this is more clearly seen in Figure 7-3 which shows the fractional impact values (P) as a function of thermal load and probit model.

For a thermal dose value of 10^7s (W/m^2)$^{4/3}$, the Eisenberg model predicts around 1% fatalities, whereas the TNO model gives around 45% fatalities. Clearly a significant difference to be considered, showing the difference in the underlying assumptions of the models.

Schubach (1995) gives a useful analysis of probit functions and shows that for long duration events, the Eisenberg probit produces extended effect distances and an overestimation of risk. He suggests that the exposure duration should be limited in applying these models.

The reduction of 85% in the fraction of fatality for the clothed skin compared to unprotected skin is considered optimistic. In risk analysis, when considering impact on vulnerable members of the population, it is better to make a conservative estimate by ignoring the protection offered by clothing.

7.2.2 Impact of Flash Fires on People

Flash fires due to combustion of a vapour cloud that has formed through dispersion of hydrocarbon vapour is a rapid event.

General consensus is that anyone within the cloud volume when ignition and fire occurs will be a fatality. This is a conservative assumption. Direct flame contact in these cases plus the ignition of clothing are key factors in determining the impact.

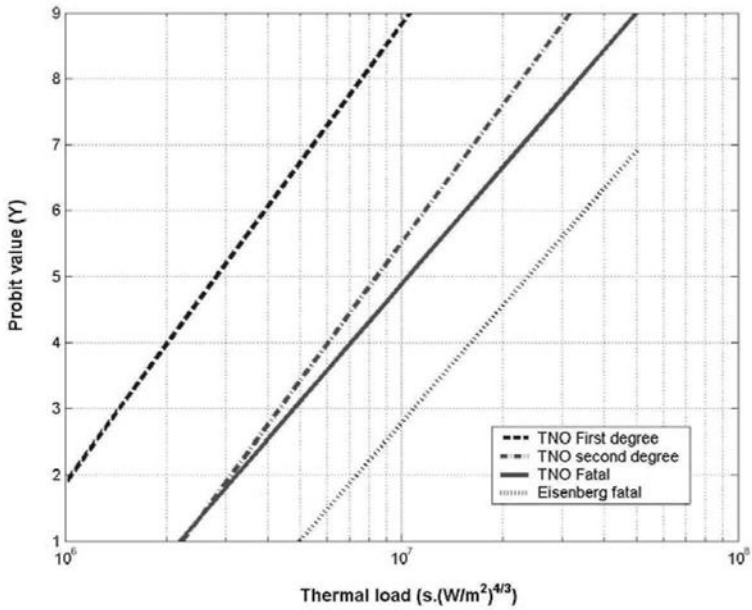

FIGURE 7-2 PROBIT VALUE VS. THERMAL LOAD FOR BURNS PROBITS

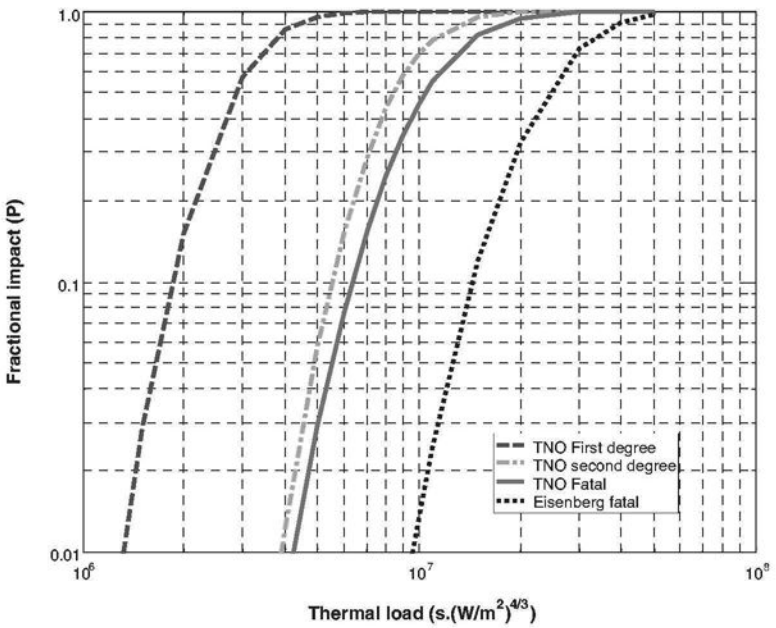

FIGURE 7-3 FRACTIONAL IMPACT VS. THERMAL LOAD FOR BURNS PROBITS

7.3 ESTIMATION OF EXPLOSION IMPACTS ON PEOPLE

In section 6.7.1 the characteristics of explosions and the effects from the blast wave were discussed. In particular, the peak overpressure and positive phase duration were key factors in the potential impact.

In considering the effects of blast on people there are many complexities that make predictions difficult. These include (HSE, 1998):

(i) Type of explosive and the quantity
(ii) Presence of reflecting surfaces that can magnify blast effects.
(iii) Location of explosion with respect to the targets of interest

and in certain cases,

(iv) The explosive device, its shape and primary fragments.

In terms of the potential impacts on people there are direct and indirect effects from the blast (TNO 1992a). These include:

(i) Direct effects: injury and death from pressure change that affects internal organs (lungs, gut etc.)
(ii) Indirect effects: include
  a) impact of fragments and debris generated by the blast
  b) bodily displacement causing impact of body parts (e.g. head) or whole body on nearby structures.
  c) building or structural collapse, in the case of people inside structures.

There are also the associated effects of heat radiation from the blast. The main direct and indirect impacts are:

(i) Rupture of eardrums
(ii) Lung damage (haemorrhage)
(iii) Head impact
(iv) Whole body displacement
(v) Impact from fragments and debris (non-cutting)
(vi) Glass fragments (cutting)

Table 7-4 gives typical blast effects related to a range of overpressures. Tables 7-5 and 7-6 give a range of probit functions that are applicable to these situations from several sources (TNO 1992a, Lees 2001). The references from Lees (2001) were originally developed by Eisenberg et al. (1975). Prugh (1999) gives a very useful coverage of blast effects on structures and personnel. However it must be stressed that many assumptions underlie these functions and data is often related to very specific circumstances. Hence, extreme caution is needed in applying them. As a first estimate of potential impact they can be useful. For further assessments it is advisable to refer to primary sources based on field data. Evenso, much of the literature is based on impacts from dense phase explosions, whereas most industrial accidents involve hydrocarbon based vapour cloud

explosions (HSE, 1998) that have quite different pressure-time profiles and hence impact patterns.

TABLE 7-4 TYPICAL BLAST EFFECTS FROM EXPLOSION OVERPRESSURE

Overpressure (kPa)	Effects
0.3	Loud noise
1.0	Threshold for breakage of glass
4.0	90% window breakage. Damage to cladding. Minor structural damage.
7.0	Glass fragments fly with enough force to injure. Roof tiles removed.
14.0	Houses uninhabitable but not totally irreparable. Cement block buildings flattened.
21.0	Reinforced structures will distort. 20% chance of fatality inside a building
35.0	On-set of severe structural damage. House demolished. Large storage tanks could rupture. 15% chance of fatality outdoors, 50% chance indoors.
70.0	Almost complete demolition of all ordinary structures. Almost 100% chance of fatality indoors.

In many cases an approximation of the pressure-time profile to a triangular shape is made, as seen in Figure 7-4. Here P_o is atmospheric pressure; P_s is the peak-overpressure and t_p is the positive phase duration.

The pressure impulse i is then approximated as:

$$i \cong \frac{P_s \cdot t_p}{2} \tag{7.9}$$

which represents the area under the pressure-time profile above atmospheric pressure P_o.

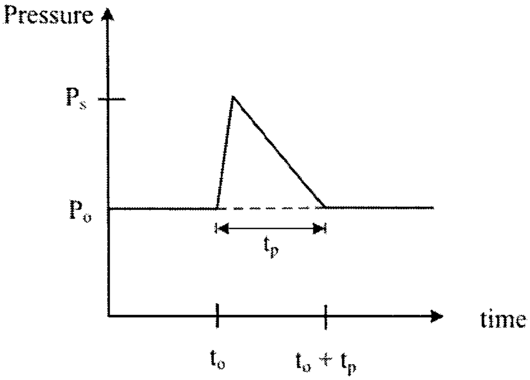

FIGURE 7-4 EXPLOSION PRESSURE-TIME PROFILE APPROXIMATION

TABLE 7-5 PROBIT EQUATIONS - BLAST IMPACTS (TNO 1992A, LEES 2001)

1.	Eardrum damage:	$Y = -12.6 + 1.524 \ln P_s$	(TNO)	(7.10)
		$Y = -15.6 + 1.93 \ln P_s$	(Lees)	(7.11)
		where P_s = peak overpressure (Pa)		
2.	Lung damage and death:	$Y = -77.1 + 6.91 \ln P_s$	(Lees)	(7.12)
		$Y = 5 - 5.74 \ln S_1$	(TNO)	(7.13)
		where		
		$S_1 = \frac{4.2}{\bar{P}} + \frac{1.3}{\bar{i}}$		
		$\bar{P} = \frac{P}{P_o}$; $\bar{i} = \frac{i}{P_o^{\frac{1}{2}} \cdot m^{\frac{1}{3}}}$		
		P = actual overpressure on person depending on orientation		
		P_o = atmospheric pressure (Pa)		
		i = impulse $\left(\sim \frac{Pt_p}{2} \right)$		
		t_p = positive phase duration (s)		
		m = body mass (kg)		
3.	Head impact:	$Y = 5 - 8.49 \ln S_2$	(TNO)	(7.14)
		where		
		$S_2 = \frac{2.43 \times 10^3}{P_s} + \frac{4 \times 10^8}{P_s \cdot i_s}$		
4.	Whole body displacement:	$Y = 5 - 2.44 \ln S_3$	(TNO)	(7.15)
		where		
		$S_3 = \frac{7.28 \times 10^3}{P_S} + \frac{1.3 \times 10^9}{P_S \cdot i_S}$		
		$P_s < 9 \times 10^5 Pa$		

TABLE 7-6 PROBIT EQUATIONS - BLAST FRAGMENTS/DEBRIS

1.	Debris:	$Y = -13.19 + 10.54 \ln V_o$	(TNO)	(7.16)
		where V_o = velocity of fragment (m/s); m = mass of fragment (kg) > 4.5 kg		
		$0.1 < m < 4.5$ $\quad Y = -17.56 + 5.30 \ln S_4$	(TNO)	(7.17)
		where		
		$S_4 = \frac{1}{2} m V_o^2$		
		$0.001 < m < 0.1$ $\quad Y = -29.15 + 2.10 \ln S_5$	(TNO)	(7.18)
		where		
		$S_5 = m V_o^{5.115}$		

EXAMPLE 7-2 EARDRUM RUPTURE FROM EXPLOSION

Using the probit equation:

$$Y = -12.6 + 1.524\ln(P_s) \tag{7.19}$$

where P_s is the peak overpressure (Pascals), the following fractional responses are seen from the variation in overpressure.

Percentage Affected	Probit	Peak Overpressure (Pa)
1	2.67	21500
10	3.72	42800
50	5.00	103800
90	6.28	240400

ref: TNO (1992a).

EXAMPLE 7-3 BLAST FRAGMENT IMPACT

A small fragment of 0.1 kg from the rupture of a pressure vessel impacts on a person some 60 metres from the event. The velocity of the fragment is estimated at 40 m/s.

Using equation (7.17) the value $S_4 = \frac{1}{2}(0.1)(40^2) = 80$

and the probit value
$$Y = -17.56 + 5.30\ln(80)$$
$$Y = 5.66$$

Hence the probability of fatality is approximately 70%.

7.4 DOSE-RESPONSE MODELS FOR TOXIC SUBSTANCES

7.4.1 Toxic Exposure Effects

The area of toxicology is complex and highly specialised. Most data on the toxic effects of substances are derived from animal experiments and then extrapolated or scaled to the human population. Some data exists for human exposure to certain substances such as chlorine and ammonia. These arise from actual incidents that were documented or from effects observed during times of war when certain agents were used as chemical weapons.

In general there are several observable effects and these depend on the chemical nature of the substance and its interaction with the body. Table 7-7 sets out the major exposure effects from irritation to asphyxiation and systemic damage.

TABLE 7-7 TOXIC EXPOSURE EFFECTS

IRRITATION
- respiration (Cl_2, SO_2, NH_3)
- skin
- eyes

NARCOSIS (hydrocarbons)

ASPHYXIATION
- simple (N_2, He)
- chemical (CO, HCN)

SYSTEMIC DAMAGE

Effects are often addressed through the use of limiting values of the substance's concentration for assumed exposure periods. In most cases these are applicable to occupational situations and not directly applicable to acute, accidental releases of materials. Such measures include:

a) Threshold limit values (TLV)
b) Short Term Exposure Limit (STEL)
c) Immediately dangerous to life or health (IDLH)
d) Permissible exposure limits (PEL): A maximum amount of concentration of a chemical that a worker can be exposed to under US-OSHA rules.

The above measures have limited application in most acute event situations. Definitions of the terms are given Section 5.2.2.3 in Chapter 5.

An approach originating in the USA that has been used for land-use planning issues relies on Emergency Response Planning Guidelines (ERPGs) that set three levels of possible exposure that relate to increasing effects on individuals in a community exposed to various substances. These include:

ERPG-1 level: maximum gas concentration for 1 hour exposure where only mild transient effects such as objectionable odour can be experience by most individuals.

ERPG-2 level: maximum gas concentration for 1 hour with no irreversible health effects or symptoms.

ERPG-3 level: maximum gas concentration for 1 hour not causing life threatening health impacts for nearly all individuals.

In some cases, the ERPG levels have been applied to risk based land-use planning guidelines to provide criteria for injury levels from toxic exposure from hazardous industry developments (DIPNR, 2003).

Some values of ERPG levels are given in Table 7-8 for selected substances. The complete listing is available from the American Industrial Hygiene Association (AIHA 2004). They are updated every 5 years and there are currently about 100 substances listed.

TABLE 7-8 ERPG LEVELS FOR SELECTED SUBSTANCES (PPM)

Substance	ERPG-1	ERPG-2	ERPG-3
ammonia	25	150	750
benzene	50	150	1000
chlorine	1	3	20
hydrogen sulphide	0.1	30	100
methyl isocyanate	0.025	0.5	5
nitrogen dioxide	1	15	30
sulphur dioxide	0.3	3	15
vinyl acetate	5	75	500

Of primary use are probit relations that permit a wider range of acute impacts to be assessed. The following section deals with those dose-response representations.

In an important comparison of probit expressions for toxic exposure, Schubach (1995) points out the significant difference between the CCPS and TNO (1992) relations. He suggests that the TNO values are preferred because they recognize species differences in inhalation rates and sites of damage. Specific human data is always to be preferred over extrapolations and manipulations of animal toxicological data. However specific data only exists for certain substances such as chlorine and ammonia due to their past use in chemical warfare.

7.4.2 Vulnerability Models

Impact from exposure to toxic gases is commonly handled through the use of specific probit equations. Some are based on actual human exposure to the substance, many are extrapolated from animal testing. A number of sources quote specific probit relations including the US Coast Guard (1980), Director-General of Labour, The Netherlands (TNO 1992a) and the World Bank (1988). Other specific studies on chemicals such as chlorine and ammonia are available (Withers and Lees 1985a, 1985b, MHAP, 1987, 1988).

The key factors in assessing impact include:

(i) Exposed concentration and time of exposure
(ii) Whether the exposure is transient or sustained
(iii) The breathing rate of the individual
(iv) Opportunities of shelter indoors or escape from the toxic cloud

Table 7-9 gives a selected summary of currently available probit equations for a number of important substances indicating some alternatives. These are drawn from US Coast Guard data and from the Director-General of Labour, The Netherlands. In the case of The Netherlands, alternate probits based on extrapolation of LC_{50} values were used (TNO 1992a).

TABLE 7-9 PROBIT EQUATIONS - TOXIC EXPOSURE

The general form is: $Y = k_1 + k_2 \cdot \ln(tC^n)^*$

Chemical	k_1	k_2	n
acrolein	-9.931	2.049	1
ammonia	-35.9	1.85	2
	-15.8	1.00	2 (TNO)
bromine	-9.04	0.92	2
	-12.4	1.00	2 (TNO)
carbon monoxide	-37.98	3.7	1
	-7.4	1.00	1 (TNO)
chlorine	-8.29	0.92	2
	-14.3	1.00	2.3 (TNO)
hydrogen cyanide	-29.42	3.008	1.43
	-9.8	1.00	2.4 (TNO)
hydrogen sulphide	-31.42	3.008	1.43
	-11.5	1.00	1.9 (TNO)
nitrogen dioxide	-13.79	1.4	2
	-18.6	1.00	3.7 (TNO)
phosgene	-19.27	3.686	1
	-0.8	1.00	0.9 (TNO)
sulphur dioxide	-15.67	2.10	1
	-19.2	1.00	2.4 (TNO)

* In the case of TNO relations C = mg/m^3 otherwise C = ppm and t = minutes.

EXAMPLE 7-4 PREDICTED IMPACTS FROM HF RELEASES

Hydrogen fluoride (HF) is commonly used in petroleum refinery alkylation units. Escape of HF and its subsequent dispersion is an important risk issue for nearby communities.

There exist several probit relations for HF impacts (HSE 1995). These include:

ten Berge (1986) $$Y_{tb} = -7.35 + 0.71\ln(C^2 t) \quad (7.20)$$

Rausch (1977) $$Y_r = -25.8689 + 3.3545\ln(\hat{C}t) \quad (7.21)$$

de Weger (1991) $$Y_{dw} = -8.4 + \ln(C^{1.5} t) \quad (7.22)$$

Mudan (1989) $$Y_m = -48.33 + 4.853\ln(\hat{C}t) \quad (7.23)$$

where t = minutes exposure
C = mg/m^3
$\hat{C}$ = ppm

Figure 7-5 shows the comparative predictions of the probit relations for 15 minutes exposure to HF gas. It is clear that there is a significant spread in predictions of fatality. At a gas concentration of 1000 ppm the fatality predictions range from 90% (Rausch) to 0% (Mudan) with the other probits in the 20 to 30%

fatality range. This variance reflects the differences in some of the underlying data, mainly animal experiments, and the subsequent scaling treatment of that data for use in human dose-response predictions.

The probit relationship developed by Mudan (1989) is widely used for longer duration exposures (30 to 60 minutes often quoted), where the c-t relationship is linear (HSE 1995, Lees 2001). This linear relationship has been used by the HSE (1993) to derive a Dangerous Toxic Load (DTL). A value of 2400 ppm is listed for a 5 minute exposure. DTL does not represent a lethal concentration, but could reflect serious injury requiring prolonged medical treatment.

What is clear is that significant variations can occur in vulnerability analyses and these variations must be addressed in the decision making process. It also emphasizes that the underlying assumptions of the probit functions should be clearly understood and the expressions not used blindly. ■ ■ ■

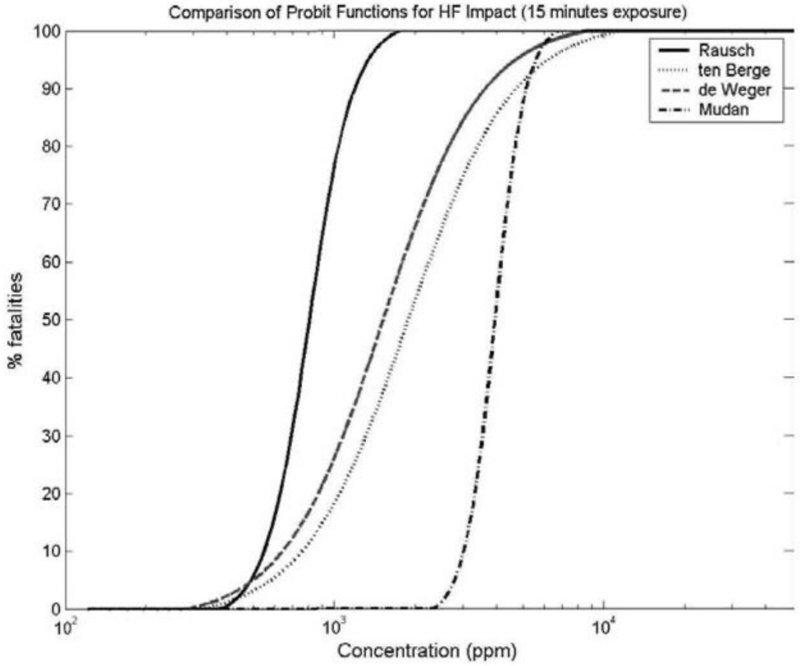

FIGURE 7-5 PROBIT COMPARISONS FOR HF EXPOSURE

7.4.3 Eco-system Impacts

Eco-system impacts require knowledge of:

(i) The receptor type (fish species, bird, animal, ...)
(ii) The uptake rate to determine the dose
(iii) The chemical of concern (COC)
(iv) The ecological endpoint being considered, such as mortality.

As shown in Figure 5-7, the environmental risk assessment framework can be extremely complex with many pathways for the COC to impact the ecological receptor.

In assessing impact on the receptor it is typical to use toxicity data such as that found in the ECOTOX database (USEPA, //www.epa.gov/ecotox/) or from the Registry of Toxic Effects of Chemical Substances (RTECS). Data from these sources are presented using various measures including:

Acute toxicity measures:

LD_{LO}, LD_{min}	:	the lowest dose of a substance that may cause death under defined conditions. Typically in mg/kg of body weight.
LD_{50}	:	lethal dose to 50 percent of a population
LC_{50}	:	lethal concentration in an environmental medium to 50 percent of a population following a certain period of exposure. Typically expressed as mg/L for aquatic toxicity and mg/m^3 for inhalation toxicity.

In the case of lethal dose, it is important to recognize the routes of exposure. These can be via dermal (skin) or oral routes. In the case of lethal concentrations the exposure time needs to be considered as well as the uptake rate into the species.

Other important measures include:

NOEC	:	No observed effect concentration, which is the concentration that causes no observable effects on the organism, or
NOAEL/NOEL	:	No observed (adverse) effect level.

Chronic toxicity measures:

In these cases, where exposure occurs over long time scales there are no simple LC or LD measures available. Specialised studies, data and models are necessary to assess chronic impacts. Short-term testing protocols can provide some estimates of chronic toxicity (USEPA 2002).

Other important sources of toxicological information are to be found in:

TOXNET (//toxnet.nlm.nih.gov/) which includes

- IRIS: Integrated Risk Information System
- HSDB: Hazardous Substances Database
- GENE-TOX: Genetic Toxicology (Mutagenicity)
- ITER: International Toxicity Estimates for Risk

European Chemicals Bureau (//ecb.jrc.it/)

Ecological impacts can be complex to assess and especially to quantify. The use of predictive models and toxicity data must be used carefully and cautiously. Expert assistance is normally required to provide credible analyses.

7.5 STRUCTURAL RESPONSE TO FIRES

Section 7.2 discussed the response of humans to heat radiation. This section considers the effects of heat radiation on structures. This is often an important aspect in domino effects where thermal impacts from an event lead to further system failures and propagation. This was the case in Mexico City in 1984 when the Pemex LPG facility was completely destroyed.

There are several important aspects that need to be considered, including:

(i) Direct flame impingement on vessels and structures and its impact.
(ii) Radiant impact on vessels and structures from nearby flames.

7.5.1 Direct Flame Impingement or Engulfment

In the case where a jet fire directly impinges on a structure or vessel, localised heating will take place and if no action is taken then structural failure will eventually occur. This will be determined by the state of the vessel contents, the location of the impingement (vapour or liquid space), the structural design as well as the emergency response taking place, e.g. water sprays or deluge systems.

Jet flame temperatures are typically in the range of 1300°C to over 1500°C depending on the degree of turbulent mixing. Failure of steel is dependent on the load or stress it carries but temperatures in the vicinity of 400°C to 600°C can precipitate structural failure. On unprotected structural steel or a pressure vessel shell, the time to the failure temperature can be less than a few minutes. Complex heat transfer calculations are required in order to assess the specific situation. Field studies of LPG vessels subject to propane and butane jet fires show that hot spots of over 500°C can occur on vessels even with conventional deluge systems (HSE 2000). These temperatures take in the order of 10 minutes to achieve.

Engulfment of vessels or tanks by pool fires is covered in many codes of practice that deal with vessel pressure relief or venting (AS1940 1993; AS1210 1997). Heat absorption is expressed in terms of a "wetted" area of flame and a correlation constant, typically as:

$$Q = cA^{n} \tag{7.24}$$

where Q = heat absorbed (kW)
A = area (m^2)
n = index
c = constant

Various standards such as API RP520, API Std 2000 for storage tanks recommend the use of estimates similar to equation (7.24). Engulfing fire heat fluxes of $150 kW/m^2$ are typical of these situations (Lees 2001). What is of importance here is the use of dynamic models that capture the heat transfer

mechanisms in order to predict time-varying temperatures and pressures in the system.

7.5.2 Structural Response by Heatup Modelling

Heatup modelling is a useful tool for predicting the temperature-time history of structures subject to pool fire engulfment and jet fire impingement. The main uses are:

- Determination of the extent of passive fire protection (PFP) requirements for steel columns supporting pipe bridges in process plants, if there is a potential for pool fire engulfment.
- Determination of PFP requirements for primary steel supporting the equipment and modules in offshore structures.
- Estimation of time to failure of vessels containing volatile hydrocarbon inventory (time to BLEVE), with and without depressuring, and with and without deluge protection. The results provide optimum depressuring rates to prevent BLEVE, estimate PFP requirements, and emergency response planning to protect emergency crew.

Exposure of a vessel to external fire engulfment or impingement involves interaction between the physical components of the system (Hunt and Ramskill 1985, Davenport et al 1992). Specific parameters are:

- Fire characteristics (flame size, surface emissive power, area of engulfment, flame temperature)
- Vessel structure (dimensions, wall thickness)
- Vessel contents (physical and thermodynamic properties of the liquid and vapour, and the vessel fill level)
- Vessel vents (pressure safety valve (PSV) and capacity)
- Process flows in and out of the vessel
- The surroundings (ambient conditions, attenuation of thermal radiation by fixed water sprays).

A set of heat and mass balance equations need to be setup involving the following:

- Heat input to vessel by radiation and convection (liquid and vapour parts have to be separately modelled)
- Heat conduction from heated side of vessel wall to unheated side
- Heat absorbed by vapour and liquid in the vessel (in many instances, boiling heat transfer in the case of liquid)
- Heat losses from reflected radiation and convection to ambient air
- Thermodynamic equilibrium between the vapour and liquid phases within the vessel (complicated for mixtures)
- Heat and mass loss through PSV discharge as pressure rises from heatup (generally this is modelled as a intermittent discharge with reseating of the PSV, referred to as "chattering")

A number of temperature nodes may be selected, and constitutive equations developed. These have to be numerically integrated for each time step, with physical and thermodynamic properties calculated at the vapour and liquid temperature corresponding to temperatures at that time step. The longitudinal and hoop stresses are calculated, along with the reduction in the ultimate tensile strength with rising temperature. The computations are quite complex, especially maintaining the mathematical constraint of thermodynamic equilibrium within the vessel. Obviously, for load bearing structures, the heatup calculations are simpler.

In order to obtain more accurate estimates, it is necessary to interface the heatup calculations with a dynamic finite element model, where the stress distribution is calculated at each time step, using the existing temperature at that time. No commercial software is currently available.

A number of heatup modelling studies and experiments have been carried out on fire engulfment of vessels storing flammable inventory. Many of these studies have originated from offshore oil and gas industry, where there is no luxury of separation distance and the level of congestion, and hence fire engulfment potential, is high (Davenport et al 1992; Steel Construction Institute, 1992a; Roberts et al. 2000). Other studies focus on vessels containing liquefied flammable gas (LPG) subject to external flames (Moodie 1985; Moodie et al. 1985, 1988; Benyon, 1988; Birk 1988; Dancer and Sallett 1990; Venart 2000). None of the existing models for predicting the response of LPG vessels exposed to fire are ideal, but have been validated against experiments with small vessels.

There have also been experiments on the effectiveness of fixed water spray in attenuating fire impact and prevention of escalation (Schoen and Droste 1988; Gosse and Alderman 2001; Roberts et al. 2001).

The findings from various studies are summarised below:

1. The convective heat transfer coefficient from tank wall to liquid is greater than the corresponding value for vapour in the nucleate boiling regime, causing the vapour side wall temperature to rise faster than the temperature of a surface in contact with liquid.
2. For a vessel subjected to external flame impingement, the time taken for the initial discharge through the PSV is a function of the vessel inventory. The higher the level, the sooner the discharge occurs, as the vapour space available is smaller and therefore the pressure rise from thermal expansion is faster.
3. A two-step failure mechanism for vessel failure has been postulated – plastic deformation leading to an initial crack, following by a shear fracture. Time of failure is difficult to predict, but wall temperatures of 500–550°C have been suggested.
4. For process vessels containing LPG, which generally tend to contain less than 10 tonnes in inventory, the failure time is between 3 and 10 minutes, depending on the size of vessel.
5. Water spray cooling is effective against pool fires, as the radiative heat flux can be reduced by 55% for design water spray density of 10 L/min/m^2.
6. Conventional water spray of 10 L/min/m^2 applied from the top of the vessel, using standards such as NFPA 15 (1996), is ineffective against a jet fire attack, where most of the heat transfer is through convection

rather than radiation. Further, the water film breaks down in the region of blocked nozzles.

7. Higher water deluge density (2 to 3 times conventional value), directed specifically at the fire impingement area, would protect the vessel. However, the water spray quantity must be assessed as quantity actually applied to the surface rather than nozzle discharge rate, as the application is not uniform.
8. Passive fire protection (PFP) for jet fire attacks has been developed (Steel Construction Institute 1992a,b). The data suggest that an adequate PFP system can reduce the heat transfer to the vessel by a factor of 10 (HSE 1998).
9. Emergency depressuring of the target inventory to flare extends failure time, and may prevent failure in some instances. In general, a depressuring system designed to API 521 (1997) has been shown to be inadequate to prevent a BLEVE, even with fixed water sprays designed to NFPA 15 (1996). Larger depressuring rates would be required to protect against vessel failures (Institute of Petroleum 2003).
10. For atmospheric storage tanks designed with separation distances specified by NFPA 30 (2000), in the case of tank surface fires and bund fires, the flame drag and flame tilt may result in event escalation even at moderate wind speeds.
11. For an atmospheric storage tank designed to API 650 (1998) and engulfed by a bund fire, the time for vapour generated to exceed the vent capacity varies from 15 to 30 minutes. External cooling increases the failure time by 10 minutes. This means that the external fire from a leak could escalate to a tank surface fire unless a foam blanket system is used within that time.

The above summary indicates that, unless emergency action is effective within the first 5 minutes for a small pressure vessel containing LPG, or within 15 minutes for an atmospheric storage tank, the potential for escalation is high.

7.5.3 Radiant Heat Impact

In the case of nearby, non-engulfing fires, radiant heat is the mechanism of concern. These situations can be treated using view-factor methods as outlined in section 6.1.4.3. Care needs to be taken to obtain good estimates of flame shape and surface emissivity. View factor estimates need to be accurate.

In the case of steel ‘I’ beams, note that for a critical temperature of 500°C and an incident heat flux of 100 kW/m^2, the 90% failure limit is reached after 20 minutes for beams where the heat discharge area of the beam is 4 times the heat incident area. Where this ratio decreases, times to failure rapidly decrease TNO (1992a).

7.6 STRUCTURAL RESPONSE TO EXPLOSIONS

Buildings, tanks, vessels and other structures can sustain significant damage due to explosion overpressures and impulses. In turn, this can also lead to human injury and fatality. This area of vulnerability analysis is well studied and is complex by

virtue of the blast wave interactions with other nearby structures as well as the many variations in the shockwave or pressure wave profiles.

The key concepts are given in Table 7-10 which outlines issues for consideration in analysing explosion responses.

TABLE 7-10 PRINCIPAL FACTORS IN STRUCTURAL RESPONSE TO EXPLOSIONS

- Blast wave time characteristics: shock and pressure waves
- Blast interaction with structure: diffraction and reflection
- Air displacement: explosion wind and dynamic pressure
- Natural frequency of vibration for structure
- Pressure-impulse characteristics
- Structural materials: brick, steel, wood, concrete structures

Excellent discussions on structural responses to explosions are available from many sources. Useful summary references are given by TNO (1992a), Lees (2001) and CCPS (2001).

A number of useful probit functions have been developed to predict a range of structural responses to explosions. These are given in Table 7-11. These are sometimes based on scarce data and are often related to specific building types. So, again care needs to be exercised in their application. This is the key message of recent explosion and vulnerability reviews (HSE 2000).

TABLE 7-11 PROBIT EQUATIONS - EXPLOSION (TNO, 1992A)

Explosion	Buildings up to 4 storeys	
Minor damage:	$Y = 5 - 0.26 \ln V$	(7.25)
	$V = \left(\frac{4600}{P_s}\right)^{3.9} + \left(\frac{110}{i_s}\right)^{5.0}$	(7.26)
where:		
P_s	= overpressure (Pa)	
i_s	= impulse (½ P_s t_p)	
t_p	= positive phase duration (s)	
Major structural damage:		
	$Y = 5 - 0.26 \ln V$	(7.27)
	$V = \left(\frac{17500}{P_s}\right)^{8.4} + \left(\frac{290}{i_s}\right)^{9.3}$	(7.28)
Collapse:	$Y = 5 - 0.22 \ln V$	(7.29)
	$V = \left(\frac{40000}{P_s}\right)^{7.4} + \left(\frac{460}{i_s}\right)^{11.3}$	(7.30)
Glass breakage:	$Y = -11.97 + 2.12 \ln P_s$ (single pane, older buildings)	(7.31)
	$Y = -16.58 + 2.53 \ln P_s$ (double glazed, newer buildings)	(7.32)

It should be noted that the damage levels refer to work by Jarrett (1968) in the UK and are for brick constructions where:

a) minor damage: refers to window breakage, door displacement and roof damage.
b) major damage: refers to wall cracks, and collapse of some walls
c) collapse: refers to a total collapse of the building.

Prugh (1999) provides a summary of blast impacts through useful charts for a range of damage to industrial structures such as tall columns, reinforced masonry and concrete structures.

7.7 REVIEW

This chapter has presented the basic links between the predictions from effect models and estimation of impact impacts on vulnerable receptors. The chapter has focused on safety related vulnerabilities. There is a significant body of literature dealing with environmental impacts that requires specialized toxicological knowledge.

The techniques for vulnerability analysis rely heavily on field data. In some cases the field data is specific to certain building types or in the case of toxic effects relies on extrapolated or scaled data from animal experiments to predict human impacts. The chapter makes clear that the analyst needs to be aware of the underlying assumptions in the predictive models, and the breadth of data used in their development. Where possible reliable field data is always to be preferred over extrapolated data. The message is: "User beware"!

7.8 REFERENCES

American Industrial Hygiene Association (AIHA) 2004, Available at: http://www.aiha.org/.

American Petroleum Institute. *Guide for Pressure Relieving and Depressuring Systems*, 4th edn, American Petroleum Institute, Washington D.C. API 521: 1997.

American Petroleum Institute. *Welded Steel Tanks for Oil Storage*, 10th edn, American Petroleum Institute, Washington D.C. API 650:1998

Beynon, G.V., Cowley, L.T., Small, L.M. and Williams, I. 1998, 'Fire Engulfment of LPG Tanks: HEATUP, a Predictive Model', *Journal of Hazardous Materials*, vol. 20, pp.227-238.

Birk, A.M. 1988, 'Modelling the Response of Tankers Exposed to External Fire Impingement' *Journal of Hazardous Materials*, vol. 20, pp.197-225.

Dancer, D. and Sallet, D.W. 1990, 'Pressure and Temperature Response of Liquefied Gases in Containers and Pressure Vessels which are Subjected to Accidental Heat Input', *Journal of Hazardous Materials*, vol. 25, pp.3-18.

Davenport, J.N., Richardson, S.M. and Saville, G. 1992, *Thermal Response of Vessels and Pipework Exposed to Fire*, Prepared by Steel Construction Institute for Health & Safety Executive – Offshore Technology Information, OTI 92 610, HMSO, London.

CCPS 2000, *Guidelines for Chemical Process Quantitative Risk Analysis*, 2nd edn, Centre for Chemical Process Safety, AIChE, New York.

de Weger, D., Pietersen, C.M. and Reuzel, P.G. 1991, 'Consequences of exposure to toxic gases following industrial disasters', *Journal of Loss Prevention in the Process Industries*, vol. 4, pp. 272-276.

DIPNR 2003, *Hazardous Industry Planning Advisory Paper No 4: Risk Criteria for Land-use Safety Planning*, NSW Government Bookshop, Sydney, Australia.

Eisenberg, N.A., Lynch, C.J. and Breeding, R.J. 1975, *Vulnerability Model: A simulation system for Assessing Damage Resulting from Marine Spills*, Report CG-D-136-75, Enviro Control Inc., MD., USA.

Gosse, A.J. and Alderman, J. 2001, 'The Effectiveness of Water Deluge Systems in Mitigating Offshore Fires', *35th Loss Prevention Symposium*, American Institute of Chemical Engineers, Houston, Texas, Paper LPS-1a.

HSE 1993, *Toxicology of Substances in Relation to Major Hazards: Hydrogen Fluoride*, Health & Safety Executive, UK.

HSE 1995, *A Review of the Manufacture, Uses, Incidents and Hazard Models for Hydrogen Fluoride*, HSE Contract Research Report No. 79/1995 by WS Atkins Consultants Ltd, Health & Safety Executive, UK.

HSE 1998, *Review of Blast Injury Data and Models*, Research Report 192/1998, Health & Safety Executive, UK, ISBN 0717616177.

HSE 1998, *Review of Test data on the Performance of PFP Materials in Jet Fires*, Offshore Technology report – OTO 97 078, Health & Safety Executive, UK.

HSE 2000, *Efficacy of water spray protection against butane jet fires impinging on liquefied petroleum gas (LPG) storage tanks*, Res. Report 298/2000, HSE, HMSO, Norwich, UK.

Hunt, D.L.M. and Ramskill, P.K. 1985, 'The Behaviour of Tanks Engulfed in Fire - The Development of a Computer Program', *Institution of Chemical Engineers Symposium Series No. 93*, Assessment and control of major hazards, pp. 71-86.

Hymes, I, Boydell, W. and Prescott, B. 1996, *Major Hazards Monograph: Thermal Radiation: Physiological and Pathological Effects*, IChemE, Rugby, UK.

Institute of Petroleum UK 2003, *Guidelines for the Design and Protection of Pressure Systems to Withstand Severe Fires*, March.

Jarrett, D.E. 1968, 'Derivation of the British explosives safety distances', *Annals of the N.Y. Academy of Sciences*, vol. 152, pp. 18.

Lees, F.P. 2001, *Loss Prevention in the Process Industries*, Butterworths-Heinemann.

MHAP 1987, *Chlorine Toxicity Monograph*, Major Hazards Assessment Panel, IChemE., Rugby, UK.

MHAP 1988, *Ammonia Toxicity Monograph*, Major Hazards Assessment Panel, IChemE., Rugby, UK.

Moodie, K. 1988, 'Experiments and Modelling-An Overview with Particular Reference to Fire Engulfment', *Journal of Hazardous Materials*, vol. 20, pp.149-175.

Moodie, K., Billinge, K. and Cutler, D.P. 1985, 'The Fire Engulfment of LPG Storage Tanks', *Institution of Chemical Engineers Symposium Series No. 93*, Assessment and control of major hazards, UMIST, pp. 87-106.

Moodie, K., Cowley, L.T., Denny, R.B., Small, L.M. and Williams, I. 1988, 'Fire Engulfment Tests on a 5 Tonne LPG Tank', *Journal of Hazardous Materials*, vol. 20, pp. 55-71.

Mudan, K. 1989, 'Use of toxicity data in quantitative risk assessment of HF Alkylation Units', *American Institute of Chemical Engineers Summer National Meeting*, August.

National Fire Protection Association. *Standard for Water Spray Fixed Systems for Fire Protection*, National Fire Protection Association, Quincy, Massachusetts, USA. NFPA 15:2001.

National Fire Protection Association. *Flammable and Combustible Liquid Code*, National Fire Protection Association, Quincy, Massachusetts, USA. NFPA30:2000.

Prugh, R.W. 1999, 'The Effects of Explosive blast on Structures and Personnel', *Process Safety Progress*, vol. 18, no. 1, pp. 5-16.

Roberts, T., Buckland, I. and Beckett, H. 2001, 'Directed Water Deluge Protection of Liquefied Petroleum Gas Vessels', Hazards XVI, *Institution of Chemical Engineers Symposium Series No 148*, pp. 193-212.

Roberts, T.A., Medonos, S. and Shirvill, L.C. 2000, *Review of Response of Pressurised Process Vessels and equipment to Fire Attack*, Offshore Technology Report – OTO 2000 051, UK Health & Safety Executive, June.

Rausch, A.H., Tsao, C.K. and Rowley, R.M. 1977, *Third-stage development of the vulnerability model, A simulation system for assessing damage from marine spills,* US Coast Guard Report No. CG-D-5-78.

Schubach, S. 1995, 'Thermal Radiation Targets used in Risk Analysis', *Transactions of Institution of Chemical Engineers*, vol. 73, Part B, pp. 265-270.

Schubach, S. 1995, 'Comparison of probit expressions for the prediction of lethality due to toxic exposure', *Journal of Loss Prevention in the Process Industries*, vol. 8, no. 4, pp. 197-204.

Standards Australia. *The Storage and Handling of Flammable and Combustible Liquids*, Standards Australia. AS1940:1993.

Standards Australia. *Pressure vessels*, Standards Australia, ISBN 0733710123. AS1210: 1997.

Schoen, W. and Droste, B. 1988, 'Investigations of Water Spraying Systems for LPG Storage Tanks by Full Scale Fire Tests', *Journal of Hazardous Materials*, vol. 20, pp. 73-82.

Steel Construction Institute 1992a, *Experimental Data Relating to the Performance of Steel Components at Elevated Temperatures*, Prepared for the Health and Safety Executive – Offshore Technology Information, OTI 92 604, HMSO, London.

Steel Construction Institute 1992b, *Passive Fire Protection: Performance Requirements and Test Methods*, Prepared for the Health and Safety Executive – Offshore Technology Information, OTI 92 606, HMSO, London.

ten Berge, W.F. 1986, 'Concentration-time mortality response relationship of irritant and systemically acting vapours and gases', *Journal of Hazardous Materials*, vol. 13, pp. 301-309.

TNO 1992a, *Methods for the determination of possible damage*, CPR16E, Director General of Labour, The Netherlands, ISBN 90-5307-052-4.

TNO 1992b, *Methods for the Calculation of Physical Effect*, CPR 14E, Director-General of Labour, Voorburg, The Netherlands.

USEPA 2002, *Short-term methods for estimating the chronic toxicity of effluents and receiving waters to freshwater organisms*, US-Environmental Protection

Agency, Office of Water, 4th edition, EPA-821-R02-013, October, Washington DC.

USCG 1980, *Study to Modify the Vulnerability Model of the Risk Management System*, Report CG-D-22-80, Washington DC, US Department of Transportation.

Venart, J.E.S. 2000, 'Boiling Liquid Expanding Vapour Explosions (BLEVE) - Possible failure mechanisms and their consequences', Hazards XV, *Institution of Chemical Engineers Symposium. Series No.147*, pp. 121-137.

Warren Centre 1986, *Major Industrial Hazards: Technical Papers*, Sydney University, Australia, ISBN 09492629-37-9.

Withers, R.M.J. and Lees, F.P. 1985a, 'The assessment of major hazards: the lethal toxicity of chlorine, Pt 1: Review of information on toxicity', *Journal of Hazardous Materials*, vol. 12, no. 3, pp 231.

Withers, R.M.J. and Lees, F.P. 1985b, 'The assessment of major hazards: the lethal toxicity of chlorine, Pt 2: Model of toxicity to man', *Journal of Hazardous Materials*, vol 12, no. 3, pp 283.

World Bank 1988, *Techniques for assessing industrial hazards*, Technical Report 55, Washington DC.

7.9 NOTATION

$\hat{C}$	Concentration, ppm
AIChE	American Institute of Chemical Engineers
AIHA	American Industrial Hygiene Association
API	American Petroleum Institute, USA
BLEVE	Boiling Liquid Expanding Vapour Explosion
C	Concentration, mg/m^3
CCPS	Centre for Chemical Process Safety, AIChE
Cl_2	Chlorine
CO	Carbon monoxide
COC	Chemical of Concern
DIPNR	Department of Infrastructure, Planning and Natural Resources, NSW, Australia
DTL	Dangerous Toxic Load
ERPG	Emergency response planning guidelines
HCN	Hydrogen Cyanide
He	Helium
HF	Hydrogen Fluoride
HSE	Health and Safety Executive, UK
IChemE	Institution of Chemical Engineers, UK
IDLH	Immediately dangerous to life or health
kg	kilograms
kW	kilo-Watts
kW	kilo-Watts
kW/m^2	kilo-Watts per square metre
LC_{50}	Lethal concentration for 50% mortality to exposed species
LD_{50}	Lethal dose for 50% mortality to exposed species
LD_{min}	Minimum lethal dose

LPG	Liquefied Petroleum Gas
mg/L	milligrams per Litre
mg/m^3	milligrams per cubic metre
MHAP	Major Hazards Assessment Panel, UK
N_2	Nitrogen
NFPA	National Fire Protection Association, USA
NH_3	Ammonia
nm	nano-metres
NOAEL	No Observed Adverse Effects Level
NOEL	No Observed Effects Level
OSHA	Occupational Safety and Health Administration, USA
P_0	Atmospheric pressure, Pa
Pa	Pascals
PEL	Permissible exposure limits
PFP	Passive Fire Protection
ppm	parts per million
P_S	Peak overpressure, Pa
PSV	Pressure Safety Valve
q	Heat flux (W/m^2 or kW/m^2)
RTECS	Registry of Toxic Effects of Chemical Substances
s	seconds
SO_2	Sulphur dioxide
STEL	Short Term Exposure Limit
TLV	Threshold Limit Value
TNO	Netherlands Organization of Applied Scientific Research
t_p	Positive phase duration, s
USCG	United States Coast Guard
USEPA	United States Environment Protection Agency
W/m^2	Watts per square metre