

FLIXBOROUGH VERSUS SEVESO - COMPARING THE HAZARDS

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The control of major hazards in the chemical industry requires identification of the relative quantities of different substances which pose a similar hazard, even when the nature of those hazards are very different. A practical approach to this difficult problem is presented which combines a study of past accidents with simple calculations, and refers the various hazards to a common "damage zone", taken as being an area of one square kilometre. The derived quantities are in broad agreement with those which will be notifiable under proposed U.K. regulations. Two possible problem areas are materials in transit and the identification of toxic reaction intermediates or byproducts.

INTRODUCTION

Recent major accidents in chemical plants or involving chemicals in transit, such as those at Flixborough, Seveso or San Carlos de la Repita in Spain, have led to political pressure to ensure that adequate safety standards are being met by the chemical industry. Proposed regulations to control static installations are under discussion both in Britain (1) and in the E.E.C. as a whole (2).

Any system of control, whether voluntary or regulatory, requires identification of the relative quantities of different substances which pose a similar potential hazard, even when the nature of those hazards are very different. The purpose of this contribution is to present a semi-empirical approach to this difficult problem; a study of past accidents ("experiment evidence") is combined with simple calculations (theory) based on clearly defined assumptions and conditions.

The type of installation which could potentially constitute a "major hazard" is defined here as one where a sudden loss of containment or process control could lead to a significant threat to the safety of the public, employees or the environment. The method proposed for comparing different materials is based on the concept of a common "damage zone" beyond which the effects on people are tolerable. Distinction is made between situations where the damage potential is short term, such as a release of toxic gas, an explosion or major fire, and those involving a release of toxic substance which may contaminate an area of land for some time. Comparing the immediately catastrophic accident, such as that at Flixborough, with the more insidious threat of long-term damage, as at Seveso, is particularly problematical.

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REVIEW OF MAJOR ACCIDENTS

The discussion begins with an examination of available information on past accidents, aimed at assessing its usefulness as a guide to the relative hazards posed by different substances. Two preliminary comments are necessary:

- the number of serious accidents recorded worldwide is relatively small, particularly when compared to the quantities of chemicals manufactured and used
- very few of the accidents reviewed here occurred in the United Kingdom. The safety record of the chemical industry in the U.K. is excellent.

Liquefied toxic gases

Information on accidents which involved a release of toxic gas and which resulted in four or more deaths is summarised in table 1. Although this listing may not be complete, a number of salient points emerge:

- all but two of the accidents listed involved the complete failure of the basic tank and the virtually instantaneous release of its content. Such accidents are uncommon, but account for the great majority of deaths caused by toxic gas releases.
- a much more common accident is that which allows the liquid to escape slowly, for example, when a tank is punctured, valves damaged or a pipeline springs a leak. Such an accident will release the pressure and allow some liquid to flash off, the remaining liquid evaporating more slowly. If liquid spills onto the ground, evaporation will be more rapid. This gradual release of the gas results in generally lower casualty rates than when the basic tank fails. Note that if the liquid is completely refrigerated, then puncture of the tank above the liquid level will result, not in an initial flash of vapour and entrained liquid, but simply in slow evaporation.
- it is not possible to relate the severity of past incidents, in terms of human casualties, either to the absolute quantity of gas released or even to the apparently more important rate of gas release. This is undoubtedly due in part to providence, that the wind happened to disperse the cloud over an area of low population density, and in part to the evacuation procedures adopted.
- a detailed analysis of accident records is hampered by incomplete reporting. This is particularly true of "near miss" situations, where a serious accident is averted by prompt action or by good luck.
- most recorded accidents have involved either chlorine or ammonia: this should not be taken to mean either that accidents involving other gases have not occurred or that they pose less of a hazard if released, but rather that their use has been and still is less widespread.
- it is not possible to use the information on past accidents to compare in any detail the relative quantities of different gases which pose a similar hazard.

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Table 1. Serious Incidents Involving Releases of Liquefied Toxic Gases

Year	Location	Description	Quantity Lost (Tonnes)	Fatalities	Casualties
A. Failure of the Basic Tank					
(a) <u>Chlorine</u>					
1926	St. Auban, France	Tank burst - no details	25	19	?
1939	Zarnesti, Roumania	Tank burst - no details	21/25	68	400
1947	Rauma, Finland	Tank burst from over filling	30	19	120
1952	Wilsum, Germany	Tank burst - no reason given - converted oil boiler	15	7	200 +
1975	USA	Tank burst - ex rail tank car used in chlorine recovery system	?	4	89
1978	Florida, USA	Rail car ruptured in collision	25	8	90
(b) <u>Phosgene</u>					
1928	Hamburg, Germany	Cover flew off the tank - old wartime stock	11	11	200 +
(c) <u>Ammonia</u>					
1929	? USA	Tank ruptured - no details	?	35	?
pre 1952	?	Tank exploded - possibly failure of a welded seam	?	15	20 +
1968	Lieven, France	Semi-trailer road tank suddenly ruptured	19	5	15
1969	Nebraska, USA	Rail tank car disintegrated after a collision	64	6	53
1973	Potchefstroom, S. Africa	Static tank burst while being filled	38	18	65 +
1976	Texas, USA	Road tanker crashed from elevated roadway	19	6	200
(d) <u>Sulphur Dioxide</u>					
1938	Finland	Rail car ruptured in collision	?	13	?
B. Other Incidents Resulting in Four or More Deaths					
(a) <u>Chlorine</u>					
1974	Spain	Drums rolled and knocked off a tank plug	1	4	100 +
1957	USA	No details known	?	8	210 +

Liquefied flammable gases

A release of liquefied flammable gas may result in an explosion by at least three separate mechanisms, although the distinction is not always clear in the description of past accidents:

- a confined explosion may occur when the release is inside a building. Such incidents are both serious and relatively common, but in general they do not affect the general public beyond the factory fence.
- a boiling liquid - expanding vapour explosion or BLEVE occurs primarily when a tank of liquefied gas, under pressure, is heated in an external fire following an accident, until it vents and torches. For an explosion to occur the initial heating of the venting tank must be sufficiently intense to cause the internal pressure to rise above the tank's bursting pressure, even with venting. Damage is caused by the blast wave, by the scattered fragments and by the spectacular airborne fireball. Most recorded accidents which resulted in a BLEVE have involved rail tank cars or road tankers. In one study, the damage from 84 explosions is evaluated (3).
- an unconfined vapour cloud explosion may occur when a massive quantity of flammable vapour is released to the atmosphere. Both the Flixborough, and the San Carlos de la Repita road tanker, explosions were of this type. The mechanism of explosion is not completely understood, but an examination of accident records (table 2) does give a good idea of the circumstances when an explosion is to be expected. Three conditions must apparently be fulfilled:
 - (a) the cloud of vapour must be large, a lower limit of about 5 tonnes being suggested for normal hydrocarbons
 - (b) the rate of release of vapour must be large, of the order of 1 tonne/minute or more
 - (c) a significant delay to ignition, usually greater than 30 seconds, is required so that a large cloud has time to form.

If the cloud of vapour is small, or if ignition occurs immediately then the result is either a fireball or a flash of fire back to the leak site and torching of the leak. Such a fire may of course initiate a BLEVE.

Other explosions

Flammable gases are only one of the possible causes of explosions in industry. Others include:

- bursting pressure vessels
- bursting reaction vessels

Table 2. Unconfined Vapour Cloud Explosions

Including only selected incidents prior to 1970

Date	Location	Process	Material Released	Liquid Spill (Tonnes)	Vapour Qty (Tonnes)	Cloud Dia. (m)	Cloud Yield (Tonnes)	Ignition Delay	Fatalities	Serious Injuries	Property Loss (\$)
1944	Cleveland, Ohio	Storage	LNG	(2,200)	180	-	-	-	213	-	Sev \$M
1943	Ludwigshafen	Railcar rupture	Dimethyl ether	27.5	(27.5)	-	-	-	245	2,500	\$15
1959	Naldrin, Georgia	"	LPG	27.5	18	-	-	-	23	-	\$0.2
1962	New York	"	LPG	(27.5)	17	150	-	mins	10	17	\$0.2
1964	Nevada	"	Hydrogen	-	0.10	-	0.03 (18)	-	0	0	\$4.8
1966	W Germany	"	Methane	-	0.3*	60+	2-3	secs	3	83	\$16K
1966	Louisiana	"	Butadiene	1	1	15+	-	-	3	63	\$3
1966	Feyzin, France	Synthetic Rubber	Propane	1	1	-	-	-	18	-	\$35
1967	Lake Charles, Louisiana	Propane storage	Isobutylene	11	11	140	10 (108)	15 mins	7	-	\$28
1967	Lake Charles, Louisiana	Refinery alkylation	Hydrocarbons	(50)	50	18	(-)	>13 mins	2	70	\$35
1968	Perris, Holland	Heated sllops tank	Propane	27	45 (108)	100	45 (108)	13 mins	0	4	\$30
1970	Port Hudson, Missouri	Refinery, Y-oil units	Hydrocarbons	(900)	(900)	100	50 (48)	-	0	0	-
1970	New Jersey	"	Hydrocarbons	(900)	(900)	100	50 (48)	-	0	0	-
1971	Louisiana	"	Ethylene	4	4	-	1.5 (-)	-	0	8	\$2.6
1971	Texas	"	Polyethylene	-	0.5*	-	-	-	3	7	\$8.8
1971	Texas	"	Butadiene	-	12	-	-	8-10 mins	1	6	\$0.16
1971	Texas	"	Petroleum Refinery	-	-	-	-	-	-	-	-
1971	Tennessee, England	"	Hydrogen/Naphtha	65	(53)	150	1-2.5 (0.38)	>5 mins	0	230	\$7.5
1972	St Louis, Illinois	Tank car ruptures	Propylene	-	-	-	-	-	37	53	\$84
1972	Brazil	"	Butane	-	-	-	-	-	1	-	\$16
1972	Japan	Refinery	Ethylene	1,100	-	20	-	-	1	23	-
1973	Tokyo, Japan	"	Vinyl Chloride	27.5	-	-	-	-	6	-	\$2.2
1973	St Almand-les-Eaux, Fr.	Transport Incident	Propane	-	-	30+	-	-	7	-	\$10
1973	Lodi, N Jersey	"	Hydrocarbon vap	-	10	-	-	-	-	0	\$1
1973	Koln, W Germany	"	Vinyl Chloride	(25)	-	15	-	-	0	0	\$1
1974	Florida	"	Propane	-	-	-	-	-	0	0	-
1974	Climax, Texas	"	VCM	-	75	-	-	-	0	0	-
1974	Decatur, Illinois	"	Propane	65	65	-	5-10 (23)	>5 mins	7	-	\$15
1974	Fixborough, England	Cyclohexane oxidation	Cyclohexane	(50)	80	1,000	300 (25-504)	>1 min	28	89	\$100
1974	Illinois	"	Isobutane	80	80	1,000	300 (25-504)	9 mins	7	356	\$18.4
1974	Mississippi	Railcar puncture	Butane	-	2*	-	-	-	0	24	-
1974	England	Storage	Ethylene	-	1-3	-	-	-	0	2	-
1974	England	"	Polyethylene	(96)	-	-	-	3 mins	0	235	\$13.3
1974	Texas	Tank car puncture	Butadiene	-	-	-	1 (18)	-	2	9	\$13.2
1974	Baumont, Texas	"	PCs hydrocarbons	80	-	-	-	-	6	13	\$26.5
1975	Antwerp, Belgium	Isoprene	Ethylene	-	5.5	50	-	-	14	104	\$40
1975	Beek, Holland	"	Propylene	-	-	-	-	-	0	4	\$2.75
1975	Germany	Refinery hydroformer	Hydrogen/Naphtha	-	0.3	10	0.02 (0.24)	-	0	2	\$10
1975	California	Hydrogen	Oil vapours	-	-	-	-	-	16	-	-
1975/6	Philadelphia	Oil refining	Light hydrocarbons	-	-	-	-	-	1	15	\$18
1976	Czechoslovakia	"	Ethylene	-	-	-	-	-	12	40	-
1978	Maverly, Tennessee	"	Ethyl Alcohol	(60)	(60)	-	-	-	0	0	-
1978	Louisville, Arkansas	"	Propane	(100)	(100)	-	-	-	0	0	-
1978	San Carlos de la Repita	Railcar puncture	Vinyl Chloride	-	-	-	-	-	180	200+	-
1978	Spain	Road transport	Propylene	(50)	(50)	-	-	-	0	0	-
1978	Mexico City	"	LPG	(30)	(30)	-	-	-	8	-	-

References 4-8. Notes: - Information not available
* Explosion partially confined

- dust explosions
- unstable and very reactive materials

The potential hazards are well known and plants are designed to minimise the risk, although major accidents have occurred. In the last case in particular, explosions have been less frequent than simple theory might lead one to expect. For example, ammonium nitrate has caused major explosions, including that at Oppau in Germany in 1923 which killed 1,100 people; however, an explosion has only occurred when three conditions have been fulfilled simultaneously:

- the quantity of material is large, greater than about 250-500 tonnes
- an impurity such as an organic material is present
- initiation is caused by a detonator or by external heating.

Fires

Fires involving flammable liquids are relatively common, particularly in the oil refining industry. However, it is rare for the effects of such fires to extend far beyond the factory fence. If a fire occurs during transportation, when the liquid is not retained within a bund, then much damage can be done by burning, flowing streams of liquid.

Materials which are spontaneously flammable on contact with air rely for their safety on adequate containment. Materials such as aluminium alkyls could potentially pose a major hazard if present in sufficient quantity. Another hazard is the release of toxic fumes in a fire: the dangers of materials such as polyurethane foams and compound fertilisers are well known to the fire services.

Liquid oxygen may, if released, cause vigorous fires or even explosions if it comes in contact with both a flammable material and a source of ignition. A release, at a rate of about 200 tonnes per hour, at New Martinsville, West Virginia in February 1978 spread through a gully and, about 20 minutes after the initial pipe rupture, claimed the lives of two pedestrians and of three people in a lorry in separate incidents.

Extremely toxic materials

Accidents involving the contamination of an area with extremely toxic materials had until recently not been seriously considered in the context of potential major hazards in the chemical industry. However, the accident at Seveso in Italy on July 10th 1976 focussed public attention on this issue. The bursting disc on a 2,4,5-trichlorophenol reactor vented, and an aerosol cloud of gases and vapours, together with entrained liquid droplets and solid particulates, spread over the surrounding area. The only damage initially expected was that caused by the caustic soda and by the phytotoxic trichlorophenol in the cloud; however, much more serious effects soon became apparent, caused by the extremely toxic contaminant 2,3,7,8-tetrachlorodibenzo-p-dioxin (TCDD). The consequences of this incident are still uncertain nearly four years later. Many animals died but the initial human symptoms, mainly chloracne, have now largely disappeared (9). Long term effects including deaths from cancer may result, but any causative relationship will probably never be conclusively proven.

An area of some 100 hectares of land is still contaminated and uninhabitable.

One of the worrying aspects of the Seveso incident is that TCDD was only a very minor byproduct of the normal reaction; its presence in significant quantity was due to an unwanted side reaction which occurred under fault conditions, the exact cause still being unknown (10). The prediction of other processes where a similar accident could occur is thus fraught with difficulty. In a complex reaction mixture it may be difficult to identify all the chemicals normally present, never mind those which could conceivably occur under fault conditions. The prospect of screening all such materials for toxicity is daunting.

The Seveso incident is not unique. Previous accidents in trichlorophenol manufacture also resulted in TCDD contamination and even deaths, but the effects were always confined within the factory building itself. A similar but little known incident occurred just two months after that at Seveso, at Manfredonia, also in Italy. An explosion at a petrochemical plant released a cloud of toxic substances which contained arsenic dioxide. After a few days delay, decontamination was initiated, first inside the plant and then over an area of 500 hectares, larger than that affected at Seveso. Thanks to the prompt action and active cooperation of the local authorities and the factory management, the consequences of the accident were minimised (11).

QUANTITIES OF CHEMICALS WHICH POSE SIMILAR HAZARDS

Principles and definitions

It is extremely difficult to compare the consequences of accidents involving different chemicals, particularly if, for example, one is a toxic gas and the other a flammable liquid capable of creating an unconfined vapour cloud explosion. Nevertheless, some idea of the relative quantities of different substances which represent a similar "major hazard" can be obtained by the use of simple calculations based on clearly defined assumptions and conditions. It is first necessary to establish some common benchmark of hazard against which each material can be measured. There are three basic alternatives:-

- the quantity of material which would result in a defined death toll if released under standard conditions over an area with a given population density.
- the quantity of material which, if released under standard conditions, would produce a "damage zone" covering an area of defined size
- an empirical estimate of the "major hazards" quantity of one material, based on past experience, combined with a theory relating the various parameters so that predictions can be made for other materials.

The first of these benchmarks, based on the likely death toll, is particularly problematical as it requires assumptions to be made on the likely evacuation procedures, the degree of panic prevailing and the variable human response to toxic exposures. In addition, population densities may vary in practice from zero to many thousands per hectare, and may also depend on the time of day.

For such reasons, the second benchmark based on a common "damage zone" is preferred for use here. For materials where the damage potential is primarily short term, the damage zone is defined as:

- an area of one square kilometre beyond which the concentration of toxic gas, the peak overpressure from an explosion or the radiation intensity from a fire are at a "reasonably safe" level.

The term "reasonably safe" must be defined in each case. The choice of an area of one square kilometre is arbitrary, but the principles will remain the same whatever area is chosen.

The definition needs to be expanded for the case of contamination of an area of land by an extremely toxic material. The main hazard arises from continuing contact over a period of time. The damage zone is defined as:

- an area of one square kilometre of land which is rendered uninhabitable for a period of one year. (If the period of contamination is likely to be less than one year, then the area will increase correspondingly).

It should be noted that the consequences of an accident may be minimised both by evacuation and by decontamination measures.

In some cases, it is only possible to derive the relative quantities of different chemicals which pose a similar hazard and it is then necessary to use the third benchmark. In addition, the evidence of past accidents often shows that the quantity of a material, which could in theory affect an area of 1 km² if it were to explode, cannot in fact produce an explosion. In such cases, the major hazard quantity is set at the threshold level below which an explosion will not occur, even though the damage zone so produced would exceed 1 km².

Application

These principles have been applied to calculate the threshold quantities of a large number of bulk chemicals which could pose a "major hazard". The more significant results are summarised in table 3, where they are compared to the quantities which will be notifiable as constituting a "hazardous installation" under proposed regulations (1). The agreement is generally good, although there are some differences by a factor of up to 5.

The rationale and assumptions used in deriving these quantities are now summarised for the main categories of hazard.

Toxic gases. The principal method of calculation used classical wind dispersion theory and a hazardous cloud defined by a concentration at the periphery of twice the short term exposure limit (STEL) for occasional 15 minute exposures at work. This ad-hoc concentration limit was used in lieu of the more relevant "public emergency exposure limit" which in general has not yet been defined. Three points should be noted:

- it is assumed that the tank is punctured above the liquid level: if the complete tank was to disintegrate, then an equivalent hazard would be provided by a much smaller quantity, perhaps 2 tonnes of chlorine rather than 10.

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Table 3. Recommended Criteria for Major Hazards

All quantities in tonnes unless otherwise stated

CATEGORY AND SUBSTANCE(S)	This Paper	UK Draft Regulations (1)
<u>Toxic Gases</u>		
carcinogenic	2	2
Fluorine	2	-
Boron trifluoride	2	-
Chlorine	10	10
Hydrogen chloride	10	-
Hydrogen sulphide	10	-
Hydrogen bromide	20	-
Hydrogen cyanide	20	20
Sulphur dioxide	25	20
Nickel carbonyl	30	-
Bromine	30	40
Nitrogen dioxide	40	-
Ammonia	100	100
<u>Highly Reactive Materials</u>		
Acetylene	1	-
Hydrogen	1	2
Ethylene Oxide	5	5
Propylene Oxide	10	5
Organic Peroxides	5	5
Nitrocellulose compounds	50	50
Bulk polymerisable materials	50	-
Ammonium nitrate	250	500
Sodium chlorate	500	500
Liquid oxygen	500	1,000
<u>Mixed Hazards (Toxic and reactive)</u>		
Acrylonitrile	20	20
Carbon disulphide	20	20
<u>Flammable Materials</u>		
Flammable gases not specified elsewhere	5	15
Flammable liquids above their boiling point (at 1 bar pressure) and under pressure greater than 0.34 bar gauge		
(i) hydrocarbons	10	(20)
(ii) halogenated hydrocarbons	20	(20)
Liquefied gases used as fuel (LPG - propane/butane)	(10)	30
Refrigerated flammable gases which have a boiling point below 0°C at 1 bar pressure and are wholly or partly liquefied at a pressure of 0.34 bar gauge or less	50	50
Flammable liquids with flashpoint less than 21°C	5,000	10,000
<u>Pressure Vessels</u>		
Stored pressure energy (volume times pressure) at a pressure greater than 50 bar	10,000 m ³ -bar	10,000 m ³ -bar
<u>Dust Explosions</u>		
A silo for the storage of grain, animal feedstuff, flour, refined sugar or powder	volume 50,000 m ³	-
<u>Materials which could emit toxic gases in a fire</u>		
Flammable brominated or chlorinated material, including solvents and plastics	100	-
Any organic compound containing isocyanato- isothiocyanato-, cyano- or isocyano- groups	100	-
Any organic compound containing more than 20% by weight of sulphur	250	-
Plastic foam	250	500
Compound fertilisers	250	500
Any organic pesticide or herbicide	250	-
<u>Very Toxic Materials</u>		
Letal to man in quantities less than 1 milligram	-	0.1
Any material which could lead to an airborne release of a toxic substance (LD ₅₀ in mg/kg body weight)	400 LD ₅₀ (oral) 200 LD ₅₀ (dermal)	-
<u>Toxic and Persistent Materials</u>		
Any material which could lead to an airborne release of a toxic and persistent substance (half-life t _{1/2} in weeks)	400 LD ₅₀ (oral)†t _{1/2} 200 LD ₅₀ (dermal)†t _{1/2}	-
<u>Carcinogenic Materials</u>		
Any selected carcinogenic material	not specified	

- it is assumed that the liquid is stored at ambient temperature under its own vapour pressure. The appropriate major hazard quantity for a refrigerated liquid might be rather higher, while that for a pressurised gas at high temperature would be much lower.
- the "damage zone" of one square kilometre is approximately sausage-shaped and points downward.

This basic calculation was supplemented by several other approaches:

- for heavy gases, several recent theoretical models were reviewed (12,13). The results suggest that, for the average weather conditions assumed here, classical theory overestimates downwind spread of the cloud by about 20-40%, and underestimates lateral spread by a factor greater than 2. Thus the overall area of hazard may be underestimated; allowance was made for this in appropriate cases.
- it can be shown that the quantity of any volatile liquid required to produce a vapour cloud of constant area is approximately proportional to the ratio χ/Mp , where χ/M is the public emergency exposure limit in parts per million and p is the vapour pressure. Relative quantities of a wide range of liquids were calculated using both the STEL and animal LC_{50} values to define χ . These were converted to absolute values by defining the major hazard quantity of chlorine as 10 tonnes.

Liquefied flammable gases. A release of liquefied flammable gas may result in a confined or an unconfined explosion or a BLEVE. In general, the greatest damage potential is associated with an unconfined explosion. The evidence of past accidents suggests that a large cloud, of at least 5 tonnes of vapour for a normal hydrocarbon but perhaps as little as 1 tonne for hydrogen, acetylene or ethylene oxide, is required if an explosion is to occur. A cloud of this size will give damage over an area rather larger than one square kilometre.

For most hydrocarbon liquids held under pressure at ambient temperature, the quantity of liquid necessary to give an initial vapour cloud size of 5 tonnes is in the range 6-20 tonnes. This applies equally to LPG as to other hydrocarbons. Our suggested major hazard inventory of 10 tonnes for hydrocarbon gases compares to the notifiable quantities (1) of 20 tonnes, or 30 tonnes for LPG. For refrigerated gases, the surface area of the spill is very important. An initial cloud size of 5 tonnes will be formed from a pool of radius about 30m on soil.

A BLEVE results in three distinct damage mechanisms:

- the blast wave is usually fairly minor
- the most spectacular damage mechanism is the fireball, which is due to subsequent massive burning of the contents of an exploded tank in the air. Using empirical data given by High (14) and a safe distance of two fireball diameters from the edge of the flame (15), a major hazard quantity of 200 tonnes is calculated.
- missile damage can be severe as large fragments can be scattered over long distances due to the ductile nature of the tank's rupture and the rocketing of pieces by reaction forces. From

an examination of 84 explosions, Siewert (3) recommended a safe evacuation radius of 600m (giving an area about 1 km²) in all cases where a tank-car containing a liquefied flammable gas is being heated in an external fire.

Other explosions. The method used to calculate the damage potential from explosions is based on the classical method of TNT equivalence. The damage zone is defined as that beyond which the probability of serious damage is less than 0.05, corresponding to a peak overpressure of 2 kN/m² (16). It can then be shown that a damage zone of area 1 km² corresponds to an inventory of material with a TNT equivalence of 2 tonnes. If a less conservative definition of damage zone is used, with a peak overpressure at the periphery of 5 kN/m² giving some structural damage, then the TNT equivalence is increased to about 8 tonnes.

This method of calculation has been applied to a wide range of unstable and very reactive materials. In general, the quantities which could theoretically give blast damage over an area of 1 square kilometre are quite small, although the evidence of past accidents often points to a much higher threshold quantity which must be present if an explosion is actually to occur. Exceptions, where quantities of 5 tonnes could produce a serious explosion, include ethylene oxide and organic peroxides.

General criteria are listed in table 3 for both pressure vessel and dust explosions, but not for reaction vessel explosions. The identification of chemical processes where runaway reactions could conceivably lead to explosions of "major hazard" proportion would be difficult and time consuming.

Fires. A large fire involving flammable liquids in a bund will cause damage at a distance primarily by radiating heat. The damage zone is defined here by a radiation intensity at its periphery of 4,000 watt/m², which can be tolerated by personnel for about 30-60 seconds. This suggests that a circular pool fire of diameter about 90m will constitute a major hazard, giving a quantity of 5000.h tonnes, where h is the height of the bund in metres. The definition of a standard "major hazard" quantity is difficult. As the escape time even at a distance of 500m from the fire is less than 1 minute, a conservative value of 5,000 tonnes is suggested here.

In the absence of containment, the hazards, particularly from flowing streams of liquid, are greatly enhanced: the major hazard quantity during transportation should therefore be considerably lower than 5,000 tonnes.

Many chemicals decompose in a fire with the emission of toxic fumes. When comparing such materials with the toxic gases themselves, several points should be noted:

- the rate of release of volatile gases in a fire might be much lower than if they were released from storage under pressure
- conversely, gases which are relatively involatile might be released more quickly in a fire
- the hot combustion gases will dilute the toxic gases and disperse them upwards more quickly than in a simple release. The effect is more complex for the dense gases which normally spread largely under their own weight.

The major hazard inventories in table 3 were based on the quantities which could evolve x times the major hazard inventory of the toxic gas in question. Two values of x were gestimated, namely 10 for normally volatile gases and 2 for relatively involatile gases (which are liquids at room temperature).

The major hazard quantity of liquid oxygen is particularly difficult to estimate. Theoretical considerations might yield a quantity about 1000 tonnes, while the possible knock-on effects of spreading fires and the evidence of a recent major accident would suggest a rather lower figure. On balance, a value of 500 tonnes was selected here.

Extremely toxic materials. The calculation of major hazard quantities for materials such as TCDD poses many problems. Although some theoretical work has been published (17, 18), a very simple approach based on a gaussian distribution pattern of contamination was preferred here. This suggests that the major hazard quantity Q, in kg, may be expressed as

$$Q = \frac{k C_L}{t_2}$$

where k is a constant

C_L is the maximum permissible concentration of the material in mg/m^2

and t is the "half-life" of the material in weeks

This expression raises as many problems as it solves. For example:

- the concentration limit C_L has not generally been defined. Experience at Seveso suggests that $5 \mu\text{g}/\text{m}^2$ for TCDD is the "acceptable" level outside buildings. In practice, the best which can be done is to relate C_L to animal toxicity data. This is particularly difficult if the material is suspected of being carcinogenic even at low, single doses
- what is meant by the "half-life" t_2 ? For organic materials, the half-life in soil may be measured, but inorganic materials do not degrade. Is removal from the surface sufficient? Even readily biodegradable materials will persist if deposited on buildings. Photodegradation may be relevant in some cases.

The criteria based on this approach and shown in table 3 are far from ideal. They require a knowledge of toxicity and perhaps also persistence data which would be difficult to acquire, even if a satisfactory definition of the latter could be achieved. An alternative strategy would be to define broad bands of toxicity corresponding to a certain inventory limit. For carcinogenic materials, the only feasible approach would be to list selected materials and appropriate quantity limits.

DISCUSSION AND CONCLUSIONS

A practical working method has been presented which enables one to compare the relative quantities of different materials which could potentially pose a similar "major hazard". The method combines a study of past accidents with simple calculations, and refers the various hazards to a common "damage zone", taken as being an area of one square kilometre.

The primary purpose of this study was the identification of threshold quantities of materials above which some measure of independent control would appear prudent. It was thus general in approach, and the results should not be applied directly to any specific chemical plant. Quantities of materials far in excess of those derived here can be and are handled safely, while much smaller quantities could, in certain unfavourable circumstances, give rise to a major accident. When any potentially hazardous material is being handled, there is no substitute for a detailed hazard assessment study.

Any attempt to simplify a complex problem must have its limitation, and this paper is no exception. In addition to the many assumptions build in to the individual calculations, several general points should be noted:

- this paper was concerned mainly with the magnitude of potential hazards, and not with the likelihood or risk of an accident happening. This approach is justified in this instance, as the purpose of independent control is to ensure that appropriate measures are taken to reduce the risk to an acceptable level
- the choice of a hazard area of one square kilometre is arbitrary. A comparison of our results with the proposed notifiable quantities (1) however suggests that such an area corresponds to official thinking. Stating the damage zone explicitly in this way should enable a more informed public debate of safety issues.
- the location of the damage zone varies with the type of hazard. For example, an explosion will usually produce a circular damage area centred at or near the storage location. A cloud of toxic gas, on the other hand, will give an elongated hazard area pointing downwind: the total area which could potentially be affected is thus larger. Such considerations are vital to planning authorities.
- the comparison of short term hazards with those involving potential long term damage presents many conceptual difficulties. The relative rating of the Flixborough and Seveso accidents on some hypothetical "Richter scale of disasters" is a matter of personal and political judgement. The proposed approach here takes a fairly neutral stance in this particular debate, treating both types of accident as equally undesirable.

The threshold quantities which could constitute a major hazard, as derived here, compare well with those which will be notifiable as constituting a "hazardous installation" under proposed regulations in Britain (1). A few exceptions may be noted:

- major hazard quantities of 10 tonnes for hydrogen chloride and 2 tonnes for fluorine are suggested here
- owing to the possibility of explosive self-heating reactions due to polymerisation, a major hazard quantity of 50 tonnes for "bulk polymerisable materials" is suggested
- the quantities suggested here for flammable gases and liquids are generally lower than those in the regulations

- six separate major hazard categories are suggested for materials which could give rise to a toxic gas in the event of a fire. Of these categories, only two are included, with rather higher inventory limits, in the draft regulations
- the treatment of very toxic materials suggested here is more comprehensive but perhaps less pragmatic than that in the regulations. The regulations give a very low threshold quantity for the most toxic materials, but do not control materials with an LD₅₀ greater than about 50 ug/kg body weight.

The system currently proposed for the control of hazardous installations represents a reasonable balancing of interests between industry and the general public. However, this discussion pinpoints at least two respects in which the regulations are either lacking or may prove difficult to implement:

- the regulations will apply only to hazardous installations, not to materials in transit. For example, a 10 tonne chlorine storage tank will be notifiable, but the 15 tonne tanker which services it can travel wherever it likes. The risk of an accident for a road or a rail tanker must be greater than for a static storage tank, irrespective of design considerations. In addition, the area around a hazardous installation is known to be at risk, and appropriate precautions can be taken: a transport accident can happen almost anywhere. A similar system of notification and survey could be applied to regular shipments of defined quantities of materials between a producer and user factory. Among the factors which should be considered are (19):

- design of tankers
- load size
- road vs rail transport
- route taken
- refrigerated vs pressurised storage
- for liquefied gases

- the regulations are at present vague in respect of very toxic materials. One problem in implementing any system of control is the difficulty of identifying all the possibly toxic intermediates or byproducts present in a reaction mixture or which could be formed under conceivable fault conditions.

Acknowledgements

The author is grateful for helpful discussions with colleagues from many organisations: Dr. S. Waring of Harwell deserves special mention. This paper is published by kind permission of the Director, Harwell Laboratory, UKAEA.

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Table 3. Recommended Criteria for Major Hazards

All quantities in tonnes unless otherwise stated

<u>CATEGORY AND SUBSTANCE(S)</u>	<u>This paper</u>	<u>UK Draft Regulations (1)</u>
<u>Toxic Gases</u>		
Phosgene	2	?
Fluorine	2	-
Boron trifluoride	2	-
Chlorine	10	10
Hydrogen chloride	10	-
Hydrogen sulphide	10	-
Hydrogen bromide	20	-
Hydrogen cyanide	20	20
Sulphur dioxide	25	20
Nickel carbonyl	30	-
Bromine	30	40
Nitrogen dioxide	40	-
Ammonia	100	100
<u>Highly Reactive Materials</u>		
Acetylene	1	-
Hydrogen	1	2
Ethylene Oxide	5	5
Propylene Oxide	10	5
Organic Peroxides	5	5
Nitrocellulose compounds	50	50
Bulk polymerisable materials	50	-
Ammonium nitrate	250	500
Sodium chlorate	500	500
Liquid oxygen	500	1,000
<u>Mixed Hazards (Toxic and reactive)</u>		
Acrylonitrile	20	20
Carbon disulphide	20	20
<u>Flammable Materials</u>		
Flammable gases not specified elsewhere	5	15
Flammable liquids above their boiling point (at 1 bar pressure) and under pressure greater than 0.34 bar gauge		20
(i) hydrocarbons	10	(20)
(ii) halogenated hydrocarbons	20	(20)
Liquefied gases used as fuel (LPG - propane/butane)	(10)	30
Refrigerated flammable gases which have a boiling point below 0°C at 1 bar pressure and are wholly or partly liquefied at a pressure of 0.34 bar gauge or less	50	50
Flammable liquids with flashpoint less than 21°C	5,000	10,000
<u>Pressure Vessels</u>		
Stored pressure energy (volume times pressure) at a pressure greater than 50 bar	10,000 m ³ bar	10,000 m ³ bar
<u>Dust Explosions</u>		
A silo for the storage of grain, animal feedstuff, flour, refined sugar or powder	volume 50,000 m ³	-
<u>Materials which could emit toxic gases in a fire</u>		
Flammable brominated or chlorinated material, including solvents and plastics	100	-
Any organic compound containing isocyanato- isothiocyanato-, cyano- or isocyano- groups	100	-
Any organic compound containing more than 20% by weight of sulphur	250	-
Plastic foam	250	500
Compound fertilisers	250	500
Any organic pesticide or herbicide	250	-
	(subsequent quantities in kg)	
<u>Very Toxic Materials</u>		
Lethal to man in quantities less than 1 milligram	-	0.1
Any material which could lead to an airborne release of a toxic substance (LD ₅₀ in mg/kg body weight)	400 LD ₅₀ (oral) 200 LD ₅₀ (dermal)	-
<u>Toxic and Persistent Materials</u>		
Any material which could lead to an airborne release of a toxic and persistent substance (half-life t _{1/2} in weeks)	400 LD ₅₀ (oral); t _{1/2} 200 LD ₅₀ (dermal); t _{1/2}	-
<u>Carcinogenic Materials</u>		
Any selected carcinogenic material	not specified	