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Shell Stanlow fluoroaromatics explosion — 20 March 1990: Assessment of the explosion and of blast damage

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Abstract

At 3.20 a.m., 20 March 1990, a violent explosion at the fluoroaromatics plant in the Shell Stanlow Manufacturing Complex injured six people, destroyed the plant and caused considerable damage to nearby buildings and plant. The level of blast was considerably above that expected from a runaway reaction and vessel rupture. This paper contains a description of the blast damage caused by the explosion, and an analysis of the type of events that might have caused such damage. The chemical mechanisms involved in the runaway reactions are the subject of another paper. The most likely sequence of events is indicated as a vessel rupture followed immediately by a highly congested jet fireball, where a large quantity of flammable material was released at high speed and instantly ignited in a very congested structure.

1. Introduction

At 3.20 a.m. on 20 March 1990, there was an explosion at the fluoroaromatics plant in the Stanlow Manufacturing Complex during the manufacture of difluoroaniline. The explosion was quite energetic. Missiles were thrown up to 500 m away. The fluoroaromatics plant itself was devastated, and nearby buildings suffered serious structural damage. Windows and door frames over 500 m away were damaged. A subsequent xylene fire burned for over an hour. Six people were injured, one of whom died later in hospital from post-operative complications following lower limb surgery. A long secondary fire was caused, involving the inventory of nearby vessels, including four xylene tanks. The secondary fire followed the primary explosion quite quickly.

This paper contains a description of the blast damage, and a discussion of the blast-generating processes involved in the event. The initiating event, which was almost certainly a chemical runaway reaction, is discussed elsewhere [1,2]. The consequences, granted that such an event took place, are discussed in detail here.

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2. Blast and missile damage

2.1 General observations

Analysis of the blast damage from the explosion was complicated by both missile damage and fire damage. Examination of the damage was restricted by the precautions necessitated by contamination. The missiles and blast damage were erratic and very directional.

We draw attention to four features of the blast damage:

(1) The damage level decayed very slowly with distance.

(2) The level of damage was at least an order to magnitude too high to be accounted for a simple vessel rupture.

(3) Damage to individual structures showed evidence of a long time duration event.

(4) A lot of the damage was associated with the rarefaction part of the pressure wave.

These features are discussed in detail below. Each of these features is significant in working out the nature of the blast-generating event(s). The nature of the event indicated by these features is discussed in Sections 4 and 5, where other supporting evidence is given.

2.2 Nature of near-field damage and missiles

The distribution of missiles is included in Appendix A and Fig. 3. The near-field damage (within 10 m of the reactor vessel) was severe (Plate 1), and is discussed in more detail in Appendix B and Fig. 1.

The vessel itself was torn into at least three large pieces, with the top piece being flung a considerable distance (200 m). As far as can be worked out from a visual examination of the vessel, the vessel first burst near the top weld, at about 320° with respect to plant north. It was then torn vertically downwards and horizontally around, close to the weld, before the horizontal tears joined up near the top of the vessel. The burst was therefore towards the north-west leg which supported the concrete roof above the reactor vessel. Most plant structure within about 5 m of the vessel was either turned into missiles, or badly buckled. Much of the major structural damage was associated with the collapse of the north-west leg.

The major vessel fragment ended up outside the plant structure, apparently having been propelled north-west. The rupture itself (if we are correct about the orientation of the blast and the vertical tear) would have pushed this piece of vessel into the structure.

A rough estimate of the rupture pressure of the vessel, and of the tear forces, is included in Appendix C. This estimate gives a value of around 60–80 bar for the rupture pressure of the vessel, and is supported by our own metallurgist's report. A detailed examination of the vessel top has been conducted by the UK HSE, but reached different conclusions on the failure pressure.

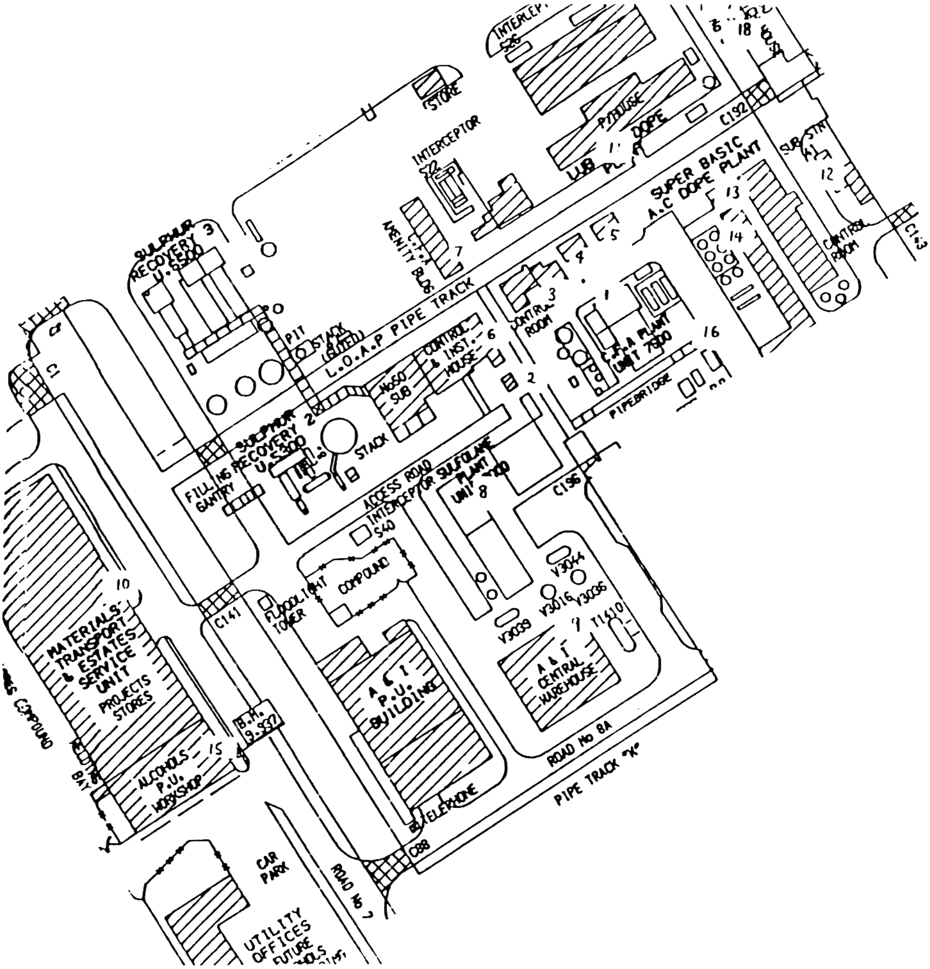

Fig. 1. Map of site damage around CFA plant (see Appendix A).

Missile 47 (Plate 2) is relevant to understanding the nature of the explosion event. This missile was a light fitting which was originally in the neighbourhood of the reactor vessel. Half of this light fitting is badly burnt, and the other half is not damaged. The light fitting was found 75 m away from the explosion, well away from the zone of the subsequent fire. The burning took place before the blast event. Despite the blast, and impact on landing, both the box cover and one glass tube were intact. This missile is discussed in more detail below.

The area behind the plant structure was shielded from missiles by the plant structure, and nearly all the missiles were found within 80° either side of plant north.

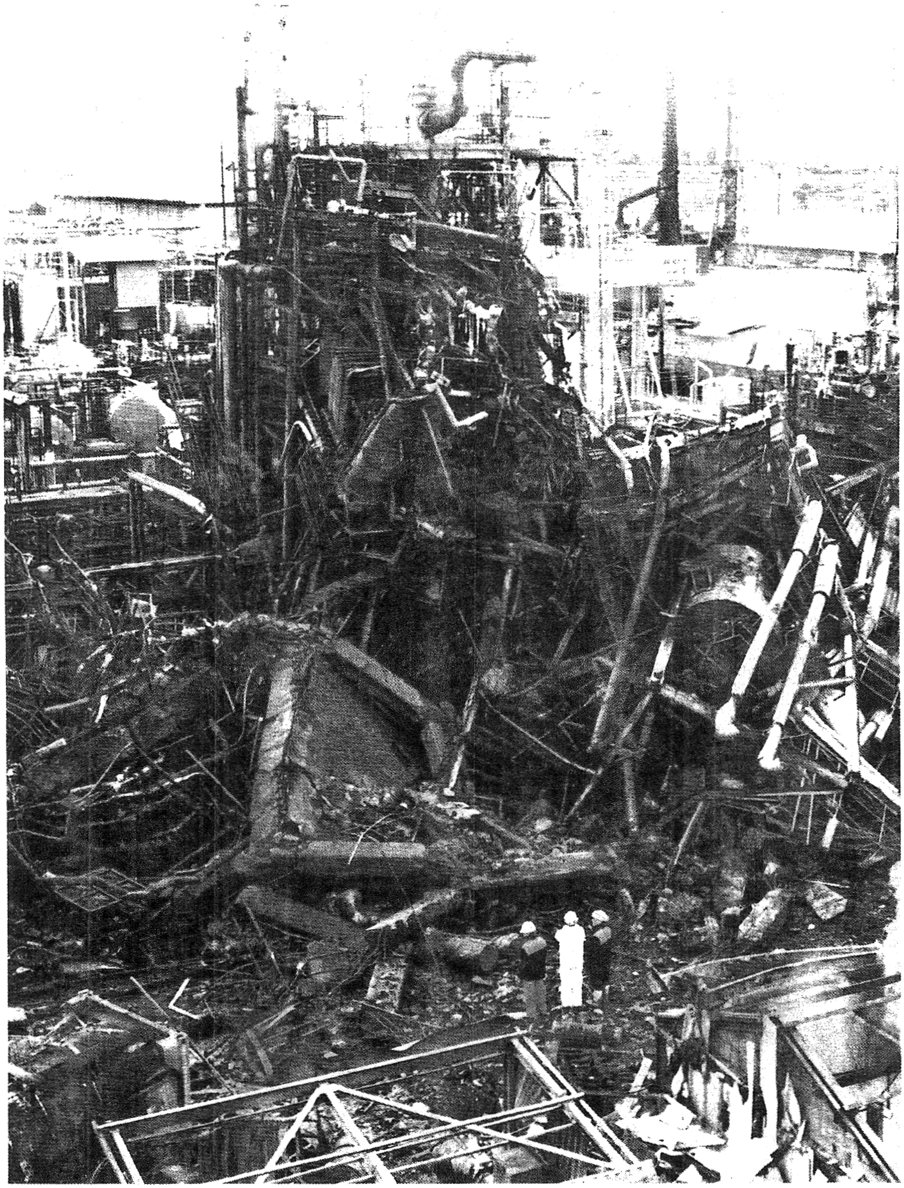

Plate 1. Near-field damage (within 10 m from the reactor).

2.3 Nature of intermediate field damage

The damage in the 10–150 m range is discussed in detail in Appendix B. The damage pattern in this range is very erratic. This was partly because the source

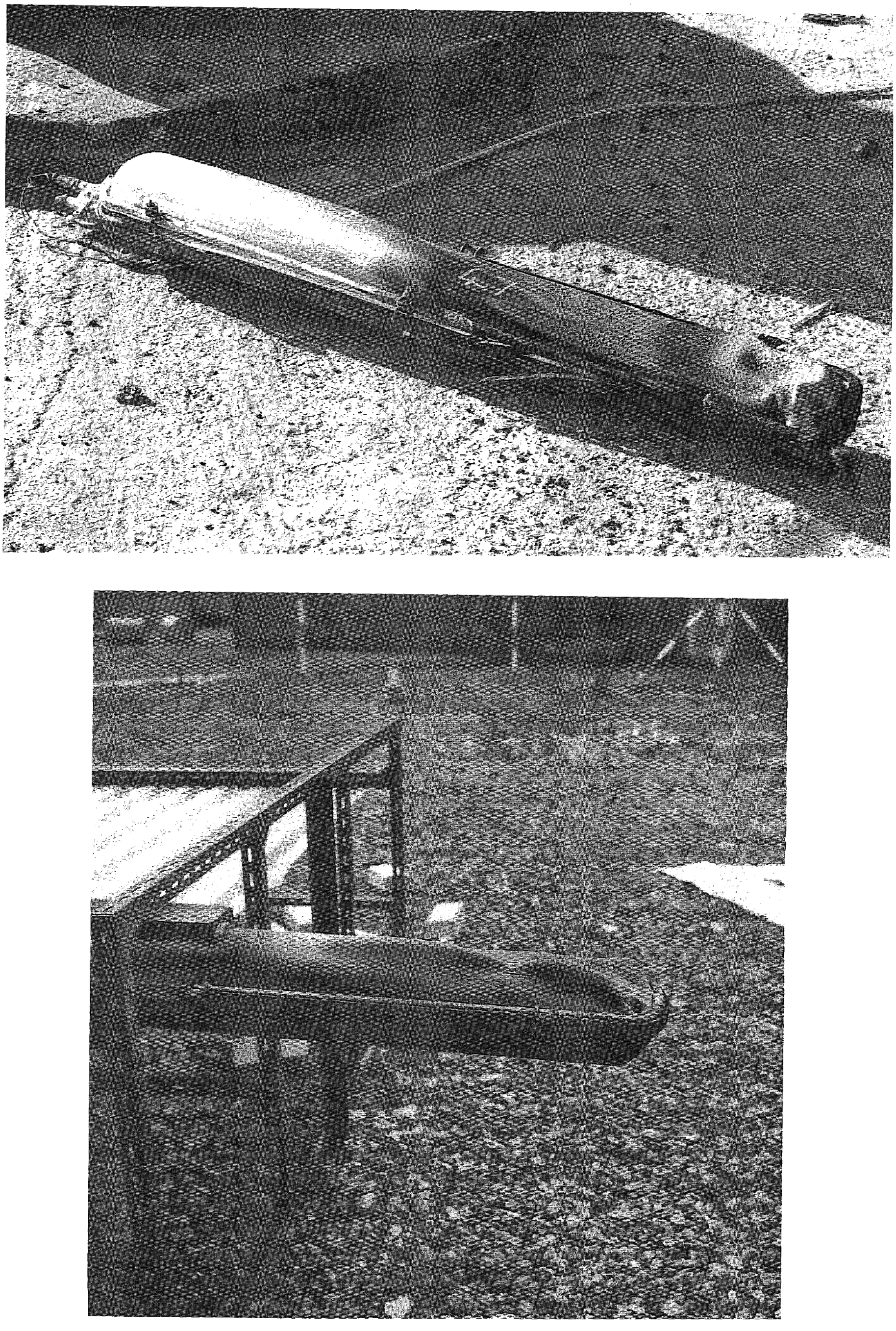

Plate 2. Two burned lightboxes.

of the blast was very directional, and partly because there was a good deal of shielding by plant and other buildings. The pressure field was probably dominated by an aerial hemispherical pressure wave. Most of the medium-field damage was caused by the downward diffraction of this pressure cap.

A plot of the likely pressure required to cause the damage seen versus distance is given in Fig. 2. The erratic level of damage should be noted. It is interesting that, although in the near-field, the highest levels of damage are plant north of the vessel; in the medium and far-field the two major areas of damage (the Materials and Transport Building and Thornton Research Centre) are at 90° in either direction to this.

Many of the pressures estimated (particularly for damage to brittle targets) are taken from TNT (trinitrotoluene) data lists [3]. These are marked as crosses in Fig. 2. Since the pressure pulse that the structures were subjected to was quite different from the spike of a TNT wave, the estimated pressures are likely to be quite different from the actual overpressures exerted. In this regard, the far-field overpressure estimates are likely to represent the pressure that occured more accurately, and the near-field overpressures are likely to be consistently underestimated. There are no reliable data available for the damage caused to brittle structures, such as brick walls, from pressure pulses other

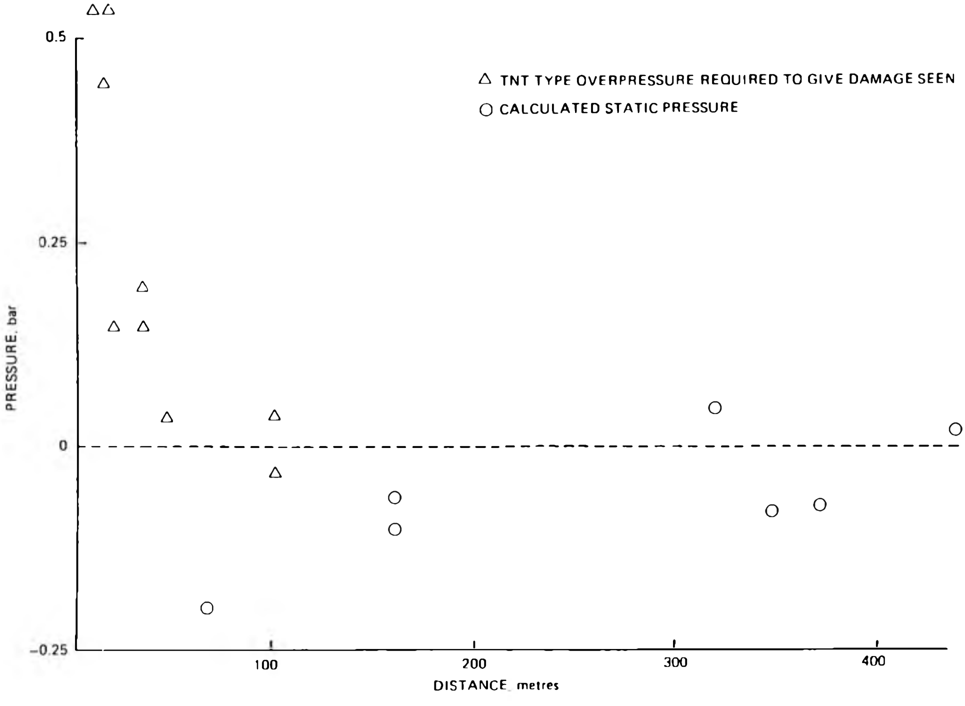

Fig. 2. Pressures required to produce observed damage.

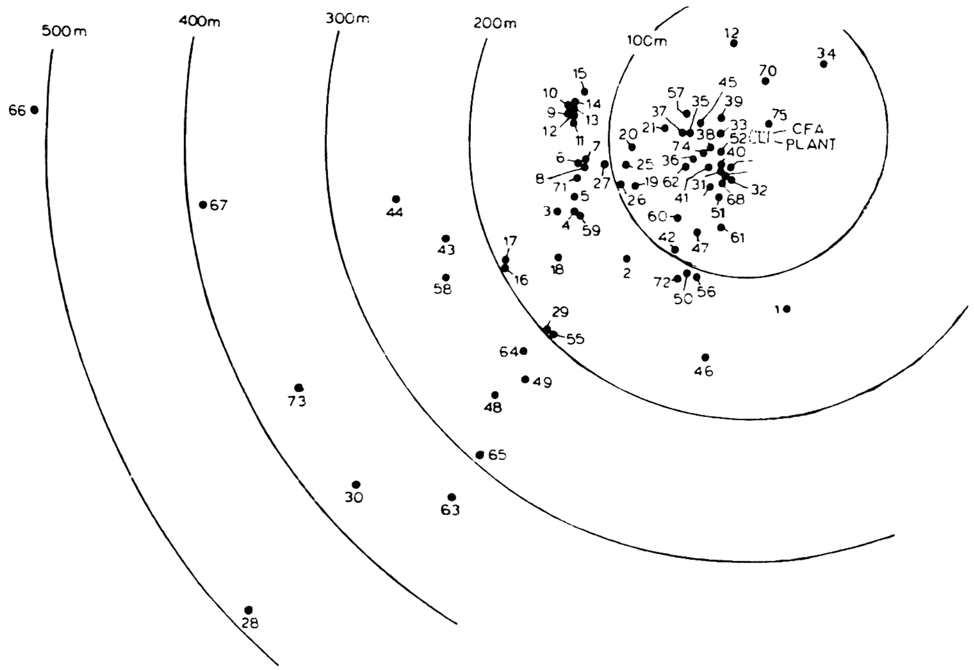

Fig. 3. Map of missile scatter (see also Appendix G for a description of each number).

than TNT or nuclear blast. The pressure loading experienced was generally in the quasistatic, rather than dynamic, response regime.

2.4 Nature of far-field damage

Thornton Research Centre is adjacent to Stanlow Manufacturing Complex, with its boundary about 350 m north-east of the explosion centre. The far-field damage to Thornton Research Centre is detailed in Appendix D. This site was a good indicator of the level of far-field pressure, as it contained a number of relatively sensitive buildings. The near edge of the site was just over 300 m from the explosion centre, and damage on the site extended to more than 500 m from the explosion centre.

The pressure experienced on the Thornton site was undoubtedly aggravated by the site being on slightly raised ground, so that acoustic reflection off the slope increased the level of compression and rarefaction. Even allowing for this effect, the amount of damage at the Research Centre was very high compared to the medium and near-field damage. Weather data supplied by the Meteorological Office rule out the possibility of aggravation by a temperature inversion, since the mixing layer was around 900 m deep.

Two points are drawn from points (2) and (13) in Appendix D. The first is that the duration of the compression phase was, at the very least, 30 ms; and the second is that the far-field shows an energy yield of at least 500 MJ. The actual energy yield must be considerably higher, since we shall argue that the pressure wave was of a very long duration, and therefore a very low "efficiency" event (in TNT efficiency terminology).

A typical far-field energy yield for a long duration event such as a vapour cloud explosion would be a few per cent, which would lead to an estimate of 25 000 MJ released at source. Since this event was unusually long, even compared to that from a vapour cloud explosion, the efficiency is likely to be less than this, and the energy release at source even more.

Although the damage was erratic, some consistent patterns arose. A lot of damage was caused by rarefaction, but this is partly because most fixtures are more sensitive to rarefaction than to compression. Roller-type doors were consistently pushed inwards, which would have required a compression phase of around 50 mbar. The largest rarefaction damage corresponded to an underpressure of at least 75 mbar. It can be expected that the compression phase was of larger amplitude and shorter duration than the rarefaction phase, but there were few fixtures sensitive to compression, so the real level of compression was never seen.

A reasonable estimate is that the site was exposed to a patchy blast wave consisting, at the fence, of up to 40 mbar overpressure followed by 40 mbar underpressure, with ground effects and acoustic reflection meaning that some targets experienced twice this. The decay of the pressure wave across the site was rather slow. with buildings several hundred metres from the site edge experiencing significant damage.

It should be noted that pressure is expected to decay inversely with distance in the far-field from a long duration event. It should also be noted that the areas (pressure multiplied by duration) of the compression and rarefaction parts of the wave are expected to be equal. In general, the compression phase is of a larger magnitude, and of shorter duration.

2.5 Time duration of blast wave

We have a variety of reasons for asserting that this was a long time duration event.

2.5.1 Comparison of near and far-field damage

The survival of an unprotected brick wall 10 m from the explosion centre, compared to the level of far-field damage, also implies a very slow event. The brick wall at point 3 on the Fig. 1 was cracked, but not fully pushed over. This wall would not have been able to withstand a pressure differential across it much in excess of 50 mbar. However, if we naively assume a spherical decay to a pressure of around 50 mbar 150 m away (at point 10 on Fig. 1), this would imply a pressure of 750 mbar or more at the site of the wall.

This assumption is obviously crude, since some of the blast may have been generated more than 10 m from the centre of the explosion, and also because the damage at a greater distance was fairly directional. None the less, if we take a reduced figure of, say, 400 mbar for the pressure at 10 m, take the wall size at 2 m, and take the pressure wave as travelling outwards at the speed of sound, then we reach an estimate of at least 50 ms for the rise time of the event. This implies hundreds of milliseconds for the duration of the whole event.

2.5.2 Comparison of near and far-field damage

A figure of hundreds of milliseconds for the time duration of the event is also supported by similar comparisons between the near and far-field damage levels which are shown in Fig. 2. For an inefficient non-shocked pressure wave of time duration T, pressure is expected to decay inversely with distance when the distance from the explosion is much more than cT (in accordance with acoustic theory), where c is the speed of sound. Here, pressure does not decay inversely with distance until hundreds of metres from the event. This suggests a time duration of hundreds of milliseconds.

2.5.3 Materials and Transport building

The nature of the damage to the Materials and Transport building (see Appendix B) gives an estimate for the duration of the rarefaction pulse or more than 100 ms. This indicates that the blast-generating event had a long duration.

2.5.4 A&I warehouse

The damage of the A&I warehouse also indicates quite a long duration event, since the damage on the sheltered side of the building is similar to that on the nearside. (When the wavelength of a pressure pulse is much less than that of building, acoustic reflection gives much worse damage on the nearside.) The similarity in damage between the sides means that the pressure wavelength was at least of the order of the size of the building, which again indicates an event of more than 100 ms.

2.5.5 Failure mode of vessel

Brittle cracks branch at propagation velocities above about $0.2c$, where c is the speed of sound in the material [4]. The speed of sound in steel is 5180 m/s. There was no significant branching in the failure of the vessel, so if the cracking were brittle it must have been going at 1000 m/s or less. A ductile crack would be even slower.

The fastest that a crack could propagate without branching around the 7 m circumference of the vessel is about 7 ms. The rupturing event must have taken longer than this, which is consistent with a pressurised vessel failure, but would not be consistent with a detonation for example (even a slow detonation). This lower bound on the time duration of energy release is mainly of use for ruling out the possibility of a "soft" liquid phase detonation.

2.5.6 *Missile 47*

Missile 47 was flung 75 m. We can calculate a minimum time for this missile to receive sufficient impulse, given that it did not receive a sufficiently great force to break the box cover.

As stated, Missile 47 was flung 75 m. This implies that it had an initial velocity of at least 55 m/s. Since the missile weighed 12 kg, we can infer that it received an impulse, I, of at least 660 kg m/s. First, we calculate whether the light cover would have responded dynamically or quasistatically to the pressure wave. The cover of the missile had an area density, D, of around 3.3 kg/m^2. The projected area, A, which the missile would have offered to an explosion would have been between 0.3 m^2 and 0.03 m^2 depending on the orientation. We taken an estimated area of 0.1 m^2. In reality, some counteracting impulse would also have been received by the opposite face of the fitting, which means that the impulse received by the face has been underestimated. If the missile received such an impulse over a time T seconds, then, if the cover responded to the impulse dynamically, it must have been displaced by a distance of

$$0.5IT^2/(DA)\approx 1000\,T^2 \text{ m}$$

The area density of (either half of) the cover was around a tenth of the area density of the light fitting itself, which implies that that this displacement must have been almost entirely relative to the fitting. Examination of the fitting allows us to conclude that 10 mm displacement of the cover relative to the fitting would have been up upper bound. Dynamic response is therefore only possible if $T<3$ ms.

We have good grounds for believing that the time duration was at least 3 ms, for example, from the vessel failure. This is also implied by the intact glass tube in the light fitting. We therefore conclude that the light box cover was subjected to a fairly static load.

We can also relate the maximum static loading experienced by the cover to the impulse received:

$$T=I/(P_{\max}A)$$

Whatever the orientation of the light fitting, the front (translucent) cover would have been subjected to a pressure close to the peak pressure.

We have tried static loading (weighting) an identical light box to find out at approximately what pressure the front cover would have failed. Throughout the testing, we tried to ensure that the test procedure would given an upper bound on the failure pressure.

A 30 cm section from the centre of the light was tested. The curved end of the light would have given a little additional strength to the light, but, as the aspect ratio of the light was more than 10:1, the additional strength would have been slight.

Under uniform pressure loading, the failure mode would have been breaking

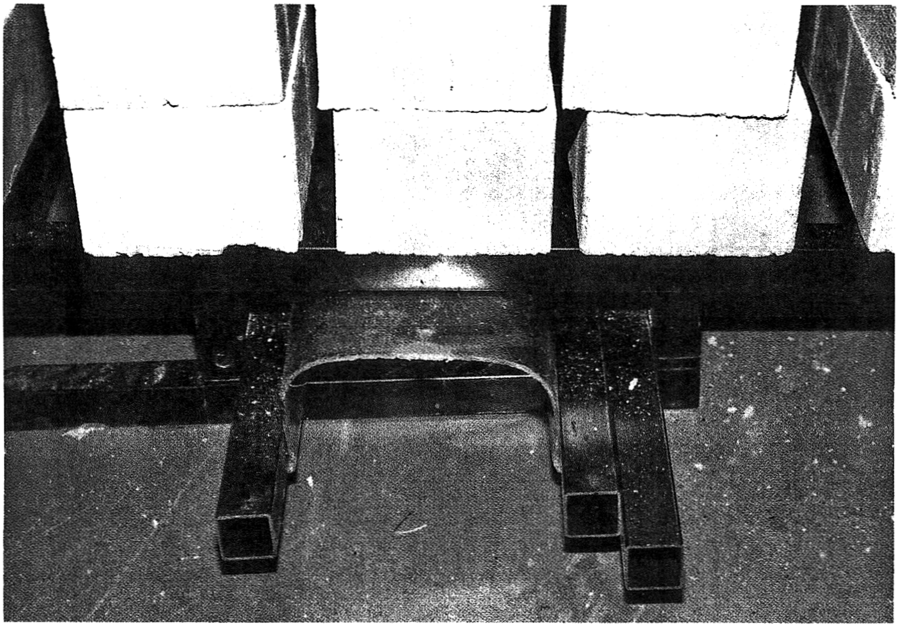

Plate 3. Light box loading.

along the maximum radius of curvature. Uneven loading would have resulted in failure at a lower average pressure. To ensure that the failure mode in the loading test was the same as it would be from a pressure wave, we clamped the edges of a section of cover, to prevent it splaying sideways (Plate 3).

The top face of the section was then steadily loaded until it failed. When it failed, it started by cracking along the line of maximum curvature, and then shattered. It failed at a loading of 3920 N. The area of the top of the section was 0.036 m^2. This corresponds to a pressure of about 1.1 bar.

From these estimates, we can conclude with confidence that the light fitting could not possibly have been exposed to a pressure of more than 2 bar, and that the pressure was probably a deal less than this. The light fitting would also have been weakened by a flame before surviving blast.

This is important for two reasons: first because it implies that the time duration of the pressure wave close to the vessel was at least 30 ms (to get sufficient impulse, taking a projected area of 0.1 m^2), and secondly because it implies that blast was generated further away from the vessel than where the light fitting was.

Straightforward expansion of a pressure wave which started from a 1 bar source with a radius of a couple of metres could not have yielded 500 MJ without an additional source of energy. The maximum blast energy (based on an ideal gas calculation) [5] from the adiabatic expansion of a gas is around:

$$P_s \cdot V[1-(P_s/P_a)^{(1-\gamma)/\gamma}]/(\gamma-1)$$

where P_s is the source pressure, P_a is atmospheric pressure, V is the source volume, and γ is the ratio of specific heats.

If we take a source pressure of 2 bar (i.e. 1 bar overpressure), and a radius of 3 m (which is an estimate of the distance between the vessel centre and the light), the available energy is 11 MJ, which is completely inadequate. After vessel failure, the contents of the vessel would expand very roughly uniformly, since they would be nucleating and forming a droplet cloud rapidly after depressurisation. This means that any subsequent release of energy, after the contents had expanded to a radius of around 3 m (which is what would be expected from a more continous release of energy from within 3 m), would also imply that most of the energy was released from outside a radius of 3 m.

This leads to an important conclusion, namely, that most of the damaging blast originated more than 3 m from the reactor vessel.

3. Other evidence on the incident

Several other pieces of evidence are important in determining the nature of the blast-generating event in the explosion.

3.1 Originating event

The pressure and temperature read-outs from the reactor vessel in Appendix E, clearly show that in the run up to the explosion, this vessel became heated and pressurised. A comparison of the temperature/pressure relationship with that expected for the vessel contents showed a far higher than expected pressure, indicating that there was probably some unknown gas being evolved within the vessel. At the process temperature of 165°C a pressure of 0.2 bar was expected, whereas the readings show around five times this.

It is unlikely that the vessel was being heated externally (e.g. by a jet fire impingement) since the vessel had a pressurised water jacket, which showed no signs of being heated and would have prevented heat flux through the sides. In addition, external heating would probably have been noticed by the operators (one of whom was on the plant structure at the time). There are signs from the read-out that the reaction started going "wrong" (shown by unexpectedly high pressure) some 35 minutes before the temperature started to rise rapidly. The water jacket was switched to cooling when the temperature in the vessel approached the intended process temperature.

It seems most likely from the evidence that the indicating event was a runaway reaction within the vessel. The possible causes of the runaway are being reported upon elsewhere [2]. The only conclusion relevant to the present discussion is that the most likely runaway mechanism involves the evolution of ketene.

3.2 Fire damage to missile 47

A study of missile 47 gives important information about the sequence of events in the incident. This missile landed 75 m from the explosion centre, and had been significantly burnt prior to being projected.

Having tested similar light fittings at Thornton Research Centre (Appendix F), we conclude that this light fitting had been burnt by direct impingement of a jet fire, rather than by radiation. The jet fire impinged the light fitting end-on. Both the front cover and the back face of the light fitting had been impinged. The jet fire had lasted between 30 seconds and 2 minutes before the explosion took place.

The damage to this light fitting (Plate 2A) was very similar to that on an identical light following exposure to a 0.7 m sooty, diffusive acetylene flame for 25 s (Plate 2B). The acetylene flame was relatively fierce (with a conductive heat flux of around 150 kW/m^2) compared to what is likely to have occurred above the vessel. So it is fairly safe to conclude that the light fitting had been exposed to a jet fire for at least 30 s, and at most for two minutes.

The form of damage on Missile 47 is much closer to that expected from a small high-speed jet flame than from a larger meandering flame, since the damaged area has a very clear boundary in two directions.

The jet was almost certainly from a flange failure above the vessel or from an opening crack above the vessel, rather than from the end of the safety valve duct. The safety valve duct ran to above the roof, where there were no lights. There were several lights above the vessel itself, and it seems very likely that Missile 47 was one of those.

The results of this test are important for three reasons: first, they establish that there was a jet fire from a flange failure before the explosion took place, for at least 40 s. This gives an indication of the rate of runaway, and also means that we can conclude that there was already a large source of ignition when the vessel ruptured. Second, they establish that there was missile-generating blast well away from the vessel (that is, missiles were generated by blast: from things that were not vessel fragments, nor in contact with vessel fragments, rather than by impact by vessel fragments). An end-on light fitting is rather streamlined, and the blast wind from the explosion must have been very considerable to blow it 75 m, particularly as the event had a long time duration. Thirdly, we can infer that one of the gases produced in the runaway reaction was flammable. This fits with a suggested mechanism for the runaway involving ketene.

3.3 Eye-witness reports

There are eye-witness reports to support the sequence of events described in the conclusions. In particular, there is a report of flames from above the vessel before the vessel rupture, and of a large fireball.

4. Calculations on explosion scenarios

It seems most appropriate to start this discussion of the blast pattern with some calculations on what the damage pattern would have been from various possible incidents.

4.1 Blast from a vessel rupture

Pressure release from normal pressurised rupture of liquid above its boiling point depends on the percentage of the liquid that immediately vaporises on depressurisation. For relatively small percentages (for example, typical propane BLEVEs, where the percentage is around 20%) only the vapour above the liquid gives significant blast.

When only a small percentage of the liquid is evolved as vapour, the rate of evolution of vapour is small, since it is limited by heat conduction (rapid boiling, which gives rise to vapour and condensate, requires a heat transfer from droplets to the gaseous phase). In this case the liquid phase does not contribute significantly to the blast.

For larger percentages (above an unknown critical value, but probably near 100%), presumably the liquid phase vaporises fast enough to contribute to the blast. Such a possibility would be unusual, but it is worth considering in view of the unusual level of blast.

We first estimate the blast energy by assuming that we are below this critical value. As a guideline, if we take 3 m^3 of vapour phase released at 80 bar, then the equation used in Section 2.5 gives 44 MJ. This is inconsistent with the level of blast. The energy yield was well over ten times, and probably hundreds of times, larger than this.

The far-field damage (at Thornton Research Centre, see Section 2.4) allows us to bound the energy yield below with a figure of 500 MJ (although this figure was from a single door bolt, it is consistent with the damage throughout Thornton) and estimate a figure of at least 25 000 MJ released at source. A vessel rupture with 3 m^3 of vapour would have to be at around 800 bar (which gives 520 MJ) to give the smaller of these figures. This pressure is totally impossible from the kind of vessel, and inconsistent with the near-field damage. An energy yield close to the higher figure would be orders of magnitude beyond what could be accounted for.

The possibility that the liquid phase might contributes should be considered. For the release of a pressurised vessel containing a single liquid or solution, this is possible. For example, if a pressurised vessel of pure DMAC were heated until it reached 70 bar, this would be likely.

As a rough calculation, liquid DMAC has a specific heat capacity of around 2 kJ/kg K. For pure DMAC to have a vapour pressure of 70 bar, it would have to be at a temperature of around 700 K. (Manufacturers' data stops at 60 bar, 670 K.) The latent heat of vaporisation of pure DMAC is around 500 kJ/kg.

The excess stored thermal energy above boiling point at 70 bar is therefore around 540 kJ/kg. This is above the latent heat of vaporisation. The evolution of vapour from 70 bar DMAC in liquid phase would not be time-limited by heat conduction (for the release of a superheated liquid there is usually a rate limit associated with the required heat transfer from the liquid to the interface near nucleation sites).

The intended vessel contents were, of course, a rather concentrated solution, and would have had thermodynamic properties quite different from those of pure DMAC. Specifically, the contents would have a higher latent heat of vaporisation, and the vapour pressure also would be lower at a given temperature.

However, it is clear from the pressure/temperature trace for the vessel before rupture that some other vapour/gas was being evolved in (or was leaking into) the vessel. The presence of a jet fire and evidence that the runaway reaction evolved ketene confirm the belief that a gas was being evolved. The evolution of vapour by the runaway would greatly lower the temperature at which the failure pressure of the vessel was achieved.

Once the temperature of the vessel reached around 230°C, the DCNB/DMAC mixtures in it would start to decompose [2]. This would also involve the evolution of gases.

Although it is impossible to perform detailed calculations on the (unknown) chemicals in the vessel at the time of failure, the presence of significant quantities of evolved gas makes it very unlikely that the temperature would have been high enough at vessel rupture to give liquid phase contribution to blast.

4.2 Missiles from a vessel rupture

Calculating drive pressures from missiles is notoriously unreliable, and always underestimates the drive pressures. Typically, pressure calculated on the basis of a naive missile model is, at most, 20% of the actual rupture pressure [6]. More sophisticated theoretical missile models have been developed recently [7], but have not yet been verified, and calculations are dominated by thermodynamic and statistical uncertainties. We will therefore analyse missiles on the basis of an empirical model.

As a very rough guide, a missile such as Missile 28, which travelled about 500 m, must have been travelling at at least 70 m/s (which assumes a 45° initial flight angle), and has an area density of about 500 $\mathrm{kg/m^2}$. According to the (experimentally derived) guidelines in [8], the upper velocity limit for a fragment from a ruptured vessel is roughly

$$v=0.88\,c\,(PR/mc^2)^{0.55}$$

in terms of the rupture pressure, P; the vessel radius, R; the area density of the projectile, m; and the speed of sound, c.

If Missile 28 were a vessel fragment, it would therefore correspond to a drive pressure of at least 40 bar. The missile was not a vessel fragment but a nozzle, and therefore we can infer that the pressure that it experienced was in excess of this. All that this does is show that there is no definite inconsistency between the missile distances and the claim that missiles originated from a 60–80 bar vessel rupture.

None the less, the number of missiles was very high, and calculations based on Missile 47 indicate that the missile-generating blast had a long duration. It is likely that the number of missiles was considerably increased by blast wind from an ongoing explosion.

4.3 Non-combustive contributions to blast

At some point during the course of the vessel failure, and subsequent depressurisation and dispersion of the reactor contents, the chemical evolution of energy would cease. Although the initial stage of the runaway reaction was complicated, it is likely that the final stages involved straightforward thermal decomposition of nitro-compounds.

It is clear that, since the calculation in Section 4.1 naively assumed that the evolution of chemical energy ceased immediately when the pressure reached the failure pressure of the vessel, it neglects any contribution from the chemistry after vessel failure. An extreme case where this calculation would be in error is that of a liquid phase detonation, where the bulk of the chemical energy would be released before dispersion could take place.

In the present case, there is no doubt that the blast from a simple vessel rupture could have been considerably enhanced by the decomposition running on during the dispersion of the vessel contents. It is, however, very unlikely that chemical run-on alone was the major cause of blast.

The first reason for asserting this is the duration of the blast-generating event. The blast wave had a duration of hundreds of milliseconds. This implies that the blast-generating event must have pushed the surrounding air (like a spherical piston stroke) for this order of time duration. During a hundred milliseconds, the event itself must have expanded to a radius of tens of metres (since it would have been expanding at close to the speed of sound). During such an expansion, a considerable amount of air would have been entrained.

It seems unlikely that non-combustive chemistry which was slow enough to be relieved by a vessel failure over perhaps 10 ms (in the sense that it did not force the vessel to fail faster) would have maintained its heat release rate after it had been dispersed over thousands of cubic metres, and been cooled by entrained air.

In addition, we conclude in Section 2.4 that the energy released at source was probably well in excess of 25 000 MJ, which is more than could be generated by non-combustive chemistry, even if *all* of the available non-combustive energy had been released.

Based on vessel contents of 4 tonnes DCNB/DFNB and 6 tonnes of DMAC, the decomposition energy available (see Appendix G) was about 8000 MJ.

4.4 Combustive contribution to blast-generation

In a sense, the distinction between non-combustive and combustive contributions to the blast is a little blurred, since it is unlikely (even without a strong ignition source) that air would not have become involved in the chemistry during this process.

There was a strong ignition source outside the vessel. Ketene (which is highly flammable) was indicated as present. The bulk contents of the vessel were also flammable (at their release temperature, although not at room temperature: DMAC has a flash point of 70°C), and the runaway reaction may have resulted in a whole range of chemical intermediates being vaporised also.

It is therefore most likely that the rupture would result in a sudden high-speed jet release of about 10 tonnes of highly flammable material from a source pressure of perhaps 70 bar, with an energetic ignition source. It is also quite possible that the whole mixture would autoignite when exposed to air, even without an ignition source.

Such a phenomenon is already a little beyond anything that has been tested experimentally, and is further complicated by a proportion (perhaps most) of this release being into a very highly congested area. High levels of congestion can greatly increase the severity of diffusion limited processes (such as vapour cloud explosions), since the congestion generates high levels of turbulence, which increase the mixing rate. This resulting combustive event is the most likely source of most of the blast observed. The fact that such an event would be rate-limited by air mixing into the fireball (albeit at a very high level of turbulence) would make such an event of long duration compared to a vapour cloud explosion (which is limited only by the diffusion of heat and radicals away from the flame-front).

The typical duration of a vapour cloud explosion is perhaps 50 ms. An unconfined fireball from a low-pressure source can last for 10 s. It is easy to see that a high-speed congested fireball might last for, perhaps, 400 ms.

The combustive energy available was around 230 000 MJ (based on 4 tonnes of DCNB/DFNB with a heat of combustion of 14.5 MJ/kg, as in Appendix G, and 6 tonnes of DMAC with a heat of combustion of 29 MJ/kg). By comparing these figures with estimates in Section 2.4, we can see that a combustive event involving about a fifth of the vessel contents in the congested region would explain the blast well.

5. Probable sequence of events

The most likely description of events from our investigation is as follows:

(1) There was a runaway reaction in the reactor vessel, evolving some gas (almost certainly ketene and carbon dioxide [2]), which caused the pressure to rise rapidly once the vessel approached its process temperature.

(2) As the pressure rose, the safety valve blew. A flange (or similiar) failed

above the vessel and gave rise to a jet fire. The jet fire carried on burning for at least 30 s before vessel failure.

(3) The vessel burst, at a pressure of around 60–80 bar. The vessel tore into two major and several minor fragments. The vessel fragments, and many surrounding pieces of plantwork, were turned into energetic missiles, which flew up to 500 m away. The contents of the vessel did not detonate.

(4) As the vessel failed, the vessel contents continued to release energy, entrained air and rapidly ignited. The entrainment of air and combustion were greatly speeded up by the highly congested environment in which the vessel failure took place. The blast wind from this combustive event probably increased the number and severity of the missiles.

(5) A large fireball extending outside the structure occurred. A secondary fire started, which quickly involved the inventory of some nearby xylene storage vessels.

We summarise the reasoning behind each of the steps above.

(1) The event seems to have started inside the vessel. This is clearly indicated by the pressure/temperature plot of the vessel (Appendix E). External heating is very unlikely not to have been noticed by the operators on the timescale concerned, and would have affected the water jacket temperatures. Some evolved gas is also shown up by the vessel data, which indicate that the event started inside the vessel. This view is supported by an investigation into the runaway processes reported on elsewhere [2].

(2) Eyewitnesses report the safety valve lifting significantly before the vessel exploded. The valve itself was ducted to outside the plant structure, and could not have been the source of the jet fire which burned Missile 47. There was therefore another leak in the vicinity of the reactor vessel (where there were light fittings). The jet fire lasted at least 30 s before the missile was blown away from the fire, since the fire damage on Missile 47 could not have been achieved in less than this.

(3) Detonation can be ruled out by the small number of large vessel fragments. The pressure in the vessel was adequately relieved on the timescale of the crack propagation, which was several milliseconds. The number of missiles was remarkably high, but not conclusively inconsistent with being from a vessel rupture.

(4) The time duration of the blast wave implies that energy continued to be released well after the vessel had ruptured. The amount of energy released into the far-field also implies energy release after the vessel had ruptured. Since the contents were rapidly expanding, this implies energy released when the contents occupied a large volume, when air would have been entrained. There was an energetic ignition source and, without combustion, it is hard to account for the total energy yield. The vessel was underneath a concrete floor, and surrounded by very congested structure, so that

for any burst point part of the contents are bound to have been expelled at high speed into a congested geometry. A highly congested jet fireball seems inevitable, and could account for the high level of damage.

(5) The fireball and xylene fire were well documented.

6. Conclusions

The CFA explosion was initiated by a runaway reaction in a reactor vessel. Before the reactor vessel failed, there was a jet fire outside the vessel for around a minute.

The main reason for the very high level of blast was that the vessel contents were released at very high speed and ignited in a very congested area. The major blast generating event was a *highly congested jet fireball.*

The blast wind from this fireball was partly responsible for the high number of missiles.

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Appendix A

The location of missiles is marked on the map in Fig. 3. There follows a brief description of each missile. The masses of most missiles were directly measured. Those estimated are marked with an asterisk (*).

No.	Description	Mass (kg)	No.	Description	Mass (kg)
1.	Instrument	0.75	37.	Pipe debris	?
2.	Pipe	*70	38.	Pipe debris	?
	Handrail	4	39.	Plate debris	?
	Flange	6	40.	Plate debris	?
3.	Vessel nozzle	56	41.	Cable tray	*7
4.	Instrument head	1	42.	Plate	<0.5
5.	Instrument base	13	43.	Reactor foot	71
6.	Instrument valve	<0.5	44.	Reactor foot packer	89
7.	Unistrut	5	45.	2 m pipe	37
	Instrument coupling	4		Pipe and flanges	38
	Handrail	*2-3	46.	Reactor foot packer	88
8.	Casing fragment	0.75	47.	Light box	12
9.	Casing fragment	0.75	48.	2 m pipe	26
10.	Casing fragment	0.5	49.	Unistrut	*3
11.	Casing fragment	0.5		Instrument probe	*3
12.	Casing fragment	1		DP cell	*3
13.	Instrument	1.5	50.	Valve yoke	*2
14.	Casing fragment	<0.5	51.	2 m pipe	*35
15.	Debris		52.	Cock	*25
16.	Pipe	4	53.	Pipe	*75
	Debris		54.	Floor grating	*45
17.	Pipe	7	55.	Valve bonnet	15
18.	Pair of flanges	15	56.	Floor grating	6
19.	Dead end lubricator +	10	57.	Vessel	probably > 1000
20.	Pipe	*70	58.	Flange	<0.5
21.	Valve actuator	70	59.	Lagging sheet	<0.5
22.	Ball valve	46	60.	Handrail	3
23.	Vessel fragment	*15		Pipe	*7
24.	Control valve fragment	3	61.	Cable tray	5
25.	Instrument stand	21	62.	Probe	38
26.	Cable tray	5.5	63.	Instrument	<0.5
	Debris		64.	Pipe fragment	<0.5
27.	Cock and flange	7	65.	Nipple	<0.5
28.	Vessel nozzle	51	66.	Instrument	6.5
29.	Reactor top fragment	675	67.	Gear box support	35
30.	Instrument level cock	<0.5	68.	Reactor drive coupling	137
31.	Flanges	2.5	69.	Debris	*3
32.	Seal cartridge (reactor)		70.	Debris	*3
33.	Instrument stand	21	71.	Floor grating	60
34.	Gear box (reactor)	365	72.	Lamp fragment	<0.5
35.	Pipe debris	(35-38 total	73.	Instrument	4.5
36.	Pipe debris	about 25 kg)	74.	Plate	*7
			75.	Reactor shell fragment	*150

Appendix B

Inspection of Stanlow site damage

Numbers refer to the number in Fig. 1.

(1) The structure around R7601 (the reactor vessel) had been devastated. I was not able to identify very much within a couple of metres of it. The damage extended some distance back into the structure, although the far side of the plant was hardly damaged at all. Even though the vessel split was along an outward face of the vessel, the bulk of the vessel ended up outside the structure. A lot of the devastation of the plant appeared to be associated with the failure of the north-west leg of the concrete roof over the vessel. The roof is clearly identifiable. Most of the visible damage was ductile rather than brittle, although this is probably because most of the structure was metal (distance from explosion centre 0–5 m). Plate 1

(2) Small one-storey brick building was completely deroofed. There was slight damage to the top couple of courses of bricks. No damage was detectable further down the wall. The roof was of corrugated construction. The bottom part of this building was well shielded from the blast. The pressure differential across the walls would have been relieved by the failure of the roof. The damage of the top was similar to the damage that would have been caused by a TNT blast wave of overpressure 150 mbar (distance from explosion centre 35 m).

(3) Single-storey control room was badly damaged structurally, but left standing. The nearest corner on this steel-framed building was debricked and deroofed, leaving only the steel frame with a little structure leaning against it. Half-way along the nearside, at about 15 m from the explosion centre, the wall was intact with only the roof missing. This indicates either quite a rapid decay in shock strength, or very directional damage (more probably the latter). From standard TNT tables [1] the damage to the near corner is similar to the damage that would have been caused by a TNT blast wave of overpressure 500 mbar shock wave, whereas the damage half-way along the wall could correspond to nearer 150 mbar.

The far side of the control room was intact (in the sense that the far wall is largely undamaged), but it had clearly been sheltered from the blast by the rest of the building. There is a strong tendency towards increasing damage with height. A first-floor brick wall (some sort of staircase?) towards the back of the control room has been moved and broken, at a distance of around 25 m from the explosion centre (distance from explosion centre 10–25 m).

(4) A single-storey steel-framed decontamination building close to the explosion centre had been completely gutted. The steel frame was bent, but probably by missiles rather than blast (a flight of stairs seems to have landed on this building). The damage to this building was similar to the

damage that would have been caused by a TNT blast wave of overpressure about 500 mbar (distance from explosion centre 15–20 m).

(5) A single-storey steel-framed corrugated sheet building had all of the sheeting ripped away on the front and back faces. A large tank had been shifted along the ground towards it. The damage to this structure probably is similar to the damage that would have been caused by a TNT blast wave of overpressure 400 mbar (distance from explosion centre: 15–20 m).

(6) Nearby (single-storey) control room mainly intact. A one-brick (9″) wall moved about 0.5 m. One window and frame bent inwards. Closest window to explosion virtually unaffected (3 of 16 panels broken). Wall movement was outwards. This is similar to the damage that would have been caused by a TNT blast wave of underpressure 200 mbar (distance from explosion centre: 30–40 m).

(7) Amenity block. This temporary block was of a wooden-framed construction and was two stories high. The end wall of this building, facing towards the explosion centre, was caved inwards, but the rest of the upper storey walls were sucked outwards. The side facing the building was sucked out much more violently than the far side, with the panel wall being nearly a metre displaced at the top. The design of such buildings is such that they are much more sensitive to rarefaction than compression, but the damage to this building probably corresponds to 150 mbar of rarefaction and compression on the sides facing the explosion centre. The building was shielded from direct line of sight from the vessel (distance to explosion centre: 40–55 m).

(8) One wall on the sulfolane plant facing towards the explosion centre had been sucked outwards. An L-shaped beam had been bent outwards and the corrugated sheeting attached to it was buckled. The sheeting had not torn much, with only two of the screws attaching the sheeting in place ripped out. Some calculations on this beam are included in Appendix C. The conclusion is that the wall was subjected to an underpressure of around 180–220 mbar (including the strength of the sheeting itself) (distance to explosion centre: 65 m).

(9) The corrugated sheeting on this warehouse was "rippled" throughout. Interior (unattached) support struts had been bent inwards, and the sheet was left bent outwards. This allowed the figures for both the compression and rarefaction part of the pulse to be estimated. The manufacturers provided the information that the sheeting (with this span) would move 2 cm elastically, if subjected to around 25 mbar, but in this case the deflections were far greater, so we performed some testing on the sheeting ourselves. The conclusion was that at an overpressure of around 30 mbar the sheeting yielded completely. The deflection of the sheeting in this regime therefore gives only an indication of the energy in the overpressure and underpressure.

Interestingly, the damage to the different sides of the building was very similar. The whole building was sheltered from direct blast, but even so the wavelength of the pressure disturbance must have been comparable to the size of the building to give similar damage to the different sides. The largest deflections measured in the sheeting were on the far side on the building from the explosion, and next to the doorway. Allowing for the structural members that also bent in the explosion gives a lower bound of 45 mbar for the overpressure, and 25 mbar for the underpressure. The degree of deflection gave a minimum figure of around 600 J/m^2 for the energy density of the compression phase, and about half that for the rarefaction phase. The degree of shelter that this building had, together with the very long duration of the pulse experienced, means that this would give an underestimate of the yield of the explosion (distance from explosion centre: 90–115 m).

(10) The materials and transport building suffered a lot of window damage, with some slight damage to corrugated sheeting (not counting missile damage). The windows facing towards the explosion centre were all pulled outwards, some completely out of their frames, others just broken and bent. The windows were wire-reinforced glass. On the far side of the building some of the windows were slightly pushed inwards, but none were sucked outwards.

The most likely intepretation for this pattern is the following sequence of events. The building was first subjected to a compression wave, which buckled many of the windows inwards, on both sides of the building. The building was not air-tight, and there would have been some air let in around the buckling, but even so, the corrugated sheeting had not failed much, which means that this overpressure cannot have been much over 50 mbar. (The span between vertical bolts on the corrugations was 120 cm, the figures supplied by the manufacturers of similar sheeting suggest that this would have failed inwards at around 70 mbar). This was followed by a rarefaction wave, which sucked many of the front windows out completely. However, once these windows had been sucked out, the pressure inside the building fell rapidly enough to prevent suction damage on the rear-facing windows. The venting of the building during the rarefaction makes it hard to quantify the level of rarefaction pulse, but probably it was also around 50–100 mbar (distance from explosion centre: 150–170 m). See Plate 4.

If we accept this sequence of events, we can estimate the time duration of the rarefaction pulse. A large sharp-edged hole with a drive pressure of 5 mbar vents air at about 30 m/s. If we take 50% of the windows as venting, the building has roughly 1 m^2 of vent per 200 m^3 of building volume. The timescale over which pressure would vent is therefore around 30 mbar. The duration of the rarefaction pulse was therefore probably at least 100 ms (since it has to have a rise time of about 30 ms). This suggests again that the pressure rise and fall was relatively slow, corresponding to a long event. It is remarkable that com-

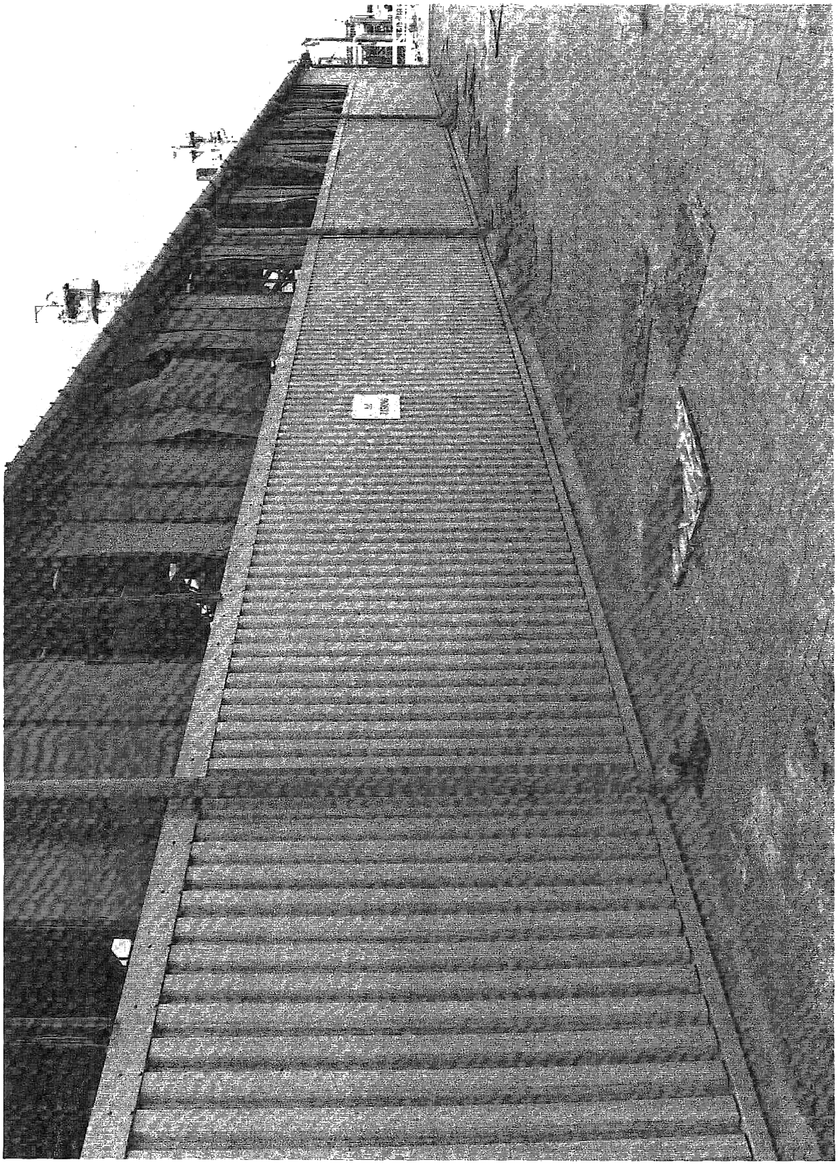

Plate 4. Damage to materials and transport building 150 m from explosion centre.

parable damage, although slightly milder (the frames moved, but no windows fell out), to this occurred to the wire-framed windows of Building 58 on the Thornton site, at a distance of 460 m from the explosion site.

(11) A high plant building was completely deroofed. The roof was a brittle corrugated sheet, which would have broken up fairly easily. The damage may have been caused by as little as 20–30 mbar, but it is impossible quantify accurately (distance from explosion centre: 35–60 m).

(12) The corrugated sheets on the roof of this substation were very slightly rippled. The overpressure required to do this was only 30 mbar. (distance from explosion centre: 70 m).

(13) Three walls of this corrugated sheet but were rippled and left been outwards. The underpressure required to do this was around 30 mbar (distance from explosion centre: 40 m).

(14) The building behind the xylene storage area was probably mainly affected by fire damage. The window frame on the near side to the explosion was presumably pushed inwards by the explosion, which would have required an overpressure of perhaps 100 mbar. The damage to this window suggests that the Keebush xylene vessels may have started leaking due to the blast damage, rather than the subsequent fire (distance from explosion centre: 40 m).

(15) One window frame on the alcohols PU workshop, facing towards the explosion, was sucked out by a few centimetres. This would require a static pressure more than 50 mbar. There was slight wall movement in this building, which again suggests that the underpressure felt here was perhaps 100 mbar. Since this building is adjoining the materials store, they probably experienced similar pressures. (There are no nearby buildings to reflect or shield pressure.) This therefore lends weight to a figure of 100 mbar rarefaction for the materials building, with damage mitigated by venting through the windows which came out, and supports the claim that the pressure pulse was long in duration (distance from explosion centre: 160 m).

(16) A 4 m high corrugated sheet building away from the main blast direction was pushed in at the top, and was bulged at the bottom. This indicates that at this location the compression was definitely stronger than the subsequent rarefaction phase (distance from explosion centre: 25 m).

(17) The corrugated roof of this building was slightly bent outwards (distance from explosion centre: 80 m).

(18) This building had slight ripples in the corrugations (distance from explosion centre: 80 m).

Appendix C

Structural calculations

This appendix collects together calculations of the internal pressure required to rupture the fluoroaromatics reactor vessel and propagate cracks in the vessel wall, and the external pressures to cause damage observed on other objects in the far field. In all cases the calculations are quasistatic. The greatest sources of uncertainty concern the properties of the materials in question.

C1 Rupture of reaction vessel by internal pressure

C1.1 Rupture of vessel head

The biaxial tensile stress σ_H, on a small circular element of the vessel head (radius δr) is given by:

$$P\pi\delta r^2 = 2\pi\delta r t_H \sigma_H \delta r / R_H \tag{C.1}$$

where P is the internal vessel overpressure, t_H is the average vessel head thickness ($=15.9$ mm), and R_H is the local vessel head radius of curvature (≈ 2 m)

$$P = 2t_H \sigma_H / R_H \tag{C.2}$$

For rupture, σ_H must be greater than the ultimate tensile strength σ_U, of the vessel material. σ_U is a function of the material composition, its history (such as any heat treatment) and temperature at rupture. A value of 30 tons/in.^{2} (465 MPa) is typical for weldable structural steels (e.g. EN2) up to 300°C. Hence:

$$P_{\text{HEAD RUPTURE}} \geq 2t_H \sigma_U / R_H \tag{C.3}$$

$$P_{\text{HEAD RUPTURE}} \geq 7.4 \text{ MPa } (\approx 74 \text{ bar})$$

C1.2 Rupture of vessel wall

By contrast, for rupture of the vessel wall, it is the hoop stress in the reaction vessel wall σ_W, that must exceed σ_U:

$$P 2R_W \delta h = 2t_W \delta h \sigma_W \tag{C.4}$$

where t_W is the average vessel wall thickness (13.8 mm), R_W is the vessel wall radius of curvature (1.25 m) and δh is an axial (ring-shaped) element of the vessel wall.

$$P = t_W \sigma_W / R_W \tag{C.5}$$

$$P_{\text{WALL RUPTURE}} \geq t_W \sigma_U / R_W \tag{C.6}$$

$$P_{\text{WALL RUPTURE}} \geq 5.1 \text{ MPa } (\approx 51 \text{ bar})$$

Thus the actual rupture of the vessel would be expected to be in the wall, at an internal pressure not less than 51 bar.

C2 Propagation of cracks following rupture

Following the initial rupture, cracks will propagate around the vessel provided the strain energy released by the crack front advancing a distance δa exceeds the surface energy required to produce the additional crack surfaces. This section considers cracks propagating axially (down the side of the vessel) or radially (around the circumference of the vessel). Both directions of cracking occurred on the reaction vessel; the removal of the top of the vessel required largely circumferential cracking, whilst the body of the vessel was split open by axial cracking.

C2.1 Axial (longitudinal) crack

$$G t_W \delta a \leq 2\pi R_W t_W \delta a (\sigma_W^2 / E) \tag{C.7}$$

where G is the surface energy per unit area of crack, E is the Young's modulus ($\approx$210 GPa for steel) and σ_W is the hoop stress in the vessel wall.

$$G = K_{IC}^2 / E \tag{C.8}$$

where K_{IC} is the critical stress intensity factor for the material. Like σ_U, K_{IC} depends on the material composition, history and temperature, larger values of K_{IC} indicating more ductile materials. For the weldable structural steel considered above (EN2), $K_{IC} \approx 100$ MNm$^{-3/2}$ at 300°C. Equations (C.5), (C.7) and (C.8) yield:

$$P_{\text{AXIAL PROPAGATION}} \geq (t_W K_{IC}) / (\sqrt{\pi} R_W{}^{3/2}) \tag{C.9}$$

$$P_{\text{AXIAL PROPAGATION}} \geq 0.56 \text{ MPa } (\approx 5.6 \text{ bar})$$

C2.2 Radial (circumferential) crack

Considering a circumferential crack propagation around the vessel wall:

$$G t_W \delta a \leq h t_W \delta a / (\sigma_A^2 / E) \tag{C.10}$$

where σ_A is the axial tensile stress in the vessel wall, and h is the length of vessel wall relieved by the crack opening (taken to be the distance from the head weld to the top of the cooling water coil $\approx$400 mm).
The axial stress in the vessel wall is given by:

$$P \pi R_W^2 = 2\pi R_W t_W \sigma_A \tag{C.11}$$

Combining eqs. (C.8), (C.10) and (C.11) gives:

$$P_{\text{RADIAL PROPAGATION}} \geq (2\sqrt{2} t_W K_{IC}) / (R_W \sqrt{h}) \tag{C.12}$$

$$P_{\text{RADIAL PROPAGATION}} \geq 4.9 \text{ MPa } (\approx 49 \text{ bar})$$

The estimated rupture pressure is therefore sufficient to account for both observed directions of crack propagation. It should be noted, however, that the internal pressure in a vessel will reduce very rapidly following the initial rupture. The internal pressure (and associated strain in the vessel wall) required for crack propagation must be maintained throughout the progress of the crack. Thus, for the almost complete removal of the vessel head, crack propagation must have been rapid and the internal pressure at rupture must have been somewhat higher than the 49 bar estimated above.

C3 Energy dissipated in crack formation

The total energy dissipated in crack formation, E_C, is given by:

$$E_C = L_C t_W G = L_C t_W K_{IC}^2/E \tag{C.13}$$

where L_C is the total length of crack, approximately 8 m for a complete circumferential crack and 3 m for a full length axial crack.

$E_C \approx 7.2$ kJ

C4 Bending of steel beam

This section concerns the bending of a beam beyond the elastic limit. The beam in question supported corrugated sheeting. The radius of curvature R_C of a beam (at the neutral axis) is given by:

$$R_C = EI/M \tag{C.14}$$

where E is the Young's modulus (≈ 210 GPa), M is the external bending moment, given by:

$$M = 0.25FL \tag{C.15}$$

F is a concentrated load at the centre of the beam span, L is the span length ($=4.75$ m), I is the second moment of inertia about the neutral axis:

$$I = \int w(r) r^2 \mathrm{d}r \tag{C.16}$$

$w(r)$ is the profile of the beam perpendicular to the plane of bending. For the L-shaped beam:

$$\begin{aligned} w(r) &= 0.06\ \text{m} \quad \text{for} \quad 0.12\ \text{m} < (n+r) < 0.13\ \text{m} \\ &= 0.01\ \text{m} \quad \text{for} \quad 0 < (n+r) < 0.12\ \text{m} \\ &= 0 \quad \text{for} \quad (n+r) < 0 \quad \text{or} \quad 0.13\ \text{m} < (n+r) \end{aligned}$$

n is the distance of the neutral axis from the inner edge, and r is measured outwards from the neutral axis.

Minimising I (to determine the position of the neutral axis) leads to:

$n = 0.0817$ m (i.e. 8.17 cm from inner edge)

$I = 3.135\ 10^{-6}\ \mathrm{m}^4$

The maximum stress in the beam is a compressive stress at the inner edge, given by:

$$\sigma_{\max} = En/R_C \tag{C.17}$$

For plastic yielding, $\sigma_{\max}$ must exceed the yield stress σ_Y. For a typical hardened steel ($Hv \approx 500\ \mathrm{kg/mm^2}$), $\sigma_Y \approx 1.6 \times 10^9\ \mathrm{Nm^{-2}}$. However, this neglects the probability that the inner edge of the beam will relieve the local stress by buckling. Thus a more realistic criterion for the onset of plastic bending is when the tensile stress at the outer edge of the beam, σ_T, exceeds the yield stress. That is:

$$\sigma_T = E(0.13 - n)/R_C \geq \sigma_Y \tag{C.18}$$

$R_C \leq 6.34\ \mathrm{m}$

The corresponding deflection of the beam δ, is given by:

$$(2R_C - \delta)\delta = (L/2)^2 \tag{C.19}$$

$\delta \approx L^2/8R_C = 0.44\ \mathrm{m}$

On substituting eqs. (C.14)-(C.16) into eqn (C.18), the concentrated force required for tensile yielding of the outer edge of the beam F_Y is:

$$F_Y \geq 4I\sigma_Y/(0.13 - n)L \tag{C.20}$$

$F_Y \geq 87\ \mathrm{kN}$ (≈ 8.7 tonnes)

If the force were evenly distributed, the total force for yielding would be doubled to 175 kN (≈ 17.5 tonnes). In order to obtain an estimate of the overpressure δP_C at this point, the force must be divided by the area of corrugated sheeting supported by the beam (2 m high along all of length L):

$\delta P_C = 18\ \mathrm{kPa}$ (≈ 180 mbar)

It should be noted that this calculation does not allow for any bending strength on the part of the corrugated sheeting bolted to the beam.

C5 Broken door bolt

C5.1 Visual description

This section concerns a door at the rear of Building 70b at Thornton Research Centre. The one and a half standard width door was pulled outwards by the pressure wave from the explosion, breaking a bolt of circular section with 1/2″ (12.7 mm) diameter. From a visual examination only, it appeared to have suffered some plastic deformation on one side from impact with the door frame, followed by brittle fracture. The grey and multi-faceted appearance of the fracture surface indicates that the material is a malleable or ductile cast iron.

C5.2 Impact energy

The fracture of the door bolt may be considered with reference to the "Charpy V-Notch Test". In this a 10 mm square section notched bar is supported between two supports 40 mm apart. The centre of the bar is struck by a pendulum to produce fracture. The energy lost by the pendulum is equivalent to the fracture energy of the specimen.

The same test can be carried out using unnotched specimens. In the case of a ferritic ductile cast iron at ambient temperature, this yields fracture energies of 150 ± 20 J, over a wide range of material composition.

To estimate the fracture energy of the door bolt, it is necessary to scale the Charpy value by the area of the bolt:

$$E_B = (\pi/4)(d/0.01)^2 E_C \tag{C.21}$$

where E_B is the fracture energy of the bolt, E_C is the Charpy fracture energy (≈ 150 J), and d is the diameter of the bolt (0.0127 m).
This energy is provided by the overpressure δP_B acting on the door:

$$E_B = \delta P_B (A/2) s \tag{C.22}$$

where A is the area of the door (≈ 2.4 m^2) (the factor of two is to allow for the door being supported at one side by hinges), and s is the distance of action of the pressure, comprising the thickness of the bolt and the maximum free movement of the door when bolted ($\approx 2d$)

$$\delta P_B = E_C (\pi/4)(d/0.01)^2 / Ad \tag{C.23}$$

$$\delta P_B \approx 6.3\ 10^3 \text{ Pa } (\approx 63 \text{ mbar})$$

Appendix D

Thornton Research Centre Damage from fluoroaromatics plant explosion

This is a revised list of the damage. It gives a reasonable impression of the level and types of damage. In all, some 119 panes of glass were broken, and not all of these are recorded below. The damage location is marked on Fig. 4:

(1) Substantial pieces of pipe lagging.
(2) Four inset metal doors in "roller" doors pushed inwards. The frames of all four doors were bent. The doors were parallel to the fence. The nature of the plastic deformation and tear suggested a long pressure pulse. The duration must also have been at least 30 ms to have time to move the doors on their free swing far enough to start damaging them. There was no sign that the doors had been pulled outwards afterwards, but it would have been harder to pull out than push in.

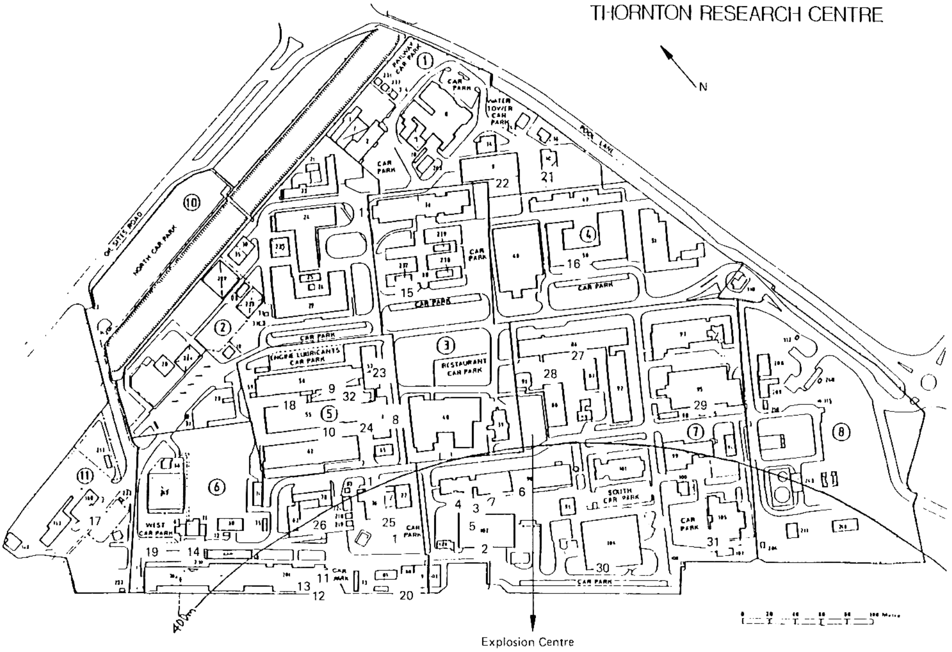

Fig. 4. Map of damage to Thornton Research Centre.

A nearby door of similar construction, perpendicular to the fence, was undamaged (although very slightly more sheltered), which suggests some directional blast.

This kind of damage to these inset "roller" doors occurred elsewhere on site (see below) and was probably caused by a force of about 5 kN, which corresponds to an overpressure of about 50 mbar. The design of these doors makes them particularly susceptible to overpressure damage.

(3) A set of fire doors had been forced open outwards. Not much force would be required to do this, but it is evidence of rarefaction.

(4) Two light covers inside the building had come off (very close to fire doors in (3)). Although the light covers were very light, and could have been lifted easily, trying to knock them back out of their fittings showed that this was not likely. Being sucked out (and flexing) due to rarefaction is more likely, and also would not have required much force.

(5) A strip light fitting had fallen down. It is impossible to work out the reason with certainty, but it was probably building shake.

(6) The detonation room is constructed with "blow-out" panels, which should vent any internal explosion. Two of these panels had partly blown out (i.e., sucked from outside). We have tested these panels and found that the movement corresponded to a force of 1 kN on small panels, which corresponds to an underpressure of 60 mbar.

(7) Two filmed windows cracked. Erratic damage is hard to quantify. Impossible to say whether it was rarefaction or compression. The windows faced in the direction of the fence.

(8) Two large wire-reinforced windows torn out of their frames outwards. The windows were door-sized. The frames had deformed by about a foot. All the nearby windows of a similar type (31 of such) were bent outwards slightly, and rendered unsafe. Eight of the 32 panes of wired glass were broken. Damage was by rarefaction, but construction meant that they would be much more sensitive to rarefaction than compression. The windows were perpendicular to the fence.

(9) Fourteen window panes just below roof level cracked. Cracking was associated with frames bending outwards. The forces required to do this were not large. The windows were parallel to the fence.

(10) Three steel doors pushed inwards, deformed by about 9 inches. Similar force required to those in (2), but doors were further from fence and sheltered from direct blast. One pair of timber doors were pulled out, damaging slip bolts.

(11) Three out of four 1 m × 1 m windows broken. All small windows intact. Should be able to calculate angle to blast. No glass left the windows, and it is impossible to assess if damage was inwards or outwards.

(12) Four out of 12 small windows broken, glass outwards. It is impossible to tell if this damage was present before the explosion.

(13) A door was ripped outwards. The damage of the door locks was considerable. The top bolt was bent and then snapped. The bottom bolt was bent and ripped the corner of the door off. The top bolt has been analysed (Appendix C) and had a yield energy of 150 J. Allowing for the lower bolt damage, this gives an energy density of at least 100 Jm^{-2} for the rarefaction phase of the blast (which is considerable at the distance). An underpressure of around 65 mbar is indicated. A total energy of at least 500 MJ is implied. (150 J of rarefaction energy on one of two door bolts 375 m away implies a rarefaction energy density of 250 $\mathrm{J/m}^2$ over a 375 m radius hemisphere, which gives an energy yield of 220 MJ just in rarefaction, implying at least 500 MJ total: although this figure is calculated from a single door bolt, it is consistent with the level of rarefaction underpressure estimated from elsewhere at Thornton.)

(14) A heavy 3 m door ripped four screws and two nails from its bolt outwards. Although the force required to do this was reasonable, the door area was large, and the required overpressure was small.

(15) One glass panel broken. One first floor window frame bent inwards, one second floor window frame bent outwards.

(16) Four glass panels cracked (rooms 6, 7, 28 and 29).

(17) One window cracked.

(18) Draught-proofing on door moved outwards.

(19) Draught-proofing on garage door moved outwards.
(20) Fire door opened outwards.
(21) Two glass panels cracked
(22) Six window panes cracked.
(23) Glass-fronted door cracked.
(24) West-facing roller door pushed inwards. Similar to damage in (2) and (10).
(25) Three glass panels broken.
(26) Glass door panel broken.
(27) Five glass panels broken.
(28) One window cracked.
(29) Cladding cracked and damaged. Timber doors sucked outwards. One window frame pushed in.
(30) Ceiling tiles blow out. One pair of double doors blown out, bolts damaged.
(31) External door lifted out of track.
(32) Roller shutter door damaged inwards. The other doors damaged outwards.

Appendix E

Reactor Data 20 March 90

Time	Reactor temperature (°C)	Jacket temperature (°C)	Reactor pressure (barg)
2:50	149.8	160	0.218
2:51	150.4	160	0.225
2:52	151.0	160	0.234
2:53	151.5	160	0.246
2:54	152.0	160	0.261
2:55	152.7	160	0.280
2:56	153.2	160	0.299
2:57	153.8	160	0.323
2:58	154.4	160	0.349
2:59	154.9	160	0.376
3:00	155.5	160	0.404
3:01	156.2	160	0.438
3:02	156.9	160	0.479
3:03	157.5	160	0.524
3:04	158.2	160	0.574
3:05	159.0	160	0.626
3:06	159.9	160	0.686
3:07	160.8	160	0.755
3:08	161.8	160	0.831
3:09	163.0	160	0.929

Appendix E (continued)

Time	Reactor temperature (°C)	Jacket temperature (°C)	Reactor pressure (barg)
3:10	164.4	160	1.031
3:11	165.7	160	1.146
3:12	167.6	160	1.203
3:13	169.4	159	1.435
3:14	171.6	156	1.614
3:15	174.2	150	1.844
3:16	177.2	144	2.113
3:17	180.6	139	2.473
3:18	185.0	132	2.976
3:19	190.3	130	3.675
3:20		Data lost	

Appendix F: Jet fire tests on light fittings

An element of the investigation concerns Missile 47, a 4′ twin-tube light fitting that is believed to have been ejected from the plant. It is not clear whether this was an active or redundant unit.

This appendix describes an investigation of the damage and associated experimental work that was carried out in a number of stages.

F1 Examination

The following observations are from examination of Missile 47. For convenience, the locations of features are referred to Fig. 5; the orientation indicated is arbitrary and is not intended to relate to its original orientation.

The unit was essentially intact; the right-hand half was fire-damaged. On

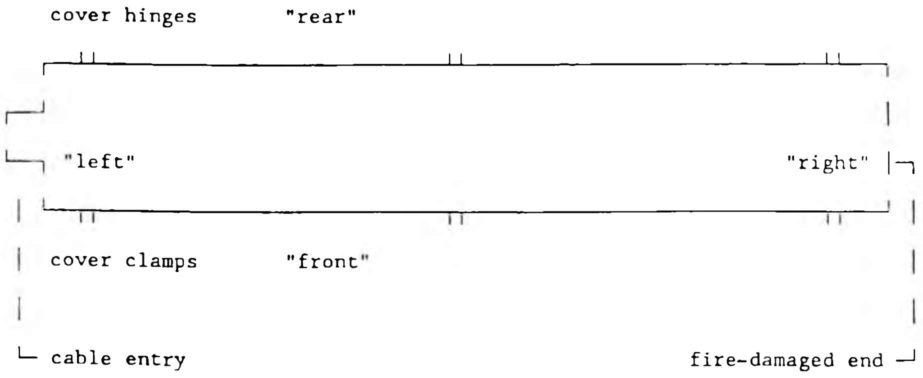

Fig. 5. Sketch plan of Missile 47.

receipt, the left-hand and central cover clamps were unfastened and the cover partly open.

The GRP casing had not suffered significant mechanical damage but a quite compact area of about 100 cm^2 at the right-hand end, extending around the sealing channel towards the right-hand cover clamp, had been burned to the extent that essentially all the resin had been lost, leaving an incoherent mass off glass fibre. This had little mechanical stiffness and was soft to touch.

The right-hand half of the cover had been burned and distorted and had partially collapsed. At the right-hand and there was an irregular hole, approximately 1 cm×2 cm. This had rounded (burned) edges, i.e. it did not have sharp, clean edges that would be expected to result from an impact fracture. The interface between the burned portion of the cover and the unaffected region was very distinct with a relatively small band of sooting.

Approximately 50 cm of the thin, outer layer of the metal securing band that fits around the periphery of the cover was missing. At the right-hand end it appears that it might have been burned away; at its left-hand end (near the centre of the front edge) it had been fractured or torn.

When the remaining cover clamp was released it was apparent that the right-hand end of the cover had become fused to the internal components. In order to release the major portion, a transverse saw cut was made at approximately 24 cm from the right-hand end to initiate a fracture which separated the required section. The adhering rubber seal was also cut in three places to secure final release.

It was noted that the front tube was broken: part of it being attached to the cover. It is fairly certain that this break was not caused by removing the cover although the damage may have been made slightly more extensive in this operation. The rear tube had remained intact, surviving the blast and subsequent impact on landing.

The rubber sealing strip had been incorrectly seated in two places toward the left-hand end; one at the front flange and one at the rear. The permanent set and witness marks indicate that it had been so fitted for some time. This would likely have impaired the explosion-proof rating of the unit.

F2 Exposure to jet fire

In order to determine what form and duration of fire had caused damage to the cover, an experiment to subject lighting units to direct flame impingement and to radiation only was set up.

An attempt was made to generate comparable damage to two similar CEAG units by exposure to a 7 MW propane jet flame. One was partially engulfed by the flame with half of the cover subjected to direct impingement at about 4 m from the jet source. The heat flux within the impinging flame would be of the order of 200 kW m^{-2}, with approximately 50% radiative and 50% convective. The other unit was positioned approximately 1 m from the edge of the flame envelope, receiving radiate heat only, estimated to be at least 20 kW m^{-2}, with half of the cover shielded by a board. Both lighting units were exposed in Test 1, in which the engulfed unit became severely damaged, whereas the other was visually unaffected. The damaged unit was removed for Test 2, in which the flame was allowed to burn for a longer period.

Test 1

The fittings were exposed to the jet fire for 25 s. From end to end of the impinged cover there was a complete range of effects from total destruction to unaffected. In the region where the edge of the flame envelope had impinged on the cover, there was a transition zone of about 150 mm containing whitened and charred material. It is estimated from the video recording that a degree of damage comparable to that on Missile 47 was achieved in 12–17 s.

Test 2

The appearance of the irradiated cover after 3 min exposure to thermal radiation was totally different to that in the impingement experiment. There was no swelling or charring of the surface. It had softened and collapsed, leaving a glossy surface with some small blisters. In further contrast to CEAG unit 1, the interface with the unaffected region that had been shielded by the board was sharp (about 15 mm wide).

The interface between damaged and undamaged portions of Missile 47 had some quite sharp delineations suggesting that the unaffected half was shielded to a certain extent. The soot pattern tended to support this. The affected surface, however, had an appearance more akin to that seen during flame engulfment of CEAG unit 1. At this stage, it was concluded that Missile 47 had been exposed to short-duration partial direct impingement of a flame rather than longer exposure to radiation from a nearby flame.

F3 Analyses

Samples of the cover material of Missile 47 were subjected to infrared and Raman spectroscopy, and both techniques give spectra that were consistent with those of polymethyl methacrylate polymer, PMMA (e.g. "Perspex"). We had some difficulty in obtaining additional examples of units with this cover, since the use of PMMA was discontinued 7–8 years ago. Eventually, two similar units were located and analyses of the covers confirmed PMMA. One of these units was used in Test 3, and a second in a blast-loading test.

The casing of each unit was analysed using pyrolysis techniques. It was presumed that all the casings were constructed from the same type of polyester composite; the results supported this.

F4 Exposure to small flame

Evidence from the casing of Missile 47 suggested that impingement of a smaller, highly directional flame, aligned essentially along the major axis of the unit, was a credible source. An acetylene torch was used to produce a luminous, sooty diffusive flame of about 0.7 m in length. The radiant component of heat flux from this flame was about 150 kW m^{-2}; the total flux could not be determined because of excessive soot deposition on the monitoring instrument.

Test 3

The lighting unit was supported horizontally with the transparent cover uppermost. Although this almost certainly bore no relationship to the orientation of the original unit, if offered the best view of the critical parts in this test.

The torch was hand-held and directed onto the corner of the casing in line with the sealing channel and at a small angle to the main axis of the unit, aiming towards its centre. This caused the flame to engulf most of the end of the unit and to wash over the cover.

The dense nature of the flame prevented much observation of the behaviour of the target, either directly or from the video recording, and it was not possible to determine when the various components ignited. A soot layer was established on the cover at between 5–10 s. After 25 s, there was definite evidence that both casing and cover were alight and at that point the torch was removed. Residual flames were extinguished with a dry powder extinguisher.

The cover had partially collapsed in a similar manner to that of Missile 47. A small hole of about 2×3 cm had formed at the end of the cover. The resin of the GRP casing had burned to an extent that the reinforcing fibres could be readily separated. At the edge of the sealing channel it had burned through, as on Missile 47.

No thermal radiation experiments were conducted on units with a PMMA cover. In light of the previous work, it is inconceivable that the associated intensive damage to the casing could be achieved in a reasonable time frame without flame impingement.

F5 Conclusion

Fire damage comparable to that observed on Missile 47 has been created on a similar lighting unit by impingement of a highly directional, energetic flame of modest proportions for 25 s. Damage to the casing and the cover, which are made of different materials, is a close match to that observed on the original.

Appendix G

Potential energy yield from DFA reactor

The aim here is to calculate the heats of decomposition of the materials present in the CFA reactor at the time of the explosion. The calculation is necessarily crude, at insufficient data on the products of decomposition have been found.

G1 Dichloronitrobenzene

The problem here is that both the heat of formation of 2,4-dichloronitrobenzene and its decomposition products are unknown. The heat of formation of the material in its standard state (i.e. solid) was estimated by inference from the known heat of formation, see Ref. [G1], of 1,4-difluoro-2-nitrobenzene of −79.4 kcal/mol. The difference between the two molecules is in the position of the halogen groups and in the substitution of two chlorine for two fluorine molecules. Taking the second problem first, the differences between the heat of formation of several fluoro-substituted compounds and their corresponding chloro-analogues, expressed per Ar–X bond, are given in Table G1.

The last figure in the list comes from Benson's Ref. [G2] tabulation of group additivity functions. Note that the values are all quite close to each other, even when other functional groups are present, except for the case of *o*-fluorotoluene, presumably due to a longer range interaction between $-CH_3$ and –F and/or –Cl. Taking the value of 37.5 kcal/mol as realistic, leads to a heat of formation of 1,4-dichloro-2-nitrobenzene of −4.4 kcal/mol. Furthermore, the differences between the heats of formation of 1,2-difluorobenzene, 1,3-difluorobenzene and 1,4-difluorobenzene are fairly small, around 5%, so we will assume that the arrangement of molecules around the ring is a second-order effect. Hence, the standard heat of formation of solid 2,4-dichloronitrobenzene is assumed to be −4.4 kcal/mol.

The prediction of the products of the decomposition is much more difficult. Taking as example, the decomposition of TNT, the actual value is not calculable by simple chemistry, because as many as 23 different products can be

TABLE G1.

Heats of formation of fluorocarbons per Ar–X bond

Fluorinated compound	(Ar–Cl)-(Ar–F) (kcal/mol)
Hexafluorobenzene (g)	36.7
m-Difluorobenzene (l)	38.6
Fluorobenzene (l)	38.7
m-Fluorobenzoic acid (s)	37.7
o-Fluorotoluene (l)	30.6
p-Fluorotoluene (l)	39.9
$(C_B\text{-}Cl)-(C_B\text{-}F)$	39.0
Average	37.5

found [G3]. The approach used here is to write down plausible overall reactions and examine their energy yield to determine a realistic value, e.g.

$$C_6H_3Cl_2NO_2 \rightarrow 2HCl(g) + 1.5CO(g) + 0.5H_2O(g) + 0.5N_2(g) + 4.5C(s)$$

$$\Delta H = -108 \text{ kcal/mol}$$

$$\rightarrow 2HCl(g) + 0.75CO_2(g) + 0.5H_2O(g) + 0.5N_2(g) + 5.25C(s)$$

$$\Delta H = -139 \text{ kcal/mol}$$

Clearly, the molecule is deficient in oxygen and so much of the potential energy is not released. None the less, formation of two HCl molecules releases a considerable amount of energy. Other reactions can be written to form alternative small hydrocarbons, e.g. formaldehyde, and the net energy release would then be lower. Taking a value of say 100 kcal/mol, gives a potential energy release for anaerobic decomposition of 2.17 MJ/kg. A more reliable estimate could be obtained by performing an equilibrium calculation considering more of the candidate products, but with much more effort.

G2 4-Fluoro-2-chloronitrobenzene

This is a product of the Halex reaction and so would be expected to be present. Taking an analogous approach to that above, the heat of decomposition for the two corresponding reactions is −112 and −143 kcal/mol, respectively. Thus, the dichloro and the fluorochloro can be treated as essentially the same in terms of their heats of decomposition.

G3 Dimethylacetamide

The heat of formation of dimethylacetamide (g) was calculated, using Benson's group additivity tables, to be −57 kcal/mol. Thus, the heat of decomposition of this molecule will be negligible, and probably endothermic. Furthermore, the heat of hydrolysis to acetic acid and dimethylamine will be essentially zero.

G4 Heat of combustion of 2,4-dichloronitrobenzene

As a rough estimate (to within about 10%), the heat of combustion of 2,4-dichloronitrobenzene can be calculated assuming the combustion products are CO_2, N_2, Cl_2 and H_2O. This gives a figure of around 2.8 MJ/mol, or 14.5 MJ/kg.

G5 References

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The assessment of major hazards: The road transport environment for conveyance of hazardous materials in Great Britain

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Abstract

The assessment of major transport hazards creates a requirement for a wide range of data on the transport environment. This environment is specific to the country concerned. The present paper gives an overview of the road transport environment in Great Britain. It gives information on the frequency of accidents involving heavy goods vehicles generally and heavy goods vehicles carrying hazardous materials in particular, on the circumstances surrounding certain types of accidents and on the probability of certain outcomes of accidents. Certain limited information is also given for comparative purposes on the road transport environment in other countries.

1. Introduction

The assessment of major hazards arising in the road transport of hazardous materials requires the use of a wide range of data on the road transport environment. As in hazard assessment generally, two situations can arise with respect to the estimation of the frequency of particular accident scenarios. Either it is possible to estimate the frequencies of these scenarios from historical data or it is necessary to synthesise the frequencies, by methods such as modelling or fault tree analysis.

Thus for scenarios such as release of materials which are transported in large quantities (e.g. gasoline and LPG) it may well be possible to obtain historical data. For other scenarios such as release of chlorine or explosion of explosives in transport it is much more difficult. Moreover, even where historical data exist, it may still be necessary to resort to modelling for reasons such as the

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need to adapt the data to the particular assessment or to explore the effect of possible mitigatory measures.

The present work was carried out in connection with a study of the risks from the road transport of explosives [1]. Explosions occurring in such transport are very rare.

An earlier review of the various transport environments has been given by Appleton [2]. The work refers particularly to the transport of radioactive materials, another example of a transport hazard for which historical data on scenarios are lacking.

As will become apparent from the data given below, a large proportion of incidents involving hazardous materials are not due to traffic accidents, but to other causes. The prime concern in this paper is with incidents which occur during transport rather than during loading and unloading or in temporary storage, but some of the data sets also cover the latter.

2. Hazardous goods

Hazardous goods are taken here to be goods defined as such under the United Nations classification and regulated by the Classification, Packaging and Labelling Regulations (CPL) 1984.

These hazardous materials are mainly flammable and/or toxic liquids and liquefied gases, reactive chemicals and explosives.

3. Some basic road transport statistics

3.1 Sources of information

The principal source of information on road transport and on road accident statistics is the Department of Transport (DoT). Other important sources are the Home Office and the Transport and Road Research Laboratory (TRRL), which is part of the Department of the Environment (DoE).

Unfortunately, as so often happens, there are difficulties in relating information from one source to that from another. For example, DoT statistics are for HGVs with unladen weights of not less than 1.5 tonne, whereas the principal TRRL study of HGV fatal accidents deals with HGVs with unladen weights not less than 3 tonne.

3.2 Road network

There are two classifications of roads used in Britain. Roads are generally classified as trunk, principal, secondary, etc., whilst in accident statistics roads are described as A class, B class, and ‘other’. Broadly speaking, trunk and principal roads are equivalent to A class roads, whilst secondary roads are equivalent to B class and ‘other’ roads [3]. Table 1 gives the length of the road network in Great Britain in 1973 [4].

TABLE 1

Road network in Great Britain 1975 (after Johnson [4])

Length of road (km)						
BUA[a]		Total	Non-BUA		Total	Motorways
Trunk/ principal	Class II and below[b]		Trunk/ principal	Class II and below[b]		
13,874	117,052	130,926	32,383	163,587	195,970	1,752

[a] BUA: built-up area.
[b] Of these totals Class II roads are 8,746 in BUAs and 19,643 in non-BUAs.

TABLE 2

Gross vehicle weight of all goods vehicles on British roads in 1985 (after JMP Consultants [6])

Gross vehicle weight (te)	Proportion of vehicles (%)
<20	70
20–22	3
22–24	3
24–26	2
26–28	2
28–30	4
30–32	6
32–34	4
34–36	2
36–38	3
>38	1

3.3 Heavy goods vehicles

The vast majority of hazardous materials are carried in heavy goods vehicles (HGVs). The most common HGV is the rigid two-axle vehicle. A total of 435,000 HGVs were registered in 1986 [5]. Table 2 gives the distribution of HGV weights for 1985 [6].

Figure 1 shows some principal heavy goods vehicles together with their classifications [7].

3.4 Distances travelled

The distances travelled by HGVs in 1986 are shown in Table 3 by axle configuration, body type and road type. HGVs travelled a total of

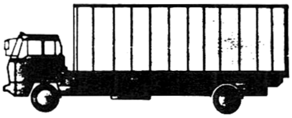
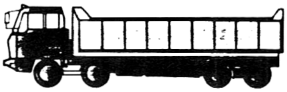
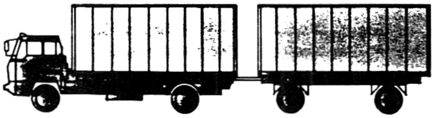
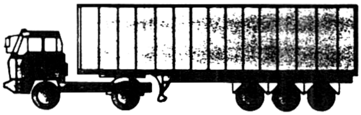
Recommended Description			Identifier	UK Maximum Gross Weight (tonnes)	Shape
LIGHT GOODS VEHICLES			2 axles	**3.500**	
LORRIES	**HEAVY GOODS VEHICLES** (Vehicles over 7.5 tonnes gross require a Heavy Goods Vehicle Driver's Licence)	SMALLER 2-AXLE LORRIES	2 axles	**Over 3.5 7.500**	
		BIGGER 2-AXLE LORRIES	2 axles	**Over 7.5 17.000**	
		MULTI-AXLE LORRIES	3 axles rigid	**24.390**	
			3 axles artic	**24.390**	
			4 axles rigid	**30.490**	
			4 axles artic.	**32.520**	
			Vehicle and draw-bar trailer	**32.520**	
			5 axles or more artic	**38.000**	

Fig. 1. A simplified guide to lorry types and weights (after Department of Transport [7]).

TABLE 3

Distances travelled by heavy goods vehicles in 1986, by axle configuration, body type and road type (after Department of Transport [5])

HGV type	Distance ($\times 10^8$ km)		
	All speed limits	Non-BUR[b]	BUR[c]
Rigid			
2-axle	131	87	44
3-axle	11	8	3
4-axle	10	8	2
Articulated			
3-axle	6	5	1
4-axle	41	36	5
5-axle	18	17	1
All HGVs[a]	221	165	56

[a] Includes cases where the axle configuration was not reported.
[b] Non-BUR includes motorways.
[c] BUR: built-up road.

TABLE 4

Proportion of heavy goods vehicles in 1986 travelling on different road classes (after Davies [1])

Road class	Proportion of vehicles (%)	
	Non-BUR[a]	BUR
A	87.0	61.0
B	6.0	11.5
Other	7.0	27.5
Total	100	100

[a] Data exclude motorways.

221×10^8 km [5]. The average annual distance travelled per vehicle is thus 50,800 km ($221 \times 10^8/435{,}000$). Table 4 gives a breakdown of the HGV distances travelled by road class.

3.5 HGVs conveying hazardous materials

It has been estimated by Kletz [8] that in 1986 there were some 14,000 road tankers in operation. The authors have confirmed that this approximate figure is still valid. Kletz also gives the annual distance travelled per tanker as 60,000 miles (96,500 km).

Estimation of the total number of HGVs carrying hazardous materials (HGV/HMs) is deferred until later.

4. Accident statistics

4.1 Accident definitions

Accidents are commonly classified in the UK as personal injury (PI) accidents and damage-only (DO) accidents.

Road accident statistics derived from police records relate to personal injury accidents. The number of damage-only accidents generally has to be estimated from the number of injury accidents. For example, Dawson [9] in a study of the cost of accidents gives the number of personal injury accidents in 1968 as 264,200 and estimates the number of damage-only accidents as 1,583,000, giving a DO/PI accident ratio of 6. Appleton states that values of the ratio given in DoT and TRRL studies are in the range 6–12. He also states that a survey by the Safety and Reliability Directorate (SRD) of a small number of local authorities found a value of the DO/PI ratio of 2–3 but the reporting was not consistent. In any event, the problem of defining what constitutes an accident is more severe for damage-only than for personal injury accidents. Moreover, an accident severe enough to endanger the integrity of a load is likely to result in some personal injury. It is convenient, therefore, to work in terms of the personal injury accident criterion.

The main exception to the above is fires. Fire brigade records allow the derivation of fire statistics. Major studies of fires have been made in 1974 by North [10] and in 1981 by McLean [11].

The significance of the definition of an accident depends on the use to which it is to be put in the hazard assessment. Broadly speaking. the definition is important if historical data on releases are lacking, but this is less so if such statistical information is available. The reason is that in the latter case it is possible to work with a definition of an accident which is to a degree arbitrary and to work in terms of the probability of release given an accident so defined. If on the other hand data are not available and it is necessary to model the accident in order to determine the probability of release, the definition of what constitutes an accident becomes more significant, since it determines the accident frequency.

In the following the UK accidents considered are injury accidents, except for fires.

4.2 Injury accidents

For vehicles generally Johnson and Garwood [12] found that the proportion of fatal accidents in the total of serious injury and fatal accidents for the period

1959–1965 was in the range 5.1–9.2% for roads with speed restrictions of 30 or 40 m.p.h. and in the range 8.3–14.5% for other roads.

A study by the DoT [13] in 1987 obtained for the ratio of fatal accidents to all injury accidents values in the range 0.018 : 1 to 0.025 : 1.

Some data on casualties in HGV accidents are given in Table 5. A study of fatal accidents involving HGVs in 1976 has been given by Riley and Bates [14].

TABLE 5

Casualties in heavy goods vehicle accidents in 1986 (after Department of Transport [13])

A. No. of casualties

Other vehicle type	Fatalities	Casualties
HGV	24	672
LGV	–	137
Bus/coach	–	47
Car	4	622
Motorcycle	–	17
Pedal cycle	1	8
SVA (no pedestrian)	32	1045
SVA (pedestrian)	171	1184
Other	28	747
Total	260	4479

B. No of HGVs involved in injury accidents: rigid HGVs

Road type	No. of vehicles involved							
	Fatal accidents				All accidents			
	2-axle	3-axle	4-axle	All	2-axle	3-axle	4-axle	All
Non-BUR	239	41	50	330	3672	714	657	5082
BUR	164	32	25	221	3988	631	463	5043
All speed limits	403	73	75	551	7660	1345	1120	10125

C. No. of HGVs involved in injury accidents: articulated HGVs

Road type	No. of vehicles involved							
	Fatal accidents				All accidents			
	2-axle	3-axle	4-axle	All	2-axle	3-axle	4-axle	All
Non-BUR	35	127	83	245	447	1444	872	2763
BUR	15	39	15	69	283	674	316	1273
All speed limits	50	166	98	314	730	2118	1188	4036

TABLE 5 (*continued*)

D. No. of casualties by road type

Road type	Fatalities	All casualties
Non-BUR		
A roads	451	6452
B roads	34	838
Other roads	37	1095
All roads	522	8385
BUR		
A roads	205	4926
B roads	34	933
Other roads	74	2316
All roads	313	8175
All speed limits		
Motorways	73	1888
A roads	656	11,378
B roads	68	1771
Other roads	111	3411
All roads	908	18,448

E. Proportion of casualties by road type

Road type	Fatalities (%)	All casualties (%)
Non-BURs	57.5	45.5
BURs	34.5	44.3
Motorways	8.0	10.2

F. No. of occupant casualties

Occupants	Fatalities			Casualties		
	Non-BUR	BUR	All	Non-BUR	BUR	All
Drivers	53	8	61	1987	773	2760
Passengers	14	8	22	354	205	559
All occupants	67	16	83	2341	978	3319

Grattan and Hobbs [15] studied injuries to occupants of HGVs. In 1975 there were 3200 occupant casualties in HGVs, of which 800 were serious or fatal, the latter numbering 71. These casualties were usually the result of collision between two HGVs or between the HGV and a roadside obstacle. A 5% sample of the serious or fatal injuries was studied. All fatal injuries were associated with either massive intrusion of the cab structure or ejection of the occupant.

Hobbs et al. [16] have examined various classifications of injury, in a study which relates the injury classifications to the length of stay in hospital.

Kletz [8] quotes figures given by Hills [17] for the number of deaths from the road transport of hazardous chemicals in the UK in the period 1970–80 as 16 deaths overall, making an average of 1.23 deaths/y. From the context these are the deaths attributable to the load. Kletz also states that the average number of deaths per fatal accident is 1.5.

4.3 HGV accident frequency

In 1986 HGVs travelled 221×10^8 km and there were 13,429 accidents involving HGVs. A number of accidents involve more than one HGV. The number of HGVs involved in accidents is thus somewhat more than the number of accidents involving an HGV. The number of HGVs involved in accidents in 1986 was nearly 15,000.

Statistics on accidents involving HGVs are given in Tables 6–13. Table 6 gives the number of HGVs involved in accidents and Table 7 the number of accidents involving HGVs by axle configuration, body type and road type. Table 8 gives a breakdown of the road class on which the accidents occurred. Table 9 gives the number of HGV accidents in 1986 by combination of vehicles involved. Table 10 gives the frequency of HGV accidents by axle configuration, body type, road type and road class. Table 11 gives the frequency of HGV accidents in built-up areas by axle configuration, body type, road class and combination of vehicles involved. Table 12 gives the frequency of HGV

TABLE 6

Number of heavy goods vehicles involved in accidents in 1986 by axle configuration, body type and road type (after Department of Transport [5])

HGV type	Roads		
	All speed limits	Non-BUR[b]	BUR
Rigid			
2-axle	7660	3672	3988
3-axle	1345	714	631
4-axle	1120	657	463
Articulated			
3-axle	730	447	283
4-axle	2118	1444	674
5-axle	1188	872	316
All HGVs[a]	14,773	7958	6815

[a] Includes cases where the axle configuration was not reported.
[b] Non-BUR includes motorways.

TABLE 7

Number of accidents involving heavy goods vehicles in 1986 by axle configuration, body type and road type

HGV type	Roads		
	All speed limits	Non-BUR[b]	BUR
Rigid			
2-axle	7264	3482	3782
3-axle	1275	677	598
4-axle	1062	623	439
Articulated			
3-axle	692	424	268
4-axle	2009	1370	639
5-axle	1127	827	300
All HGVs[a]	13,429	7403	6026

[a] The only figure in this table given in the DoT statistics is that of 13,429 for the total number of accidents involving HGVs. The ratio of the number of accidents involving HGVs to the number of HGVs involved in accidents is thus 0.948 (13,429/14,773) and the other figures in the table have been obtained by applying this ratio to the figures in Table 2.

[b] Non-BUR includes motorways.

TABLE 8

Proportion of heavy goods vehicle accidents in 1986 occurring on different road classes (after Department of Transport [1])

Road class	Proportion of accidents (%)	
	Non-BUR	BUR
A	76	60
B	10	11
Other	14	29
Total	100	100

[a] Data exclude motorways.

single-vehicle accidents by axle configuration, body type and road class. Table 13 gives the proportion of HGV accidents by junction type and by impact position.

The basic annual accident statistics for HGVs in 1986 are:

No. of accidents = 13,429/y

No. of vehicles involved in accidents = 15,000

Proportion of vehicles involved in accidents = 15,000/435,000 = 3.4%/y

Frequency of accidents = $13{,}429/(221 \times 10^8) = 0.62 \times 10^{-6}$/km

TABLE 9

Number of heavy goods vehicle accidents in 1986 by combination of vehicles involved (after Department of Transport [5])

A. All accidents

	Accidents	
	Number	Proportion (%)
Accidents involving		
Single vehicle	1994	14.8
Two vehicles	8452	63.0
Three or more vehicles	2983	22.2

B. Two vehicle and single vehicle accidents

	Accidents	
	Number	Proportion (%)
Accidents involving		
Single vehicle	890	8.5
Car	5271	50.4
Bus/coach	186	1.8
LGV	594	5.7
HGV	529	5.1
Motorcycle[a]	1012	9.7
Pedal cycle	723	6.9
Pedestrian	1104	10.6
Other	137	1.3
Total	10,446	100.0

C. Two vehicle accidents only

Accidents with	Proportion (%)
Car	62.4
Bus/coach	2.2
LGV	7.0
HGV	6.3
Motorcycle[a]	12.0
Pedal cycle	8.6
Other	1.5
Total	100.0

[a] Motorcycles include combinations.

TABLE 10

Frequency of heavy goods vehicle accidents in 1986

A. Accidents by axle configuration, body type and road type[a]

HGV type	Frequency (accidents/10^6 km)		
	All speed limits	Non-BUR[b]	BUR
Rigid			
2-axle	0.55	0.40	0.86
3-axle	1.16	0.85	2.00
4-axle	1.06	0.78	2.20
Articulated			
3-axle	1.15	0.85	2.68
4-axle	0.49	0.38	1.28
5-axle	0.63	0.49	3.00
All HGVs[a]	0.62	0.46	1.08

B. Accidents by road class (after Department of Transport [5])

Road class	Frequency (involvements/10^6 km)	
	Non-BUR	BUR
A class	0.57	1.19
B class	1.15	1.21
Other	1.30	1.28
All	0.48	1.22

C. Accidents by axle configuration, body type and road class

HGV type	Frequency (accidents/10^6 km)					
	Non-BUR			BUR		
	A	B	Other	A	B	Other
Rigid						
2-axle	0.35	0.70	0.80	0.84	0.68	0.90
3-axle	0.74	1.48	1.69	1.95	1.98	2.09
4-axle	0.67	1.35	1.55	2.14	2.19	2.30
Articulated						
3-axle	0.74	1.48	1.69	2.62	2.67	2.81
4-axle	0.33	0.66	0.76	1.25	1.28	1.34
5-axle	0.43	0.85	0.97	2.91	2.99	3.14
All HGVs	0.66	1.32	1.51	1.05	1.08	1.13

[a] Accident frequency data in Section A are derived from data given in Tables 3 and 7

[b] Non-BUR includes motorways.

TABLE 11

Frequency of heavy goods vehicle accidents on BURs in 1986 by axle configuration, body type, road class and combination of vehicles involved

A. Car, bus/coach and motorcycle

HGV type	Frequency (accidents/10^6 km)								
	Car			MC			Coach/bus		
	A	B	Other	A	B	Other	A	B	Other
Rigid									
2-axle	0.45	0.46	0.48	0.09	0.09	0.09	0.02	0.02	0.02
3-axle	1.04	1.05	1.11	0.20	0.20	0.21	0.04	0.04	0.04
4-axle	1.14	1.16	1.22	0.22	0.22	0.24	0.04	0.04	0.04
Articulated									
3-axle	1.39	1.42	1.49	0.27	0.27	0.29	0.05	0.05	0.05
4-axle	0.66	0.68	0.71	0.13	0.13	0.14	0.02	0.02	0.03
5-axle	1.55	1.59	1.67	0.30	0.31	0.32	0.05	0.06	0.06
All HGVs	0.56	0.57	0.60	0.11	0.11	0.12	0.02	0.02	0.02

B. LGV, HGV and pedal cycle

HGV type	Frequency (accidents/10^6 km)								
	LGV			HGV			Pedal cycle		
	A	B	Other	A	B	Other	A	B	Other
Rigid									
2-axle	0.05	0.05	0.05	0.05	0.05	0.05	0.06	0.06	0.07
3-axle	0.12	0.12	0.12	0.11	0.11	0.11	0.14	0.14	0.15
4-axle	0.13	0.13	0.14	0.11	0.12	0.12	0.16	0.16	0.17
Articulated									
3-axle	0.16	0.16	0.17	0.14	0.14	0.15	0.19	0.20	0.21
4-axle	0.07	0.08	0.08	0.07	0.07	0.07	0.09	0.09	0.10
5-axle	0.17	0.18	0.19	0.16	0.16	0.17	0.21	0.22	0.23
All HGVs	0.06	0.06	0.07	0.06	0.06	0.06	0.08	0.08	0.08

[a] Accident frequencies in this table have been derived from the data in Tables 9 and 10.

4.4 Impact accidents

A study of the impact speed of HGVs in accidents has been made by Davies and Lees [18] based on tachograph records. Table 14 gives the impact speeds obtained in this study. The accidents may be regarded as a biased sample in

TABLE 12

Frequency of heavy goods vehicle accidents involving only a single vehicle in 1986 by axle configuration, body type and road class

A. BUR

HGV type	Frequency (accidents/10^6 km)								
	SVA (no pedestrian)			SVA (pedestrian)			Total SVA		
	A	B	Other	A	B	Other	A	B	Other
Rigid									
2-axle	0.05	0.05	0.06	0.07	0.07	0.07	0.12	0.12	0.12
3-axle	0.12	0.12	0.13	0.15	0.15	0.16	0.27	0.27	0.29
4-axle	0.13	0.13	0.14	0.17	0.17	0.18	0.30	0.31	0.32
Articulated									
3-axle	0.16	0.17	0.18	0.20	0.21	0.22	0.36	0.38	0.40
4-axle	0.08	0.08	0.08	0.10	0.10	0.10	0.18	0.18	0.18
5-axle	0.18	0.19	0.20	0.23	0.23	0.24	0.41	0.42	0.44
All HGVs	0.07	0.07	0.07	0.08	0.08	0.09	0.15	0.15	0.16

B. Non-BUR

HGV type	Frequency (accidents/10^6 km)								
	SVA (no pedestrian)			SVA (pedestrian)			Total SVA		
	A	B	Other	A	B	Other	A	B	Other
Rigid									
2-axle	0.02	0.04	0.05	0.03	0.05	0.06	0.05	0.09	0.11
3-axle	0.05	0.09	0.11	0.06	0.11	0.13	0.11	0.20	0.24
4-axle	0.04	0.08	0.10	0.05	0.10	0.12	0.09	0.18	0.22
Articulated									
3-axle	0.05	0.09	0.11	0.06	0.11	0.12	0.11	0.20	0.24
4-axle	0.02	0.04	0.05	0.03	0.05	0.06	0.05	0.09	0.11
5-axle	0.03	0.05	0.06	0.03	0.07	0.08	0.06	0.12	0.14
All HGVs	0.04	0.08	0.09	0.05	0.10	0.12	0.09	0.18	0.21

[a] Accident frequencies in this table have been derived from the data in Tables 9 and 10.

TABLE 13

Road position and impact position for heavy goods vehicle accidents

A. Road position (after Department of Transport [5])

Junction type	Proportion of accidents (%)			
	Rigid		Articulated	
	Non-BUR	BUR	Non-BUR	BUR
Roundabout	3.4	5.5	5.0	8.9
T or staggered junction	13.7	36.0	10.0	32.9
Y junction	1.3	1.7	1.1	1.4
Crossroads	4.2	13.6	3.1	12.5
Multiple junction	0.5	1.7	0.5	2.7
Slip road	2.7	0.5	4.1	1.3
Private entrance	5.0	5.0	3.0	5.2
Other	1.0	1.6	1.0	2.1
Not at or within 20 m of junction	68.2	34.4	72.2	33.0
Total	100.0	100.0	100.0	100.0

B. Impact position (after Riley and Bates [14])

Impact position	Proportion of impacts (%)				
	Car	MC	LGV	HGV	All vehicles
Front	66	41	63	53	59.4
Side	16	31	9	15	18.6
Rear	14	26	28	24	18.1
Other	4	2	0	8	3.9
Total	100	100	100	100	100.0

that the accidents were sufficiently serious for the police to have an interest and may tend therefore to give an overestimate of impact speed in injury accidents generally.

4.5 Fire accidents

An investigation of fire in road vehicles was carried out by North [10]. Although reported in 1974, most of the data relate to 1971 and are therefore rather old. The study does, however, contain some information on certain special aspects of vehicle fires, which are given below after consideration of the main fire statistics.

TABLE 14

Impact speeds of heavy goods vehicles in accidents (after Davies and Lees [18])

A. Collisions involving other vehicles

Impact speed (m.p.h.)	Non-BUR	BUR	Motorways
0–9	1	3	0
10–19	2	4	0
20–29	1	10	2
30–39	5	12	1
40–49	9	5	2
50–60	2	2	2
>60	1	0	0
Total	21	36	7

B. Single vehicle accidents

Impact speed (m.p.h.)	Non-BUR	BUR	Motorways
0–9	1	0	0
10–19	3	4	0
20–29	2	11	0
30–39	2	5	1
40–49	1	6	1
50–60	0	0	2
>60	0	0	1
Total	9	26	5

TABLE 15

Causes of fires in road vehicle fires 1984 (after Department of Transport [19])

Cause	Number	Proportion (%)
Deliberate ignition	7434	22.0
Smokers' materials	1165	3.4
Wiring of vehicle	8980	26.6
Oil and petroleum in contact with hot components	8475	25.1
Crash, collision	881	2.6
Other	4042	12.0
Unknown	2793	8.3
Total	33,770	100.0

Information on the causes of fires in vehicles in 1985 has been given by the DoT [19]. In that year out of some 248,000 accidents there were some 33,000 fires. The causes of these fires are given in Table 15. It can be seen from the table that the vast majority of vehicle fires are non-crash fires.

Information has also been obtained from the Home Office [20] for goods vehicle fires specifically. In 1986 fire brigades attended 7,212 van and lorry fires. Not all of these were on the public highway.

Of the 2578 HGV fires, 2559 (99.3%) were non-crash fires and 19 (0.7%) were crash fires. No breakdown is available for non-crash fires by vehicle type, but for crash fires the breakdown is as shown in Table 16. The causes of the HGV non-crash fires are given in Table 17.

TABLE 16

Number and frequency of heavy goods vehicle crash fires in 1986 (after Nyman [20])

A. Number of crash fires

HGV type	Non-BUR	BUR	All speed limits
Rigid			
2-axle	5	5	10
3-axle	1	1	2
4-axle	1	1	1
Articulated			
3-axle	1	0	1
4-axle	2	1	3
5-axle	1	0	2
All HGVs	11	8	19

B. Frequency of crash fires[a]

HGV type	Frequency (fires/10^8 km)		
	Non-BUR	BUR	All speed limits
Rigid			
2-axle	0.06	0.12	0.08
3-axle	0.12	0.28	0.16
4-axle	0.11	0.31	0.15
Articulated			
3-axle	0.12	0.38	0.16
4-axle	0.05	0.18	0.07
5-axle	0.07	0.42	0.09
All HGVs	0.06	0.15	0.09

[a] Crash fire frequencies in Section B have been derived from the data in Table 10

TABLE 17

Causes of heavy goods vehicle non-crash fires (after Nyman [20])

Cause	Number	Proportion (%)
Deliberate	352	14
Smokers' materials	147	6
Electrical	720	28
Oil, petrol, other fuel	1044	41
Sparks	31	1
Overheating	24	1
Other/unknown	241	9
Total	2559	100

TABLE 18

Location of lorry and tanker fires (after North [10])

Location	Proportion of fires (%)	
	Lorries	Tankers
Road or verge	71.7	67.4
Motorway	10.5	15.2
Field, open land	6.4	4.9
Cark park, yard	10.1	9.7
Garage forecourt	0.7	0.5
Garden	0.1	0.5
Other (specified)	0.5	1.6
Total	100	100

The study by North gives some information on the location of vehicle fires. His data for lorries and tankers are given in Table 18. They show that for HGVs some 82% of fires occur on roads. About another 10% occur in car parks, yards and garage forecourts, probably for the most part in built-up areas.

North also gives information on the number of fatalities and on the damage caused in vehicle fires, which may help to determine the severity of such fires. In 1971 there were 241 vehicle fires of which 16 were in lorries and 10 in tankers and in two lorry fires there was one death in each fire and in two tanker fires one death in each. In 1972 there were 289 vehicle fires of which 19 were in lorries and 12 in tankers and in one tanker fire there were two deaths, there being no deaths in the lorry fires. Thus for lorries out of 35 fires two were fatal (6%) and for tankers out of 22 fires three were fatal (14%).

TABLE 19

Number and frequency of a certain type of load-threatening accident (after James [21]—see text)

Road type	No. of accidents	Distance travelled (miles)	Accident frequency[a]	
			(accidents/mile)	(accidents/km)
Motorway	310	3202×10^6	9.68×10^{-8}	6.0×10^{-8}
A class	740	3855	19.2	11.9
B class	47	172	27.0	10.4
Total	1097	7229	15.2	9.4

[a] Allsop et al. [22] give an accident frequency (accidents/10^8 km) as follows: motorways 11.5; A roads 36.5; B roads 114; other roads 83.1.

North gives information on the resultant damage in a sample of car fires in 1971. Out of 200 fires 73 caused minor damage, 44 damaged the original compartment, 24 damaged or severely destroyed the original compartment, 15 damaged more than one compartment, 2 damaged the exterior, 40 (20%) damaged or destroyed the whole car, and 2 had no recorded result.

From the above the following annual estimates can be made for HGV fires.

No. of crash fires = 19

Crash fires as a proportion of accidents = 19/13,429 = 0.14%

No. of non-crash fires = 2559

Non-crash fires as a proportion of accidents = 2559/13,429 = 19%

4.6 Load-threatening accidents

Investigations of accidents which might threaten the load of a large HGV transporting radioactive waste have been made by James [21) and by Allsop et al. [22]. The study by James is concerned with articulated, five-axled HGVs. For the determination of accident frequency he assumes that only serious accidents, involving death or serious injury, have the potential to threaten the load. Thus James considers only accidents where the subject vehicle was an articulated HGV of gross vehicle weight (GVW) of more than 1.5 tonnes, where death or serious injury was involved, and where the accident either was a single vehicle accident or involved another HGV of GVW greater than 1.5 tonnes. Table 19 shows his data for the number and frequency of such accidents.

Also shown in the table are the results obtained by Allsop et al. They considered all injury accidents involving either four-axle or five-axle HGVs in overturning or side damage. The accident frequencies obtained by these workers are appreciably higher. For motorways and A roads their results are higher than those of James by a factor of 2–3. The factor is greater for B roads and other roads, but James' data shows relatively little distance travelled by these large HGVs on the lower class roads.

4.7 Chemical accidents

An account of the chemical accidents attended by the UK public fire service in 1980 has been given by Maclean [11]. There were 983 special service calls in which dangerous chemicals were involved and 968 actual incidents. The incidents occurred at both fixed installations and in transport.

Table 20 gives the nature and number of these incidents. The principal chemicals involved, together with the number of incidents, were: hydrochloric acid (66), ammonia (65), LPG (42), sulphuric acid (34) and sodium hydroxide (30). There were 14 incidents involving petroleum and 10 involving ammonium nitrate. Of these incidents 132 were fires in which the presence of the chemical affected the fire fighting to a significant degree, 18 were fires in which dangerous chemicals behaved in an abnormal manner and 25 were fires at which dangerous chemicals were present and gave rise to casualties.

For all transport incidents, both road and rail, there were 419 incidents, excluding cases in which chemicals were washed ashore. Of these 105 (25%) occurred in rural areas, 187 (45%) in urban industrial areas, 113 (27%) in urban residential areas and the remaining 14 (3%) in unrecorded locations.

As far as concerns the road transport incidents, there were 335 incidents of which 21 (6%) were on motorways, 120 (36%) on A class roads, 56 (17%) on B class roads, 29 (9%) on unclassified roads, 96 (29%) occurred in a parking area off the public roads and the remaining 14 (3%) in unrecorded locations.

TABLE 20

Nature of chemical incidents attended by UK public fire services in 1980 (after Maclean [11])

Nature of incident	Number of incidents	Proportion of incidents (%)
Chemical overheated	9	1
Spillage	419	43
Leakage	211	22
Vapour, gas escape	80	8
Potential spillage	11	1
Fire	173	18
Explosion	10	1
Chemical found	19	2
Other	20	2
Unknown	16	2
Total	968	100

In 243 (73%) of the incidents the vehicle was attended. Therefore the number of incidents in which it was unattended was up to 92 (27%).

In only 36 (11%) of the cases was an accident reported as the primary cause of the incident.

4.8 Background on accidents

A discussion of the UK accident statistics is given by Johnson and Garwood [12], McBean [23] attempts to assess the influence of road features on accident frequency and Scott [3] that of traffic density, whilst Storie [24] considers the effect of driver characteristics.

A study of HGV accidents was made in 1979 by Neilson et al. [25], but the data given above are more up-to-date.

5. Collision analysis

The attempt to estimate the frequency of a particular type of event arising from an HGV collision will depend both on the probability of the event given a collision with a particular effective impact velocity, and on the frequency of a collision of sufficient severity with this impact velocity.

The effective impact velocity will depend on the closing, or impact, speed. For a single vehicle accident all that is required is the impact speed of a single HGV. Data from which may be constructed a probability density function for HGV closing speeds in accidents were given in Table 14. For an accident involving two vehicles it is necessary to combine the probability density functions of the two vehicles. In such cases the probability density function for HGV impact speed may be used for both vehicles. The determination of the probability of a given combined impact speed in head-on collision of two HGVs is described in the Appendix.

Some form of collision analysis can then be used to determine the effect on the vulnerable vehicle for collisions of particular severities. Hence the probability of the event of interest given collision can be estimated.

An early example of such an approach was the investigation by Westbrook [26] of the comparative risks of chlorine transport by road, rail and pipeline. The study included a road tanker collision analysis to determine the probability of puncture given a crash.

A series of collision analysis studies for HGVs for US conditions is available in Gardner and Moffatt [27].

6. HSE transport risk studies

The Advisory Committee on Major Hazards in its Third Report [28] recommended that although its terms of reference were restricted to fixed installations, the major hazard potential from the transport of hazardous materials should also receive attention. In pursuance of this recommendation, the Health and Safety Executive (HSE) have carried out a number of studies on transport risks. Some of these are concerned with rail transport and with consequence modelling, which are not of concern here, but others bear on the frequency of road transport incidents and the probability of hazardous events.

Canadine and Purdy [29] give a hazard assessment of the rail and road transport of chlorine. The principal producer of chlorine in the UK is ICI. The company has some 19 road tankers with payloads 15–21 tonne. Over a 60-year period there have been three leaks. Two were due to incompletely closed valves and were quickly rectified and the third was minor.

The frequency with which these tankers are involved in accidents is significantly lower than for commercial transport generally. The vehicles are fitted with various arrangements to reduce the accident rate such as high quality suspension, anti-skid devices, anti-jack-knife systems, fuel cut-off devices, additional fire protection, regular and fog lights, etc. The tankers have their liquid and vapour valves protected in a recessed valve chest at the front of the vehicle. They have excess flow valves and the two latest vehicles also have remotely operated shutoff valves.

Since 1976 the company has taken additional measures to reduce the consequences of any collision. Additional rear and side protection has been fitted to resist penetration, absorb energy and spread the load in case of collision. The value of these measures was illustrated in 1985 when the most serious accident recorded to date occurred. A chlorine tanker was hit by a 38 tonne articulated lorry travelling at an estimated 60 m.p.h. down a hill near Baslow in Derbyshire. The vehicle veered diagonally across the road and hit the chlorine tanker on its front offside, stopping it dead and driving it sideways across the road. The side protection on the tanker absorbed most of the collision energy and spread the load as it was designed to do; there was no leak.

7. Exposed population

7.1 Population density and other characteristics

A study of the density and other characteristics of the population which might be exposed to hazardous materials has been given by Petts et al. [30]. The information given includes data for the UK on population densities, both by day and by night, on the proportions of person indoors and outdoors, and on the proportion of the population which may be considered particularly vulnerable.

There have also been specialist studies of the population density along routes taken in the transport of hazardous materials. These include the TRIP program referred to in the second Canvey Report [31] and the study by Canadine and Purdy [29] already mentioned.

7.2 High density targets

Of particular interest is the probability that any incident will occur at a location where large numbers of people are exposed. An estimate of this probability for built-up areas may be made from V-2 rocket incidents. The distribution of the rockets which fell on London was effectively random. Analysis of the 517 V-2 incidents in London gives 8.9% which caused ≥ 10 deaths and 1.4% which caused ≥ 33 deaths.

7.3 Emergency services

In addition to the population who are normally in the area, personnel of the emergency services who attend the accident are also at risk. It is not uncommon in an incident involving the road transport of hazardous materials that a significant proportion of the casualties include such personnel.

A typical road accident involving injury and fire would probably be attended by one police patrol car (2 persons), one fire tender (4–5 persons) and one ambulance (2–3 persons). If the incident is considered serious and time permits, additional fire tenders may attend [32, 33].

8. Emergency services

8.1 Attendance times

In assessing the consequences of an incident, the time for the fire services to attend may be important. In accordance with Home Office guidance, fire brigades classify areas into different categories of risk. For each category there is a specified minimum number of pumps (i.e. fire engines) which are required to attend the scene and a maximum time for their arrival. Information from the London Fire Brigade [32] indicates that a vehicle fire is normally attended by one fire engine and that for the type of area through which road transport of explosives takes place, for example, the maximum attendance time is 20 minutes. The mean attendance time is between 10 and 15 minutes.

9. Some studies in other countries

There have been a number of studies in North America on the transport of hazardous materials. Several of the more recent studies are considered here.

A review of accidents involving, and releases from, vehicles carrying hazardous materials has been given by Glickman [34]. The data are based on the reporting system of the Department of Transportation, Office of Hazardous Materials Transportation. The basic data consist of the distance travelled by trucks carrying hazardous materials and the number of accidents involving a spillage.

The reporting system requires the recording of any unintentional release occurring during loading/unloading, transportation, or temporary storage. The author equates such releases to spillages. Spillages are treated as significant if they involve more than 5 US gallons or 40 lb of material. From these reporting requirements, from the data given by Maclean above and from the other data given below, it would seem that most of these spillages do not in fact occur due to road traffic accidents on the public highway.

Some data from the study are shown in Table 21. The frequency of spillages is obtained by simply dividing the number of spillages by the distance travelled by the vehicles.

There are several points of interest in these data. One is the rather high ratio of distance travelled by vehicles other than tank trucks to that travelled by tank trucks. Another is the rather lower ratio of the number of significant spillages for vehicles other than tank trucks to the number for tank trucks. Another is the striking difference in the frequencies of spillage between private trucks and trucks for hire.

The overall frequency of significant spillages is:

$$\begin{aligned}\text{Frequency of significant spillages} &= 1667/(16{,}220 \times 10^{6})\\ &= 0.1 \times 10^{-6}\ \text{spillages/vehicle mile}\\ &= 0.062 \times 10^{-6}\ \text{spillages/vehicle km}\end{aligned}$$

Harwood et al. [35] have collated information on hazardous material (HAZMAT) accidents. This information was obtained from the Department of Transportation's Research and Special Programs Administration (RSPA) Hazardous Materials Incident Reporting System (HMIR) data base. The system is based solely on self-reporting by carriers. No minimum release quantity or damage level is specified and technically any release, however, small is reportable. The requirements apply, however, only to interstate transport and carriers engaged solely in intrastate transport are not required to report HAZMAT incidents under this scheme.

Data were analysed for the period 1981–1985. During this time there were 28,433 HAZMAT incidents reported. Some data on these incidents are given in Table 22.

As the table shows, the proportion of HAZMAT incidents due to traffic was 11%. However, the proportion of severe incidents due to traffic lay between 35% and 68%, depending on the definition of severity. The authors give one definition of a severe incident as one involving injury or death, a fire or explosion or more than $50,000 dollars worth of damage.

The authors also give information from another data base, the Motor Carrier Accident Report maintained by the FHWA Bureau of Motor Carrier Safety (BMCS), now renamed the Office of Motor Carriers. This data base gives information on trucks involved in accidents, including whether the truck was carrying hazardous materials and whether a release occurred. The reporting

TABLE 21

Distance travelled and number and frequency of spillages for US trucks carrying hazardous materials in 1982 (after Glickman [34])

A. Distance travelled

Type of vehicle	Distance travelled (10^6 vehicle miles)
Trucks	
Private	6416
For hire	9804
Total	16,220
of which	
Tank trucks	
Private	4121
For hire	307
Total	4228

B. Number of spillages

Type of vehicle	No. of spillages	
	Total	Significant
Trucks		
Private	357	233
For hire	5314	1434
Total	5671	1667
of which		
Tank trucks		
Private	248	178
For hire	936	692
Total	1184	870

C. Frequency of spillages

Type of vehicle	Frequency of spillages (spillages/10^6 vehicle miles)	
	Total	Significant
Trucks		
Private	0.0556	0.0363
For hire	0.542	0.146
of which		
Tank trucks		
Private	0.0602	0.0432
For hire	3.049	2.254

TABLE 22

HAZMAT incident data from the Department of Transportation RPSA data base for 1981–85 (after Harwood et al. [35])

A. Location of incidents

Location	Proportion (%)	Number
On public highway	48	13,547
Off public highway	39	ca. 11,089
Unknown	13	ca. 3,797
Total	100	28,433

B. Failure involved in incidents on public highway

Failure type	Number	Proportion (%)
Traffic accident	1427	10.8
Body or tank failure	2741	20.2
Valve or fitting failure	3289	24.3
Cargo shifting	4945	36.5
Fumes or venting	15	0.1
Other	1100	8.1
Total	13,547	100.0

C. Hazardous materials involved in incidents on public highway

Material	All incidents (%)	Traffic incidents (%)
Flammable liquids	46	71
Toxic liquids	5	
Corrosive liquids	40	13

D. Consequences of incidents on public highway

Count	Number of incidents		
	Traffic incidents	Other incidents	All incidents
No. of incidents	1457	12,090	13,547
No. of deaths	50	4	54
No. of injuries	115	358	473

system applies, however, only to interstate carriers. Data from this source are given in Table 23.

An analysis of accident rates in three states (California, Illinois and Michigan) and of release probabilities overall in the USA has been given in a study by Harwood et al. [36], which follows on from the authors' earlier work

TABLE 23

Data on HAZMAT trucks involved in accidents from the Department of Transportation BMCS data base for 1984–85 (after Harwood et al. [35])

A. Truck accidents

Truck	Number
Non-HAZMAT trucks	71,164
HAZMAT trucks	3,703
of which	
No release	3,183
Release	530

B. Cargoes of HAZMAT trucks in accidents

Cargo	Number of accidents		
	No release	Release	Total
General freight	680	61	741
Gases in bulk	238	21	259
Solids in bulk	28	12	40
Liquids in bulk	1486	345	1831
Explosives	63	7	70
Empty	210	10	220
Other	467	62	529

C. Consequences of HAZMAT truck accidents

Count	Number of accidents		
	No release	Release	Total
No. of incidents	3183	520	3703
No. of deaths	273	53	326
No. of injuries	2514	441	2955

[35, 37]. The data were obtained from the accident reporting systems of these states. Table 24 gives data on accident frequencies and modes and Table 25 data on release frequencies and probabilities.

The accident frequencies differ appreciably between the different classes of highway. They also apparently differ appreciably between states. The probabilities of release given an accident, however, are relatively similar for rural highways as a group and for urban highways as a group.

TABLE 24

Truck accidents in three states in the USA (after Harwood et al. [36])

A. Number and frequency of accidents

Road type	California			Three states
	No. of accident involvements[a]	Distance travelled (10^6 miles)	Accident frequency[b] (accidents/10^6 miles)	Accident frequency[b] (accidents/10^6 miles)
Rural				
Two-lane	6577	3784.97	1.73	2.19
Multilane (undivided)	1070	196.58	5.44	4.49
Multilane (divided)	1801	1463.45	1.23	2.15
Freeway	5759	10850.90	0.53	0.64
Total	15207	16295.60	0.93	
Urban				
Two-lane	1778	420.69	4.23	8.66
Multilane (undivided)	2251	172.84	13.02	13.92
Multilane (divided)	4996	1427.47	3.50	12.47
One-way street	223	33.81	6.60	9.70
Freeway	28860	18107.00	1.59	2.18
Total	38108	20161.81	1.81	
Grand total	53315	39781.10	1.34	

B. Single vehicle accidents (California only)[c,d]

Road type	Proportion of accidents (%)						
	Non-collision accidents			Collisions with			
	Run off road	Overturn	Other	Fixed object	Parked vehicle	Non-motorist	Other
Rural							
Two-lane	4.5	6.6	4.4	7.0	2.4	0.6	5.7
Multilane (undivided)	3.6	7.5	3.9	7.5	4.3	0.4	5.7
Multilane (divided)	3.6	4.0	3.8	6.4	3.9	0.2	4.7
Freeway	3.5	3.3	3.8	7.4	3.8	0.4	5.0
Total	3.9	5.1	4.1	7.1	3.2	0.5	5.3
Urban							
Two-lane	1.5	2.6	3.4	5.1	3.6	0.3	3.9
Multilane (undivided)	0.2	0.6	2.6	5.1	8.5	0.8	4.0
Multilane (divided)	0.8	1.3	2.4	5.7	7.0	0.6	3.8
One-way street	0	2.2	0.9	6.3	9.4	1.3	2.2
Freeway	0.6	1.0	1.3	3.2	1.9	0.2	1.7
Total	0.6	1.1	1.6	3.8	3.1	0.3	2.2
Grand total	1.6	2.3	2.3	4.7	3.1	0.4	3.1

TABLE 24 (*continued*)

C. Multiple vehicle collision accidents[c]

Road type	Proportion of accidents (%) collisions with		
	Car	Truck	Other vehicle
Rural			
Two-lane	29.8	26.6	12.4
Multilane (undivided)	27.4	26.1	13.7
Multilane (divided)	33.4	26.4	13.8
Freeway	31.3	22.3	19.4
Total	30.6	24.9	15.3
Urban			
Two-lane	39.6	30.7	9.3
Multilane (undivided)	41.3	30.1	6.9
Multilane (divided)	43.7	28.1	6.6
One-way street	45.7	27.4	4.5
Freeway	50.6	25.6	13.9
Total	48.6	26.4	12.3
Grand total	43.4	26.0	13.1

[a] Accidents involving two or more trucks counted as two or more involvements.
[b] Average weighted according to vehicle-miles.
[c] Proportion of accidents in Sections B and C combined.
[d] There were no cases of collision with a train.

An analysis of incidents in Canada in which there were releases of gasoline or LPG has been made by Stewart and van Aerde [38]. The incidents were those reported under the regulatory system as dangerous occurrences in the period 1986 to August 1987 (1.7 years). Thus not all accidents were reported and the data are therefore not comparable with those reported under the US HAZMAT scheme.

There were 41 incidents involving gasoline. A proportion of these may not have been transport incidents. The proportion known to be transport incidents was 81%, leaving between 0% and 19% which may not have been. Table 26 gives the number of incidents by type of release.

The three major types of incident were collision, collision/overturn and overturn. The proportion of lading released in these cases was 30–40%. For fires, the release was large (98%) except in one case where it was very small (3%). Of these three types of incident, overturns caused most container damage. The authors suggest that in collision accidents a large proportion of the energy is dissipated in other parts of the vehicle.

There were four evacuations of the public in the 41 incidents.

A similar analysis is given for the LPG incidents, but there were only nine of these.

TABLE 25

Probability and frequency of release of material in truck accidents in USA (after Harwood et al. [36])

A. Probability of release by accident type: single vehicle accidents

Accident type	Probability of release
Non-collision accidents	
Run off road	0.331
Overturn	0.375
Other	0.169
Collisions with	
Fixed object	0.012
Parked vehicle	0.031
Train	0.455
Nonmotorist	0.015
Other object	0.059

B. Probability of release by accident type: multiple vehicle accidents

Accident type	Probability of release
Collision with	
Passenger car	0.035
Truck	0.094
Other vehicle	0.037

C. Probability and frequency of release by road type

Road type	Probability of release	Frequency of release (release/10^6 vehicle-miles)
Rural		
Two-lane	0.086	0.19
Multilane (undivided)	0.081	0.36
Multilane (divided)	0.082	0.18
Freeway	0.090	0.06
Urban		
Two-lane	0.069	0.60
Multilane (undivided)	0.055	0.77
Multilane (divided)	0.062	0.77
One-way street	0.056	0.54
Freeway	0.062	0.14

TABLE 26

Tanker accidents involving release of gasoline in Canada (after Stewart and van Aerde [38])

Accident type	No. of releases						Proportion (%)
	Spill	Leak	Spill/fire	Fire	Other	Total	
Collision	2			1		3	7
Collision/overturn	5		1			6	15
Overturn	19	1			1[a]	21	51
Brake failure	2					2	5
Puncture	2	1				3	7
Fitting/hose failure		1		1		2	5
Fire				2[b]		2	5
Military exercise	1					1	2
Bridge collapse	1					1	2
Total	32	3	1	4	1	41	

[a] Environmental contamination.
[b] One of these is classified as spill/fire.

Further more general data are given in the review of transportation of hazardous materials in Ontario by Gorys [39].

Griffiths and Linklater [40] have reported a study performed in 1980 of some 42 accidents involving road tankers transporting flammable materials in New South Wales (NSW). In 1979 in NSW there were some 3000 road tankers carrying flammable loads and some 100 pressurised tankers. The annual crash rate was 2.5%, which was the same as for all vehicles.

There were 42 accidents investigated, 11 involving non-articulated vehicles and 31 involving articulated vehicles. There were 18 rollovers, 5 for the non-articulated vehicles and 13 for the articulated vehicles.

In 24 cases there was no leakage of the bulk load but in three of these there was leakage of the prime mover fuel tanks. In 10 of the rollover cases there was substantial leakage. In two of the non-rollover cases the tank was punctured and burned out. Of the other non-rollover cases, one involved loss of "a lot" of product from a fractured pipe fitting, one loss from a discharge pipe and two loss from vents.

The authors state that fire occurred in 5% of cases. This would seem to cover the two cases of burnout just mentioned and to imply that none of the other cases involved a fire.

The authors obtained data on the various factors which influenced the accident under the headings: mechanical, environmental, behavioural and general.

Factors causing rollover included high centre of gravity, 'soft' roll stiffness and sloshing of the liquid. None of the tankers appeared to have side baffles.

From these data the following estimates may be made for crash fires:

No. of crash fires = 2

Crash fires as proportion of accidents is then 2/42 or 4.8%

10. Some estimates for HGVs conveying hazardous materials

Some estimates are now made for HGVs conveying hazardous materials (HGV/HMs) in Great Britain.

10.1 No of HGV/HMs

The number of road tanker HGV/HMs was given above as 14,000. There are in addition HGVs other than tankers carrying hazardous materials. The number of such vehicles which at some time transport hazardous materials may be quite large, but what matters in the present context is the number of equivalent 'full-time' vehicles. There appears to be no reliable source of information for this figure. An estimate has therefore been made. The data for hazardous cargoes in the USA given in Section B of Table 23 indicate that the ratio of non-tank truck to tank truck HGV/HMs is about 0.6. Those given in Section B of Table 21 for significant spillages indicate that the ratio of non-tank truck to tank truck HGV/HM spillages is about 0.9. The former figure is regarded as a better guide. A roadside survey conducted by the authors is consistent with this estimate. The ratio of 0.6 is used for Great Britain also, which yields:

No. of tanker HGV/HMs $= 14{,}000$

No. of non-tanker HGV/HMs $= 0.6 \times 14{,}000 = 8400$

No. of HGV/HMs $= 14{,}000 + 8400 = 22{,}400$

10.2 Distance travelled by HGV/HMs

Then for the distance travelled by HGV/HMs

Distance travelled by individual vehicle $= 60{,}000$ miles $= 96{,}500$ km

Distance travelled by fleet $= 22{,}400 \times 60{,}000 = 13.4 \times 10^8$ miles $= 21.6 \times 10^8$ km

10.3 Accident frequency for HGV/HMs

HGVs carrying hazardous materials have a higher standard of design and operation, although the extent of this is variable. It may therefore be expected that the accident rate would be less. Information obtained by the authors for munitions vehicles indicates a reduction factor of about 0.1–0.33. For HGV/HMs it seems doubtful whether such a large reduction is appropriate. Accordingly, the estimate used here is 0.8.

Griffiths and Linklater [40] found that the proportion of HGV/HMs suffering an accident was the same as for HGVs generally. Although a lower accident rate per unit distance travelled is assumed here for HGV/HMs, these vehicles travel a greater distance per year, and the net effect is to give them an annual accident rate comparable with or rather greater than that of other vehicles.

Taking the estimate

Ratio of HGV/HM to HGV accident rates = 0.8

then for HGV/HM accidents:

Frequency of accidents = $0.8 \times 0.62 \times 10^{-6}$/km = 0.50×10^{-6}/km
No. of accidents = $0.50 \times 10^{-6} \times 21.6 \times 10^{8} = 1080$ accidents/y
No. of vehicles involved in accidents = $(15{,}000/13{,}429) \times 1080 = 1206$
Proportion of vehicles involved in accidents = $1206/22{,}400 = 5.4\%$/y

For MoD munitions vehicles (MVs) taking the estimate

Ratio of MV to HGV accident rates = 0.2
Frequency of accidents = 0.12×10^{-6}/km

10.4 Release frequency and probability for HGV/HMs

An estimate of the frequency and probability of release given an accident can be made from the data given by Maclean. From his data:

No. of releases due to traffic accidents = 36

Then

Frequency of release = $36/(21.6 \times 10^{8}) = 0.017 \times 10^{-6}$ releases/km
= 0.027×10^{-6} releases/mile
Probability of release given traffic accident = $36/1080 = 0.033 = 3.3\%$

These estimates are based on attendance by a fire brigade and should be regarded as lower limits.

These results may be compared with the US figures. From the data given in Table 23, the probability of release given a traffic accident lies in the range 0.055–0.090. The estimate for the UK is somewhat low relative to these figures, but not unduly so.

For the frequency of release, the US figures are in the range 0.06–0.77 releases/10^6 miles, the higher figures being for the less common road categories. For the three dominant road categories the figures are 0.06, 0.14 and 0.19 releases/10^6 miles. The estimate for the UK is much less than these figures. This appears to be due partly to a lower probability of release given an accident and partly to a lower accident rate.

10.5 Fatal accidents for HGV/HMs

Ratio of fatal accidents to injury accidents = 0.022

No. of fatal accidents = $0.022 \times 1206 = 26.5$/y
No. of fatalities per fatal accident = 1.5
No. of fatalities from accidents = $1.5 \times 26.5 = 39.8$ (say 40)

About one death per year is attributable to the load and the rest are due to traffic accidents.

11. Individuality of incidents

It is easy in a preoccupation with incident statistics to lose sight of the individuality of some of the accidents which have occurred involving the road transport of hazardous materials. Mention has already been made of the chlorine tanker crash with a lorry travelling down hill at 60 m.p.h. Other incidents with rather unusual features include the San Carlos campsite disaster [41], which was not initiated by either crash or fire and which involved a vulnerable target, and the explosion of an explosives lorry at Peterborough [42], which involved a fire rather than a crash and occurred off the road in a company yard.

12. Discussion

The information given above is intended to provide a basic set of data which may be of assistance in the assessment of the hazards of road transport in Great Britain.

The information provided includes some data which may be used to make generic estimates based on historical event data. However, some hazards are realised so rarely that data are sparse or non-existent. In such cases it is possible to proceed using estimates of event frequency based on the statistics of a small number of events or even zero events.

Alternatively, an attempt may be made to model the event, in which case a different set of data is required. The information given includes some data of this kind also.

Moreover, enough has been said to indicate that even where historical data do exist, they may or may not be directly applicable. A case in point is the provision of side protection on tankers. This is provided on the ICI chlorine vehicles but not on the Australian road tankers described. In such cases it may be appropriate to modify any historical data to take account of the difference between the conditions to which those data apply and the conditions of the problem in hand. Again this may involve modelling and the use of data appropriate to that.

The principal aim of the paper has been to provide data relevant to events arising from traffic accidents. These events are not synonymous with hazardous material incidents involving vehicles and in fact may constitute only a small proportion of the latter. Care is needed, therefore, in interpreting data on hazardous material incidents.

Two of the principal events which may cause an incident are collision and fire. However, other events should not be neglected. For road tankers other causes of release may be leaks from valves and from overfilling.

With regard to fire, for HGVs generally non-crash fires are much more frequent than crash fires. The Australian work indicates, not surprisingly, that

TABLE 27

Summary of principal data given in this paper

A. Great Britain

Road network	Sec. 3.2
Length	Sec. 3.2; Table 1
HGVs	
Types	Figure 1
Number	Sec. 3.3
Weight distribution	Sec. 3.3; Table 2
Distance travelled	
Overall	Sec. 3.4; Table 3
Road classes	Sec. 3.4; Table 4
HGV accidents	Sec. 4.2
Number	
Overall	Sec. 4.3; Tables 6, 7
Vehicle type and road class	Sec. 4.3; Tables 5–9
Frequency	
Overall	Sec. 4.3
Vehicle type and road class	Sec. 4.3; Tables 10–12
Junction type and impact position	Sec. 4.3; Table 13
Impact speeds	Sec. 4.4; Table 14
HGV fire accidents	Sec. 4.5
Number, frequency	Sec. 4.5
Causes	Sec. 4.5; Table 15
Crash fires	
Number	Sec. 4.5; Table 16
Non-crash fires	
Number	Sec. 4.5
Causes	Sec. 4.5; Table 17
Location	Sec. 4.5; Table 18
HGV load-threatening accidents	Sec. 4.6
Number	Sec. 4.6; Table 19
HGV chemical accidents	Sec. 4.7
Number	Sec. 4.7; Table 20
HGV/HMs	
Number	Sec. 3.5; 10.1
Distance travelled	Sec. 3.5; 10.2
HGV/HM accidents	
Number, frequency	
Overall	Sec. 10.3
Release accidents	Sec. 10.4
Fatal accidents	Sec. 10.5
MV accidents	
Frequency	Sec. 10.3
Exposed population	
Population density	Sec. 7.1
High density targets	Sec. 7.2
Emergency services	
Attendance times	Sec. 8.1

TABLE 27 Continued

B. North America

HGV/HMs	
Distance travelled	Sec. 9; Table 21
HGV/HM accidents and releases	
Number, frequency	Sec. 9; Tables 21, 23–25
Vehicle type	Sec. 9; Table 21
Road class	Sec. 9; Tables 21, 22, 24, 25
Failure type	Sec. 9; Tables 22, 26
Materials involved	Sec. 9; Tables 22, 23
Consequences	Sec. 9; Tables 22, 23
Injuries	Sec. 9; Tables 22, 23

this is less so for road tankers carrying flammable materials. Nevertheless, the figures suggest that even for such tankers non-crash fires may be more significant.

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Appendix

Probability of a given combined impact speed in head-on collision of two HGVs

One problem which arises in assessing the hazards of road transport is the estimation of the probability of a head-on collision of two HGVs. Given that there is available a distribution of HGV impact speeds such as that shown in Table 14, the distribution of the impact speeds of an HGV–HGV head-on collision and the probability that the speed lies within a certain range may be obtained as follows. Consider a normal distribution of HGV impact speeds $f(x)$ on built-up roads, where x is the impact speed, with a mean $\bar{x}$ and standard deviation σ. Then for the distribution $f(x_c)$ of the combined (i.e. summed) impact speeds

$$\bar{x}_c = 2\bar{x} \tag{A.1}$$

$$\sigma_c^2 = 2\sigma^2 \tag{A.2}$$

$$\sigma_c = \sqrt{2}\sigma \tag{A.3}$$

The probability P that the combined impact speed x_c lies between x_{c1} and x_{c2} is then

$$P[x_{c1} < x_c < x_{c2}] = P[((x_{c1} - \bar{x}_c)/\sigma_c) < z_c < ((x_{c2} - \bar{x}_c)/\sigma_c)] \tag{A.4}$$

$$= P[a < z_c < b] \tag{A.5}$$

$$= I(b) - I(a) \tag{A.6}$$

$$= P \tag{A.7}$$

Values of $I(a)$ and $I(b)$ can be obtained from standard tables of the normal distribution.

As an illustration consider the following example:

$\bar{x} = 30.6$ m.p.h., $\sigma = 12.2$ m.p.h. $\bar{x}_c = 2 \times 30.6 = 61.2$, and
$\sigma_c = \sqrt{2} \times 12.2 = 17.3$ m.p.h.

The probability that the collision speed is between 110 m.p.h. and 130 m.p.h. is then:

$$P[((110 - 61.2)/17.3) < z_c < ((130 - 61.2)/17.3)]$$
$$= P[2.28 < z_c < 3.98] = I(3.98) - I(2.82)$$
$$= 0.9999 - 0.9976 = 2.3 \times 10^{-3}$$

This method provides a simple and rapid estimate of the probability of the combined collision speed, given a collision. The results are, however, only as good as the quality of fit of the distribution used. Specifically, the method relates to the tail of the distribution. The fitting and use of tails is a common problem in the use of distributions. In some cases it may be preferable to use alternative methods which give a more accurate treatment of the tail.

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Improved equation to estimate flash points of organic compounds

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Abstract

An improved correlation, non-linear exponential type has been proposed for the estimation of flash points of organic compounds and petroleum fractions as a function of their boiling temperature. This correlation was tested with 1221 compounds and found to predict the flash points with less than 1% average absolute error, over a wide range of normal boiling temperature. The constants of the correlation for various classes of compounds are also presented.

Introduction

The global awareness of the importance of safety, risk assessment and emergency planning for industrial accidents and the stringent regulations of Governmental agencies of various countries have necessitated the search for better and accurate techniques for predictions in these areas. Flash point, one of the physical properties of chemical compounds, is useful to identify the flammable nature of the substance. It has received attention in recent years from the safety point of view. It is evident from the literature that thousands of new compounds are being synthesised every year and the flash point data of these compounds are essential for hazard classification of the substances. Experimental data are always desirable but when they are not available the recourse is taken to prediction methods.

Process plant designers, safety auditors, hazard study and risk assessment experts have to predict the flash points for many in plant stocks to check the compliance with safety requirements and for several other purposes. Many correlations have been reported in the literature [1–5] to estimate the flash points of organic compounds and their mixtures as a function of normal boiling temperature. All of these correlations fall either in the class of parabolic type or hyperbolic type. Both linear and parabolic types of equation [7] are used for

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estimating the flash points of different groups of organic compounds. A hyperbolic type of equation [6] is used for predicting the flash points of hydrocarbons and petroleum fractions. When these correlations [6, 7] were applied to predict the flash points for a wide range of organic compounds, notably larger deviations (> 10 °C) were observed between the predicted and the reported experimental flash points. The reason is that either the correlations (Riazi and Daubert [6]) developed are based on a limited number of data points (< 20 samples) or the correlation (Patil [7]) of a parabolic/hyperbolic nature does not represent the experimental data satisfactorily. So it is desirable to have a more accurate prediction method. In this paper, the applicability of a non-linear (exponential) type of equation is investigated to estimate the flash points for different classes of organic compounds and petroleum fractions as a function of normal boiling temperature.

Results and discussion

Reported experimental data of normal boiling and closed cup flash point temperatures of several organic compounds were taken from Lange's Handbook of Chemistry [8], Aldrich Catalogue Handbook of Fine Chemicals [9] and the Hazardous Chemical Data Book [10]. Twelve hundred organic compounds collected from the above sources have been divided into 12 groups as given in Table 1. Twenty-one data sets on petroleum fractions were obtained from the literature [6]. The materials contained in nitrogen group do not include the amines, which are considered separately. Care has been taken to include

TABLE 1

Values of constants in eq (3)

Group	No. of compounds	Source of data	a	b	c	AAE%[a]
Hydrocarbons	230	[8, 9]	225.10	537.60	2217.00	0.410
Alcohols	150	[9, 10]	230.80	390.50	1780.00	0.186
Amines	70	[9]	222.40	416.60	1900.00	0.200
Acids	40	[8, 9]	323.20	600.10	2970.00	0.531
Ethers	80	[9, 10]	275.90	700.00	2879.00	0.343
Sulphur	40	[10]	238.00	577.90	2297.00	0.484
Esters	120	[8, 9, 10]	260.80	449.20	2217.00	0.186
Ketones	80	[8]	260.50	296.00	1908.00	0.722
Halogens	200	[8, 9, 10]	262.10	414.00	2154.00	0.672
Aldehydes	45	[8]	264.50	293.00	1970.00	0.771
Phosphorus	20	[8, 9]	201.70	416.10	1666.00	0.815
Nitrogens	125	[8, 9, 10]	185.70	432.00	1645.00	0.622
Petroleum fractions	21	[6]	237.90	334.40	1807.00	0.294

[a] AAE%—Percentage of average absolute error in predicted flash point.

a greater number of compounds in each group, so as to increase the scope of applicability of correlation and minimise the deviations to result more accurate prediction.

As already stated, the general form of the parabolic and hyperbolic equations given below are not suitable for the estimation of flash points of different organic compounds.

$$T_f = a + bT_b + cT_b^2 \tag{1}$$

$$T_f = a + bT_b + c/T_b^2 \tag{2}$$

The best equation will obviously be one containing an exponential function. A possible candidate is:

$$T_f = a + b(c/T_b)\,e^{-c/T}/(1 - e^{-c/T})^2 \tag{3}$$

where T_f denotes the flash point temperature, K; T_b the normal boiling temperature, K; and *a*, *b*, *c* are constants in eqs. (1)–(3).

Equation (3) was used to fit the flash points of 1200 organic compounds and 21 petroleum fractions as a function of normal boiling temperature. The constants in eq. (3) were evaluated by non-linear regression using the Gauss–Newton iteration method. Similarly, the values of the constants in eqs. (1) and (2) were also determined by polynomial and multiple regression analysis, respectively, for each group of compounds.

The results of the calculations for the twelve groups of organic compounds and the group of the 21 petroleum fractions are summarised in Table 1. A maximum percentage of average absolute error (AAE%) of 0.815 was observed in the case of the phosphorus group. Using eqs. (1) and (2) only gave an AAE% of 1.014 and 1.18, respectively, for the phosphorus group. Equation (3) results were also compared with those of eqs. (1) and (2) for the other groups. The sample calculations of two compounds in each group are shown in Table 2. Reasonably accurate results are obtained by the use of (3) with most of the groups. But in case of the phosphorus group, the deviation with experiment of predicted values from eq. (3) are slightly greater than found in the other groups. However, the deviations of predicted values of flash points from eqs. (1) and (2) with experiment are still higher. Table 2 indicates that the classical parabolic/hyperbolic equations give substantially inaccurate results. It is clear from Tables 1 and 2 that (3) gives more reliable predictions of flash points for all of the materials investigated.

Conclusions

The suggested non-linear correlation gave satisfactory agreement between the predicted and reported experimental data of flash points. It is further suggested that this correlation can be applied over a wide range of normal

TABLE 2

Comparison of performance of (3) with eqs. (1) and (2) for two example components in each group

Group	Compound	T_f, °C	T_b, °C	Predicted T_f, °C		
		(Data from literature)		Eq. (1)	Eq. (2)	Eq. (3)
Hydrocarbons	1. *p*-Cumene	320.00	449.00	324.00	323.08	320.40
	2. Undecane	333.00	469.00	335.83	335.09	333.35
Alcohols	1. 2-Propanol	296.00	355.00	315.57	317.79	296.10
	2. 2-Phenylethanol	375.00	494.00	369.82	370.35	375.92
Amines	1. Decylamine	358.00	491.00	355.29	355.86	358.17
	2. 1-Hexadecylamine	413.00	603.00	422.64	423.28	415.67
Acids	1. 4-Methylvaleric acid	370.00	474.00	366.61	367.11	369.81
	2. Octanoic acid	383.00	510.00	382.70	382.96	383.12
Ethers	1. Hexyl ether	351.00	502.00	375.36	373.32	350.89
	2. *N*-Propyl ether	294.00	363.00	281.60	283.38	292.00
Sulphurs	1. Ethyl disulphide	313.00	426.00	319.43	385.60	315.20
	2. Cyclohexanethiol	316.00	431.00	322.28	379.97	318.33
Esters	1. Benzyl benzoate	420.00	596.00	425.83	425.12	419.04
	2. 2-Butoxy ethyl acetate	349.00	465.00	346.45	346.60	349.08
Ketones	1. Octanophenone	383.00	563.00	375.79	375.52	383.36
	2. 2-Methoxycyclohexanone	342.00	458.00	345.39	345.49	342.73
Halogens	1. 1-Bromo-2-propanol	327.00	421.00	329.15	329.19	327.89
	2. 1-Iodooctane	368.00	499.00	365.38	365.09	367.85
Aldehydes	1. Benzaldehyde	335.00	452.00	340.00	339.91	337.21
	2. 3,4-Dimethoxybenzaldehyde	373.00	554.00	367.54	367.83	376.60
Phosphorus	1. Triethylphosphite	327.00	429.00	212.88	340.19	336.33
	2. Trimethylphosphate	300.00	385.00	290.32	317.56	307.35
Nitrogens	1. 3-Ethoxybenzonitrile	383.00	517.00	378.87	380.00	383.31
	2. 4-Nitrotoluene	379.00	511.00	375.31	376.09	379.94
Petroleum fractions	1. —	361.89	499.11	364.02	365.60	361.79
	2. —	364.11	507.44	369.33	369.86	365.52

boiling temperatures of organic compounds to estimate flash point temperature, especially when the parabolic/hyperbolic equations fail.

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Safety and stability studies on isosorbide dinitrate (ISDN)

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Abstract

A detailed study on pure, crude, acidified and diluted isosorbide dinitrate (ISDN) was carried out to evaluate thermal stability and explosive sensitivity by using differential scanning calorimetry (DSC), thermogravimetry (TG) and cap sensitivity experiments. The results indicate that thermal stability of pure ISDN is as good as pentaerythritol tetranitrate. Acidity, especially sulphuric acid, adversely affect the stability, whereas dilution with water or lactose did not affect the thermal stability. However, the dilution effect is clearly seen in explosive sensitivity and thermal decomposition energy. ISDN diluted with 30% water behaves like a non-explosive. Acid influence on the decomposition kinetics is also studied in detail. A considerable decrease in energy of activation (E_{act}) is noticed when ISDN is contaminated with sulphuric acid, whereas lactose addition increases the activation energy. A plausible explanation is provided for the change in activation energy. A good correlation is observed between the experimentally obtained activation energy and the length of the O-N bond derived from modified neglect differential overlap (MNDO) calculations.

1. Introduction

Isosorbide dinitrate (ISDN) belongs to a group of vasodilator drugs called nitrates. Related to glyceryltrinitrate and pentaerythritol tetranitrate (PETN), it is most often used to relieve the pain and frequency of angina attacks [1]. It is also used with other drugs for the control of certain type of heart failure. ISDN is fast-acting and the effects are longer lasting than some other nitrates. Unlike glycerylnitrate, ISDN can also be stored for long periods of time without losing its effectiveness.

Pure ISDN, a white crystalline material, has proven to be a powerful explosive and is, therefore, diluted with lactose or other suitable diluents to make handling, transportation and storage safer for pharmaceutical purposes. The

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normal dilutions used for pharmaceutical preparations are 25% ISDN with 75% lactose or 40% ISDN with 60% lactose.

In view of the explosive hazards associated with ISDN, a detailed study on the safety aspects of ISDN was warranted to educate and warn the users of this material, especially drug manufacturers. This paper discusses in detail the thermal sensitivity and stability of pure and acidic ISDN and ISDN diluted with lactose. Decomposition kinetics, decomposition energy and the explosive properties of dry and wet ISDN were also examined. Previously Mohan Murali et al. [2] from our laboratory published the hazardous characteristics of ISDN–lactose mixtures. The Chemical Thermodynamic and Energy Release Evaluation Program of ASTM [3] (CHETAH) rated pure ISDN as a high hazard 25/75 ISDN–lactose mixture as low hazard and 40/60 ISDN–lactose mixture as medium hazard.

2. Experimental

2.1 Equipment

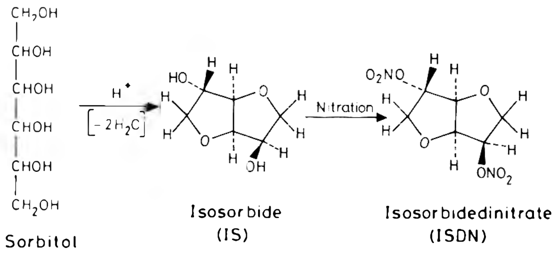
Perkin-Elmer DSC-2C and Perkin-Elmer TGS-2 were used for thermal study. The experiments were carried out under non-isothermal conditions with a constant flow of nitrogen gas. The samples were crimped in aluminium pans with a pin hole on the lids. Thermograms were recorded using percent mode which directly reads the loss of weight (%) with temperature. The sample size was kept in the range of 2–4 mg for all differential scanning calorimeter (DSC) and thermogravimetry (TG) experiments.

Cap sensitivity experiments were carried out in a sound proof bomb using a No. 6 detonator. The Nicholet digital oscilloscope 2090 series was used for measuring detonation velocity and carbon resistor probes were used for sensing the detonation wave.

2.2 Material

ISDN was prepared in our laboratory by a known procedure [4] as shown in Scheme 1 and recrystallised from acetone/water mixture to obtain pure ISDN.

A known quantity of lactose was added to pure ISDN and mixed well using agate mortar carefully to make various mixtures. (Caution: pure ISDN is hazardous to grind in a mortar.) Known quantities of sulphuric acid (10%) and nitric acid (10%) were added separately to pure ISDN and mixed thoroughly using mortar and pestle. For explosive sensitivity experiments, the material, after mixing with water, was packed in 25 mm plastic tubes and densities were determined before firing.



Scheme 1. Preparation of ISDN.

3. Results and discussion

3.1 Thermal sensitivity

DSC is a very useful technique for the evaluation of thermal sensitivity/stability of a hazardous material. DSC thermograms of pure and crude ISDN and pure ISDN diluted with 60% lactose were recorded and displayed in Fig. 1. Pure ISDN showed a melting point of 340 K and a sharp decomposition exotherm with an onset temperature of 443.0 K, whereas a crude sample showed a melting point of 335.0 K and a broad decomposition exotherm with an onset temperature of 427.0 K. ISDN diluted with lactose exhibited, in addition to ISDN melting peak at 340.0 K, another broad endotherm around 412.0 K (due to water loss). There is no change in the decomposition temperature of ISDN due to lactose dilution; but the decomposition portion of thermograms splits into two; and the area under the curve, which is the measure of decomposition energy, is drastically reduced. It may be appropriate to state here that lactose dilution does not influence the thermal stability of ISDN, but certainly minimises the exothermicity of ISDN due to dilution effect. The thermal properties are listed in Table 1.

A detailed study was carried out on various compositions, wherein the lactose dilution was increased from 5 to 75 wt%. A few DSC thermograms recorded with 10 K min^{-1} heating rate are presented in Fig. 2. The melting temperatures and decomposition temperatures are listed in Table 1. It is interesting to note that the melting point of ISDN is not affected by lactose dilution.

The DSC thermogram of pure lactose shows two sharp endotherms, one in the temperature range of 420–430 K and another in the temperature range of 480–500 K. The former peak is due to the loss of a water molecule (monohydrate) present in lactose and the latter peak is due to lactose decomposition. For up to 20% lactose in ISDN the first peak due to loss of lactose water was not noticeable, whereas more than 30% lactose dilution exhibited very broad endotherms. In fact ISDN influenced the dehydration of lactose and advanced the endothermic peak by about 20 K. Lactose did not influence the decompo-

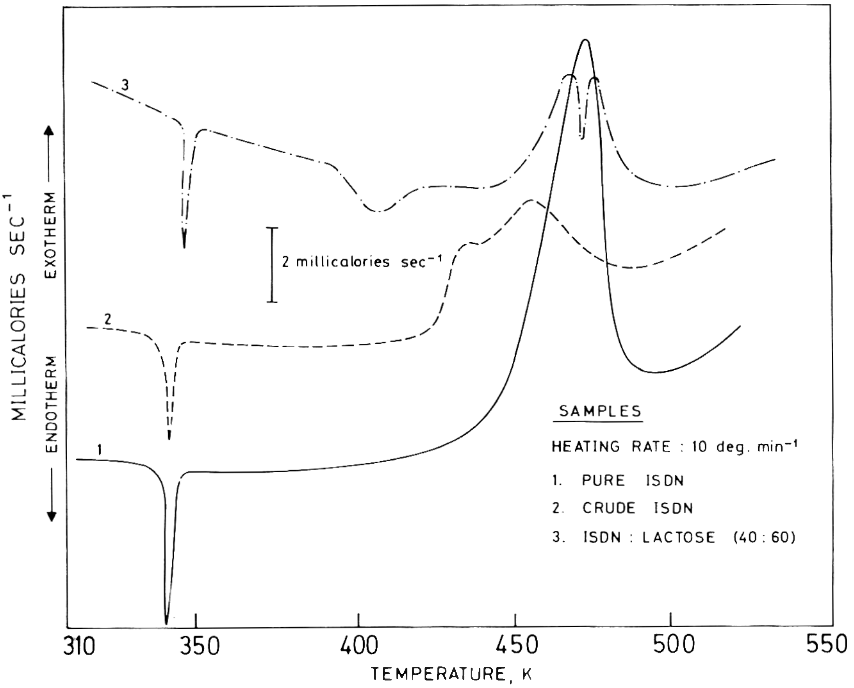


Fig. 1. DSC thermograms of (1) pure ISDN, (2) crude ISDN, and (3) 40/60. ISDN-lactose mixture.

sition temperature of ISDN, but considerably reduced the decomposition energy by acting as a heat sink. It is apparent that ISDN influenced the decomposition of lactose and was also advanced by about 20 K. Up to 20% lactose dilution ISDN showed a sharp single decomposition peak, whereas 25–35% of lactose showed a shoulder in decomposition while more than 35% lactose showed a clear split in the ISDN decomposition peak (Fig. 2). Thus, the dilution of ISDN with lactose reduces the exothermicity and enhances the safety of ISDN handling.

The split in the exotherm of ISDN lactose mixtures had given an impression that the decomposition is a two-stage process. As mentioned earlier, lactose decomposition is endothermic in nature. In diluted samples, ISDN and lactose decompose simultaneously. Decomposition due to ISDN is heat producing, while lactose decomposition is heat absorbing. The shaded areas of curves 4, 5 and 6 (Fig. 2) are due to an endothermic decomposition of lactose, which occurs during the exothermic decomposition of ISDN.

3.2 Decomposition energy

DSC is a quantitative technique to determine the enthalpy of decomposition. The area under the curve is directly related to the amount of heat released.

TABLE 1

Thermal sensitivity

Sample	Endotherms (K)		Exotherms (K)			
			T_i	T_p		T_e
Pure ISDN	340.0	–	443.0	467.0	–	482.0
Crude ISDN	336.0	–	427.0	452.0	–	480.0
ISDN/lactose (95/5)	340.0	–	445.0	468.0	–	482.0
ISDN/lactose (90/10)	340.0	–	445.0	468.0	–	482.0
ISDN/lactose (85/15)	340.0	–	444.0	468.0	–	482.0
ISDN/lactose (80/20)	340.0	–	443.0	468.0	–	481.0
ISDN/lactose (75/25)	339.0	–	443.0	468.0	–	480.0
ISDN/lactose (70/30)	340.0	–	444.0	468.0	–	481.0
ISDN/lactose (65/35)	340.0	Not clear	445.0	468.0	–	482.0
ISDN/lactose (60/40)	340.0	400.0[a]	445.0	463.0	469.0	488.0
ISDN/lactose (50/50)	340.0	400.0[a]	446.0	463.0	469.0	487.0
ISDN/lactose (40/60)	340.0	401.0[a]	448.0	463.0	470.0	485.0
ISDN/lactose (25/75)	340.0	401.0[a]	447.0	463.0	473.0	487.0
Pure lactose	420.0	477.0[b]	–	–	–	–

[a] Lactose water loss.

[b] Lactose decomposition.

T_i, Initial temperature, T_p, peak temperature, and T_e, end temperature.

High purity indium (99.9% pure) was used as a standard for estimating the decomposition heat energy of ISDN and various ISDN–lactose mixtures. Two dilutions of ISDN–lactose, 40/60 and 25/75, are commonly used for pharmaceutical preparations. The estimated decomposition energy values are listed in Table 2. Crude ISDN showed less energy compared to pure ISDN. The decomposition energy decreased as the lactose percent in ISDN mixtures increased (Table 2). Though the lactose decomposition energy is very small (165.00 J g^{-1}), its influence on ISDN decomposition is very remarkable. This study clearly indicates that ISDN diluted with lactose is less energetic and safer to handle than when pure. The common dilutions of ISDN–lactose, 40/60 and 25/75, are quite safe and their decomposition energies are 1/5 and 1/6 of pure ISDN, respectively.

3.3 Kinetics of decomposition

The kinetics of decomposition play a very important role in the assessment of the hazardous property of energetic materials. The activation energy helps in rating the hazardous potential of a given explosive. The higher the activation energy, the safer the material is to handle.

There are several methods for calculating kinetic parameters. We restricted our study to non-isothermal analysis, the Ozawa method [5], which is also the ASTM method used. The activation energy obtained by this method is inde-

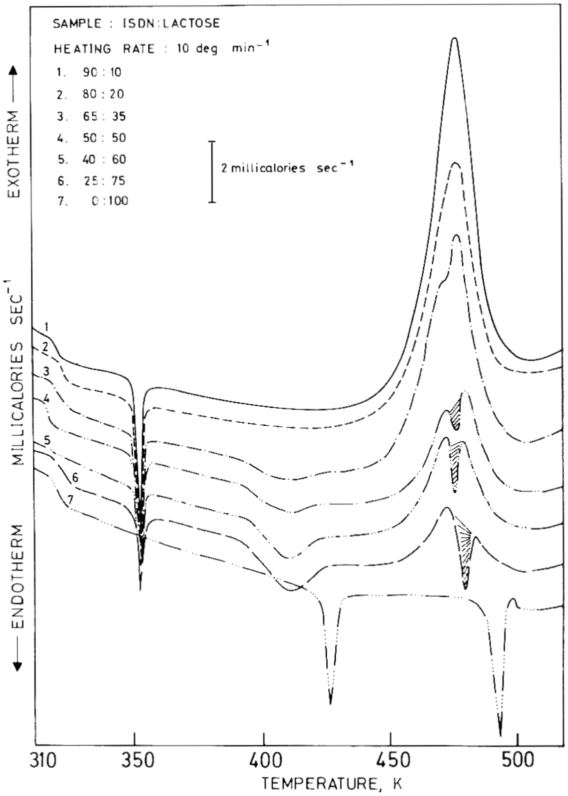


Fig. 2. DSC thermograms of ISDN-lactose mixtures.

TABLE 2

Heat of decomposition

ISDN	Lactose	Found (J/g)	Calculation for dilution (J/g)	Stabilisation (J/g)
100	0	2319.0	2319.0	0.0
95	5	2291.0	2195.0	96.0
90	10	2167.0	2071.0	96.0
85	15	1890.0	1946.0	−56.0
80	20	1815.0	1822.0	−7.0
50	50	712.5	1077.0	−365.0
40	60	505.0	829.0	−324.0
25	75	403.0	456.0	−53.0
0	100	165.0	−165.0	-

pendent of the order of the reaction. This method depends on the fact that the reaction rate depends upon the heating rate, in cases where self-heating occurs during decomposition. An increase in the heating rate shifts the peak temperature to a higher temperature. The reaction rate is maximum at peak temperatures. By this method a plot of ln (ϕ) versus reciprocal absolute peak temperature will produce a straight line with a slope equal to $-E/R$ [5].

Pure ISDN, crude ISDN and ISDN–lactose (40/60) are subjected to various heating rates (5, 10, 20 and 40 K min^{-1}) and the thermograms are shown in Figs. 3, 4 and 5, respectively. Melting and decomposition temperatures are listed din Table 3. While there was no influence of heating rate on the melting point of crude and pure ISDN, a slight shift to higher temperature was observed in the case of ISDN–lactose mixtures with increased heating rates. However, there was a clear shift in the decomposition curves. Pure ISDN showed sharp peaks, whereas crude ISDN showed broad peaks with a shoulder and ISDN–lactose mixture exhibited two peaks, Peak 1 ($T\mathrm{p}_1$) and Peak 2 ($T\mathrm{p}_2$) (Table 3). The plots of ln (ϕ) vs reciprocal peak temperatures are shown in Fig. 6, and activation energy (E_{act}) values are listed in Table 4. It is very clear from the activation energy values that crude ISDN is most hazardous and the

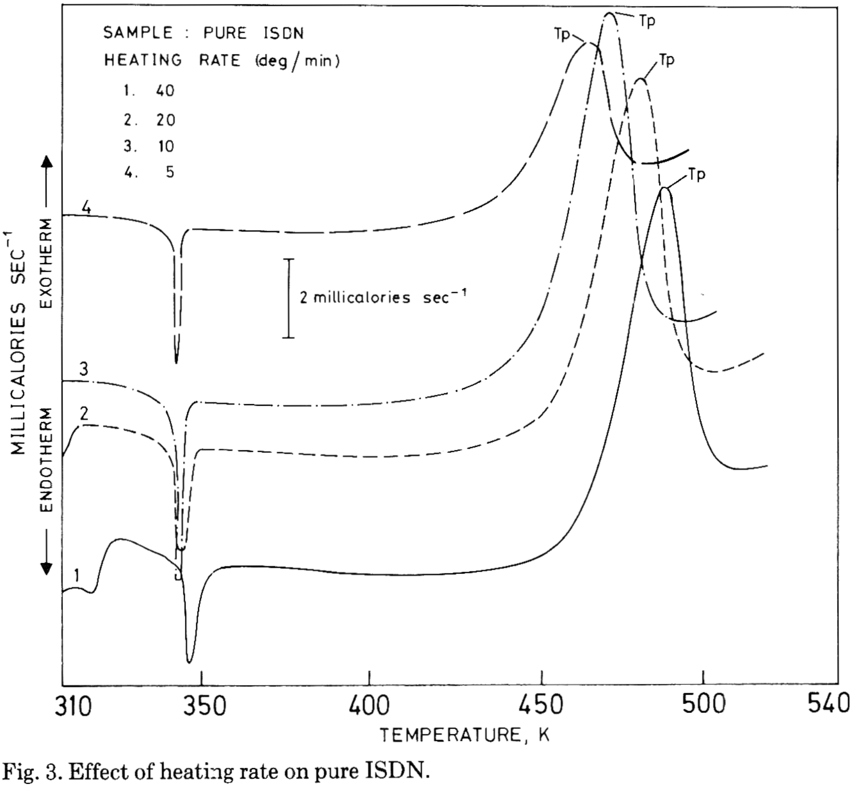


Fig. 3. Effect of heating rate on pure ISDN.

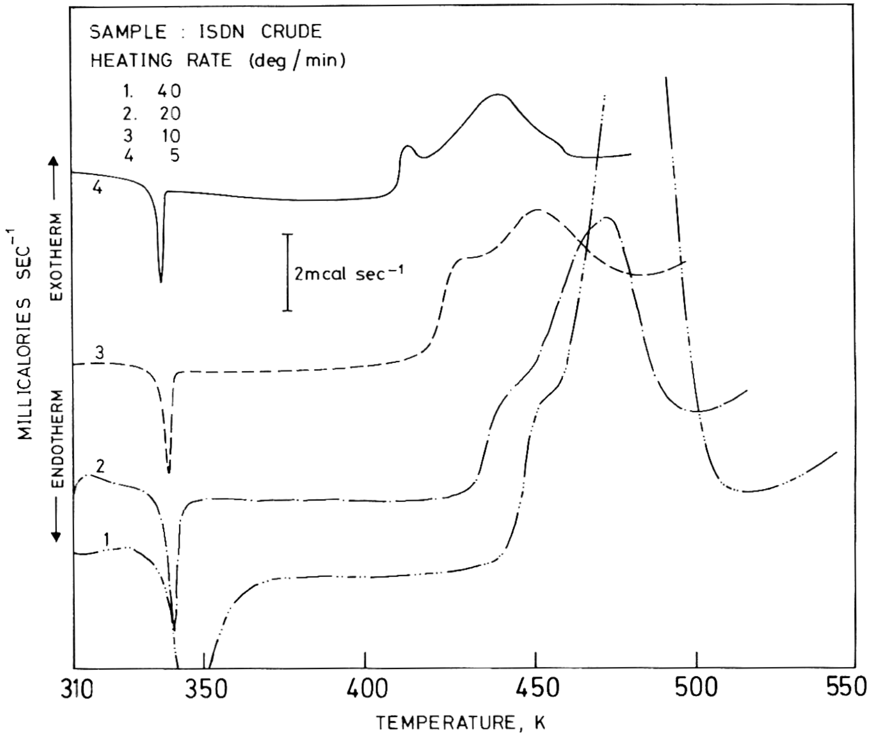


Fig. 4. Effect of heating rate on crude ISDN.

ISDN–lactose mixture is least hazardous, whereas pure ISDN falls in between. The decreasing order of hazard is given below:

Crude ISDN > pure ISDN > ISDN/lactose (60/40).

The common ISDN/lactose mixtures, 40/60 and 25/75, would be safer than the 60/40 mixture.

3.4 Thermogravimetric analysis

Weight loss measurements were carried out on pure, crude and lactose diluted ISDN. The TG thermograms of pure and crude ISDN with 10 K min^{-1} heating rates are shown in Fig. 7. Pure ISDN showed rapid weight loss compared to crude ISDN. This observation supplements previously discussed DSC data. The weight loss was in the range of 85–95%.

Ozawa [6] developed a method for the estimation of activation energy for TG analysis which states that the logarithm of the rate of heating (dT/dt) has a linear relationship with the reciprocal of the absolute temperature for the given conversion (α), regardless of the order of reaction. This method requires non-isothermal runs at different heating rates.

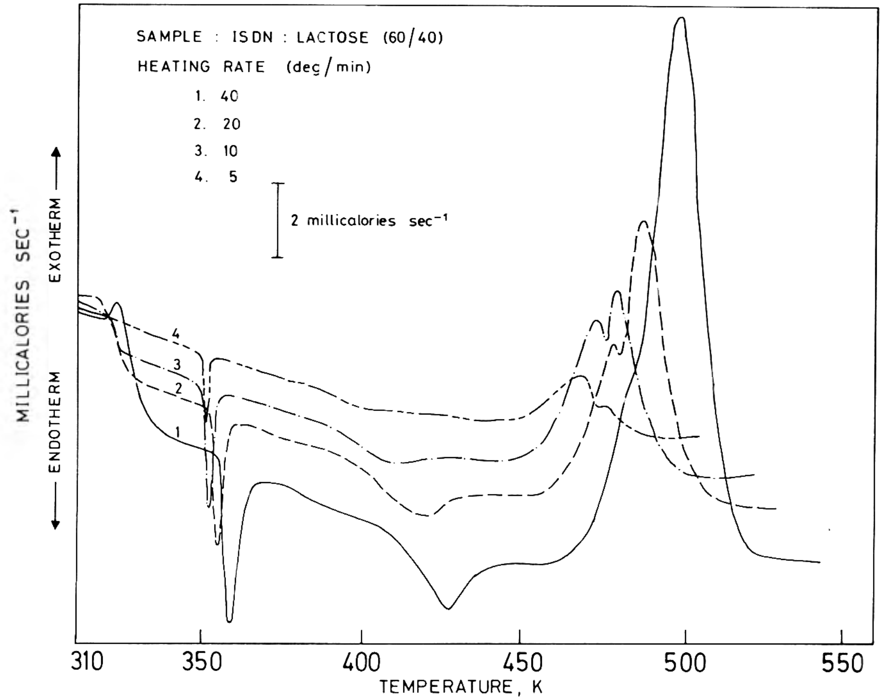


Fig. 5. Effect of heating rate on ISDN-lactose (60/40) mixture.

TABLE 3

Effect of heating rate

Sample	Heating rate (K/min)	Peak temperature (K)	
Pure ISDN	5	-	458.0
	10	-	467.0
	20	-	475.0
	40	-	481.0
Crude ISDN	5	-	440.0
	10	-	452.0
	20	-	472.0
	40	-	483.0
ISDN/lactose (60/40)	5	458.0	465.0
	10	462.0	468.0
	20	467.5	476.0
	40	-	485.0

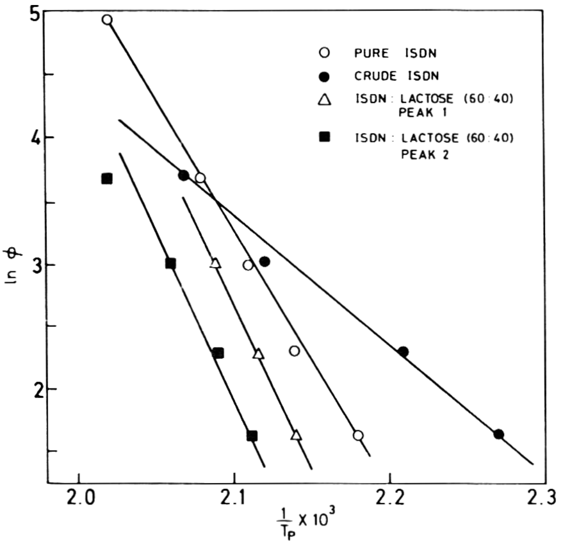


Fig. 6. Ozawa method plot.

TABLE 4

Activation energy values obtained by Ozawa's method

Sample	E_{act} (kJ/mol)
DSC	
Crude ISDN	87.36
Pure ISDN	174.70
ISDN/lactose (60/40)	233.50
TG	
Crude ISDN	68.75
Pure ISDN	158.80

Thermograms were recorded for pure and crude ISDN at four heating rates (5, 10, 20 and 40 K min^{-1}). From α-t curves, the absolute temperatures for the given conversion ($\alpha=0.5$) at different heating rates were calculated. The plot of ln ϕ vs reciprocal temperature at 0.5α is shown in Fig. 8. The calculated activation energies were 158.8 and 68.7 kJ mol^{-1} for pure and crude ISDN, respectively (Table 4). These values are slightly lower than the DSC values.

Weight loss measurement was carried out on four lactose-diluted ISDN samples: (1) ISDN–lactose (80/20); (2) ISDN–lactose (60/40); (3) ISDN–lactose (40/60); and (4) ISDN–lactose (25/75).

The weight loss data is tabulated in Table 5. The samples were heated at fixed heating rate, 10 K min^{-1}. The observed weight loss for diluted ISDN was

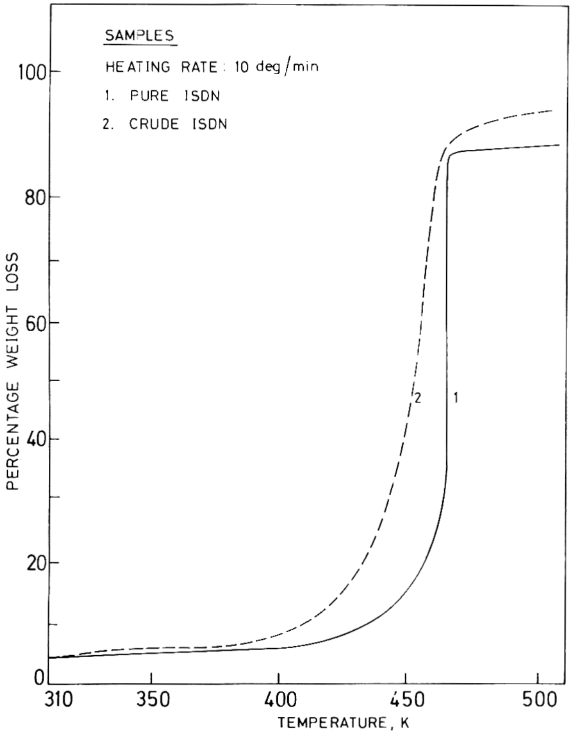


Fig. 7. TG curves of (1) pure, and (2) crude ISDN.

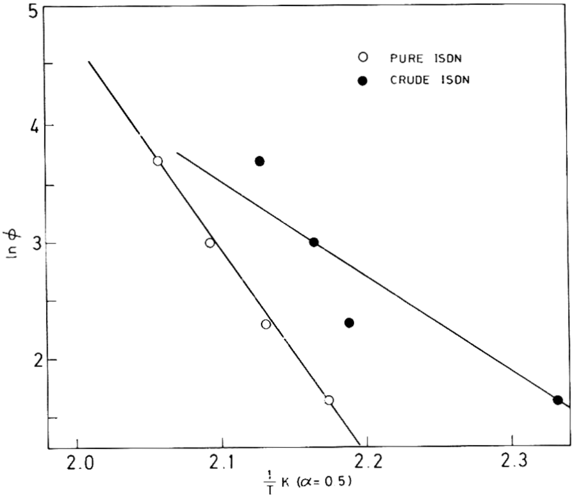


Fig. 8. Ozawa's method for TG analysis.

TABLE 5

Weight loss data TG

Sample		Temperature range (K)	Weight loss (%)	
Pure ISDN		413.0-473.0	90.5	
Crude ISDN		393.0-493.0	84.8	
ISDN/lactose 80/20	Stage I	414.0-434.0	2.0	86.1
	Stage II	434.0-493.0	64.9	
	Stage III	563.0-638.0	20.2	
ISDN/lactose 60/40	Stage I	403.0-430.0	3.1	84.1
	Stage II	430.0-498.0	49.0	
	Stage III	540.0-618.0	32.0	
ISDN/lactose 40/60	Stage I	404.0-434.0	3.9	77.5
	Stage II	424.0-480.0	30.7	
	Stage III	543.0-617.0	42.9	
ISDN/lactose 25/75	Stage I	403.5-428.0	5.6	79.1
	Stage II	428.0-473.0	24.2	
	Stage III	552.0-622.0	49.3	
Pure lactose	Stage I	414.0-447.0	4.3	70.3
	Stage II	512.0-628.0	66.0	

Stage I: Water loss,
Stage II: ISDN decomposition, and
Stage III: Lactose decomposition.

in three stages. The first stage loss is mainly due to the loss of lactose water. In the second and third stages, weight loss is due to simultaneous decomposition of ISDN and lactose. The total weight loss was in the range of 70.0–90.0%. As the lactose content increased from 20 to 75%, the percentage total weight loss decreased from 89.1 to 79.1%, while pure lactose showed only 70% loss. As the lactose content increased in ISDN formulation, the loss due to the second stage decreased while third stage weight loss increased according to the lactose percentage. As in the case of DSC analysis, in TG analysis also, the decomposition of ISDN is not really two stage, but the heat absorbing nature of lactose decomposition retards the decomposition rate of ISDN, which is reflected in the rate of weight loss.

3.5 Influence of acid on ISDN decomposition

In the manufacturing process of ISDN, isosorbide is nitrated using only nitric acid (99%) or a nitric acid and sulphuric acid mixture. After nitration and a preliminary water wash, crude ISDN is called acidic ISDN and contains about 0.5–1.0% acid. Subsequently, the acidic ISDN is neutralised with ammonia before subjecting to recrystallisation.

It is known that acidic nitrate esters such as pentaerythritol tetranitrate (PETN) and isosorbide dinitrate (ISDN) are less stable compared to the pure material. Therefore, it is essential to study the thermal stability of acidic ISDN to benefit the manufacturers. We have already noticed low activation energy and low thermal stability for crude ISDN, which is slightly acidic when compared with pure ISDN. The percentage acid in crude ISDN was found to be between 0.5–0.6%.

Further research was carried out on pure ISDN by mixing with known quantities of nitric acid and sulphuric acid separately. Nitric acid showed very little effect on the thermal behaviour of ISDN, whereas the sulphuric acid influence was alarming. The following samples were studied by DSC:
(1) ISDN+10% of 10% sulphuric acid,
(2) ISDN+20% of 10% sulphuric acid,
(3) ISDN+30% of 10% sulphuric acid,
(4) ISDN+40% of 10% sulphuric acid,
(5) ISDN+50% of 10% sulphuric acid,
(6) ISDN (pure).
The DSC thermograms are shown in Fig. 9. The thermal stability of ISDN was adversely affected with 10–40% added sulphuric acid, but at 50% sulphuric acid there was no effect on the thermal stability. The onset temperatures for Samples 1, 2, 3, 4, 5 and 6 are 410, 405, 400, 405, 440 and 445 K, respectively. In addition to the melting and decomposition of ISDN, samples with more acid also showed additional small endotherms due to loss of acid water in the temperature range of 380–400 K. This clearly indicates that small percentages of sulphuric acid catalyses the decomposition, but larger percentage of acid acts as a diluent. In fact, some of the acidic ISDN samples (prepared by mixed acid) decomposed while drying at 100°C during TG moisture content determination. Extreme care should be exercised in handling acidic ISDN. It is not advisable to store the acidic material for long periods.

To study the effect of nitric acid on ISDN decomposition, the following samples were prepared by mixing known quantities of nitric acid: (1) ISDN+10% of 10% nitric acid, (2) ISDN+30% of 10% nitric acid, and (3) ISDN+50% of 10% nitric acid.

The onset temperatures for the above samples, 1, 2 and 3, are 438, 439 and 437 K, respectively. These values fall between the onset temperature of pure and crude ISDN (Table 1). Compared to samples mixed with sulphuric acid, the nitric acid influence on ISDN stability is negligible. This may be due to the fact that the nitrate esters on decomposition produce NO_2^+ species, which will have a common ion effect in the case of nitric acid, whereas sulphuric acid favours decomposition.

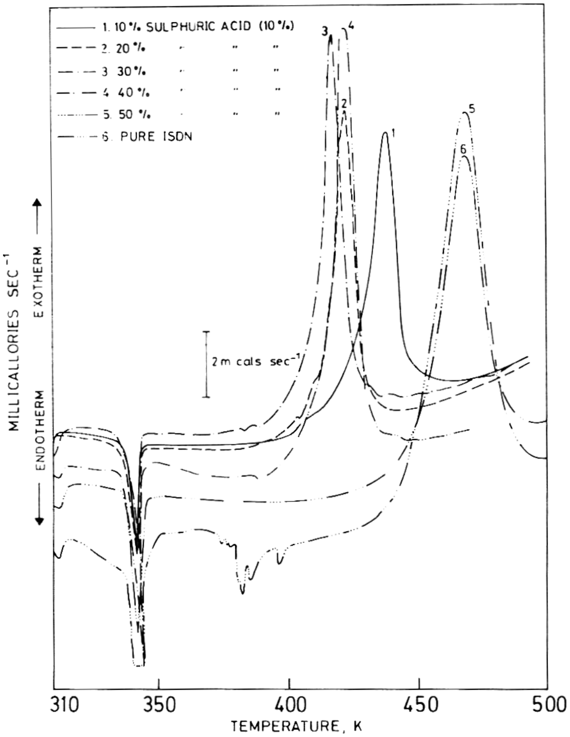
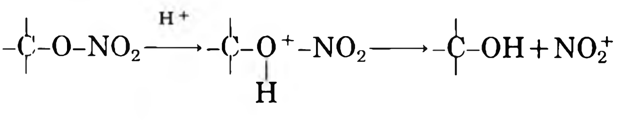


Fig. 9. DSC thermograms showing the influence of sulphuric acid.

3.6. *Mechanism of decomposition*

The activation energy values obtained by TG and DSC study suggest that breakage of the O–N bond in nitrate esters is the rate controlling step, as the activation energy was very close to the O–N bond energy (150–175 kJ mol^{-1}). The influence of sulphuric acid on the decomposition of ISDN also supports the above argument. Sulphuric acid, being a strong acid, acts as a strong protonating agent compared with nitric acid, which did not affect ISDN stability to the same extent as sulphuric acid. The influence of sulphuric acid is shown below.



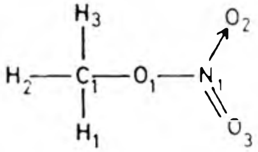
$$-\overset{|}{\underset{|}{C}}-O-NO_2 \xrightarrow{H^+} -\overset{|}{\underset{|}{C}}-\underset{H}{\underset{|}{O^+}}-NO_2 \longrightarrow -\overset{|}{\underset{|}{C}}-OH + NO_2^+$$

The nitronium ion thus formed is stabilised by sulphuric acid.

In order to understand the effect of protonation on the bond angles, bond length and charge distribution, modified neglect differential overlap (MNDO) calculations were carried out on a model compound, methyl nitrate. The effects of protonation at the alkoxy oxygen O_1 and at the nitro group oxygen O_3 (O_2)

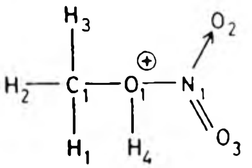
TABLE 6

MNDO calculations
(a) Methyl nitrate



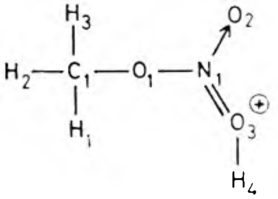
Bond angles (degrees)		Bond lengths (Å)	
$O_1N_1O_2$	119.92	N_1-O_2	1.2091
$O_1N_1O_3$	114.14	N_1-O_3	1.2088
$C_1O_1N_1$	122.89	O_1-N_1	1.3427
$H_1C_1O_1$	104.50	C_1-O_1	1.4202
		H_1-C_1	1.1162
$H_2C_1O_1$	112.50	H_2-C_1	1.1144
$H_3C_1O_1$	112.50	H_3-C_1	1.1142

(b) Methyl nitrate protonated at O_1



Bond angles (degrees)		Bond lengths (Å)	
$O_1N_1O_2$	91.52	N_1-O_2	1.1316
$O_1N_1O_3$	89.34	N_1-O_3	1.1318
$C_1O_1N_1$	126.14	O_1-N_1	2.8418
$H_4O_1N_1$	122.28	O_1-H_4	0.9474
$H_1C_1O_1$	109.37	C_1-O_1	1.4037
		H_1-C_1	1.1166
$H_2C_1O_1$	109.32	H_2-C_1	1.1170
$H_3C_1O_1$	112.87	H_3-C_1	1.1130

(c) Methyl nitrate protonated at O_3



Bond angles (degrees)		Bond lengths (Å)	
$O_1N_1O_2$	125.36	N_1-O_2	1.1820
$O_1N_1O_3$	115.58	N_1-O_3	1.3063
$N_1O_3H_4$	115.96	O_3-H_4	0.9740
$C_1O_1N_1$	124.21	O_1-N_1	1.3086
$H_1C_1O_1$	102.34	C_1-O_1	1.4533
		H_1-C_1	1.1121
$H_2C_1O_1$	111.09	H_2-C_1	1.1125
$H_3C_1O_1$	111.53	H_3-C_1	1.1178

TABLE 7

Detonation properties of ISDN/water mixtures

Shot No.	Composition	Density ($g\,cm^{-3}$)	VOD ($m\,s^{-1}$)
1	Crude ISDN + No water	0.82	3921.0
2	Crude ISDN + 5% water	0.87	3849.0
3	Crude ISDN + 7.5% water	0.92	3612.0
4	Crude ISDN + 10.0% water	0.96	Cap failed
5	Crude ISDN + 15% water	1.00	Cap failed
6	Crude ISDN + 20% water	1.04	Cap failed
7	Pure ISDN + 10% water	0.60	3129.0
8	Pure ISDN + 12.5% water	0.81	Cap failed
9	Pure ISDN + 15% water	0.90	Cap failed
10	Pure ISDN + 25% water	0.96	Cap failed
11	Pure ISDN + No water	0.49	4021.0

are shown in Table 6. It appears from the calculations that the most probable site for proton attack is O_1 not O_2 or O_3. Protonation at O_1 increases the bond length of O_1-N_1 from 1.3427Å to 2.8418Å. Furthermore O_1 aquires a negative charge, and the whole NO_2 group acquires a positive charge and becomes almost linear. This clearly suggest that protonation at O_1 weakens the O-NO_2 bond so much that little energy is required to break it. The charge distribution explains the presence of some alcohol and nitronium ions in protonated compound. This rationale for methyl nitrate holds for ISDN as well. The decrease in the activation energy of crude ISDN (which contains about 0.5% sulphuric acid) to half that of pure ISDN is due to the increase of -O-NO_2 bond length the to twice bond length of that in the pure compound.

3.7 Detonation properties of ISDN-water mixtures

ISDN is a cap sensitive explosive in pure form. The detonation properties of ISDN/lactose mixtures were reported earlier [2]. In our present investigation, crude ISDN containing about 2% moisture was diluted with water, packed in 25 mm plastic tubes, and fired with a No. 6 detonator. The results are tabulated in Table 7. Crude ISDN alone showed a detonation velocity of 3931.0 m s^{-1}. With up to 7.5% water, it was cap sensitive. With 10% or more water, it was non-cap sensitive. Water was also added to pure ISDN, but it was found that pure ISDN was cap sensitive even with 10% water. These results suggest that ISDN can be made non-explosive by mixing with about 20% water. In its manufacture, ISDN can be handled as a non-explosive by the addition of 20–30% water. However, operations such as crystallisation or drying and mixing with lactose demand the implementation of high explosive rules and regulations as with PETN. Furthermore, though safety is improved by mixing with water, long storage periods with 30% water may affect the quality due to slow hydrolysis.

4. Conclusions

1. Crude or pure ISDN is a high explosive and should be handled carefully.
2. Decomposition enthalpy data clearly shows the dilution effect in ISDN/lactose mixtures.
3. Kinetic data suggests that crude ISDN which contains about 0.5–0.6% acid is more sensitive and less stable compared to pure ISDN.
4. The influence of acidity suggests that the storage of improperly washed ISDN, especially that manufactured using mixed acids, may be unsafe over long periods.
5. Detonation velocity experiments suggest there is enhanced safety when ISDN is mixed with water.

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Removal of chemical contamination from vehicles: A comparison of weathering and active clean-up processes

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Abstract

The concentrations of chemical contamination desorbing from alkyd and polyurethane painted vehicles after exposure to sun and wind under winter conditions have been measured. A computer model has been used to determine the residual contamination level after weathering. The removal efficiency under winter conditions is compared with that under summer conditions and is shown to be approximately one eighth as effective. The weathering process is also compared with active clean-up processes involving detergent/steam and C8 emulsion/steam. The combination of C8 emulsion and steam is shown to be the most effective decontamination process.

1. Introduction

The manufacture of chemicals and the associated chemical industry are indispensable parts of our industrial society. This has been referred to as "The Chemical Age" [1]. The enormous use of chemicals is not without risk. Many chemicals are toxic to some extent and some are extremely hazardous. With increased usage the possibility of an accidental release also increases and even with excellent safety precautions accidents will occur as a result of equipment failure and human error. Transport in particular poses a major problem since the scope for accident is greatly increased. Considerable effort is expended in cleaning up spills from accidents. Emergency workers frequently must wear chemical protective suits and respirators as protection against toxic vapours. Processes which accelerate the reduction and removal of contamination will reduce the need for clean-up and also will reduce the time spent in protective clothing.

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In a previous study [2] we examined the removal of contamination from vehicles through the natural processes of weathering by sun and wind during the summer months in South Eastern Australia. We concluded that weathering in summer months would be sufficient to reduce the hazard to below the minimum risk value for all but the most toxic of chemicals. In the present study we examine the processes of weathering during the cooler winter months and compare the efficiencies of clean-up procedures using active chemicals and physical processes.

2. Experimental

2.1 Desorption chamber

The chamber in which the studies were carried out was constructed of stainless steel and was thermally insulated and temperature controlled. Total volume of the chamber was 93 m^3. Mechanical circulation of the air inside the chamber ensured rapid mixing of desorbing vapour. Methyl salicylate (MS) was chosen as a simulant because of its intermediate volatility.

2.2 Analysis

MS vapour concentrations were monitored by sampling into propylene glycol in sequential sampler bubblers. The sequential samplers each held 12 bubblers containing 5 mL propylene glycol as the absorbing medium and were programmed to sample the chamber over a 24 or 40 hour time span. The bubbler contents were analysed subsequently for MS by UV spectroscopy.

2.3 Vehicles

The vehicle chosen was the in-service Landrover complete with canvas canopy and rubber tyres. We investigated two paint systems; (i) in-service matt olive drab alkyd paint and (ii) low gloss olive drab aliphatic polyurethane paint (PUP) to GPC-P 154/3 [3].

MS containing Orasol Brilliant Fast Red (0.1%) and Tinopal SWN Conc (0.1%), as visual and fluorescent tracers respectively, was sprayed onto the side, front and windscreen of the Landrover from a hand-held pressurised sprayer. The contamination density was determined by collection of sprayed MS on felt pads (100 mm × 100 mm); after contamination these were removed for analysis. The quantity of MS on the felt pads was determined by ethanol extraction and spectrophotofluorimetric analysis of the Tinopal SWN tracer in the extract. The contamination process resulted in a fairly even distribution of simulant spread over the surface of the vehicle. In real accidents there may well be heavy and more localised contamination of the vehicle.

The contaminated vehicle was driven into the sealed chamber which was temperature controlled at 20 ± 1 °C. MS desorbing from the vehicle was monitored by collection for later analysis in four sets of sequential samplers arranged around the vehicle. Analysis of all data about the desorption of MS from vehicles in the chamber was carried out using CONSAM which is the interactive version of the SAAM modelling program and allows the user to develop mathematical models to fit experimental data [4]. All data sets have been normalised to a contamination density of 10 g m^{-2} for purposes of comparison.

2.4 Clean-up processes

In the studies on weathering, the contaminated vehicles were exposed to sun and wind under Melbourne winter conditions during August and September for 90, 135 and 180 minutes to enhance removal of contamination. The mean insolation was 0.34 kW m^{-2}, mean wind speed 1.45 m s^{-1} and mean surface temperature 11 °C.

Two active decontamination processes were investigated, a physical removal system and a chemical destruction process. The physical removal system involved a pre-wash of the vehicle for 5 minutes with degreasing detergent (0.1%) in hot water at 60 °C followed by treatment with steam at 150 °C for 5 minutes. The active chemical decontamination process consisted of a prewash for 5 minutes with a degreasing detergent (0.1%) in hot water at 70 °C, followed by C8 decontaminant. This was applied by spraying and allowed to remain on the vehicle for 20 minutes; the C8 was finally removed by steam treatment at 150 °C. Hot water, detergent and steam were supplied in both instances from a portable steam generating unit, NBC-Sanator. C8 emulsion is an active chlorine military decontaminant containing calcium hypochlorite, tetrachloro-ethylene, an emulsifier and water [5].

3. Results and discussion

In previous studies [2, 6] Amos et al. developed a computer model to describe the desorption of a liquid chemical from vehicles in an enclosed chamber. The model described was

$$Ct = P_1\,[1 - \exp(-P_2\,(t - P_4)^{P_3})] \qquad (1)$$

where P_1, P_2, P_3 and P_4 are constants that have to be evaluated. Previous studies [2, 6] have shown that P_1 is related to the contamination level of the simulant, P_2 is an estimate of the desorption rate constant, P_3 is a measure of deviation from linear kinetics and P_4 is an offset allowing for errors associated with recording early observations for the experiment.

To establish the relationship between the initial contamination level (IC) of MS and P_1, three levels of simulant contamination were studied for each of the two painted vehicles. The vehicles were not subject to weathering or decontamination in this series and were placed in the chamber immediately after contamination. The experimental data were fitted to the model and the values

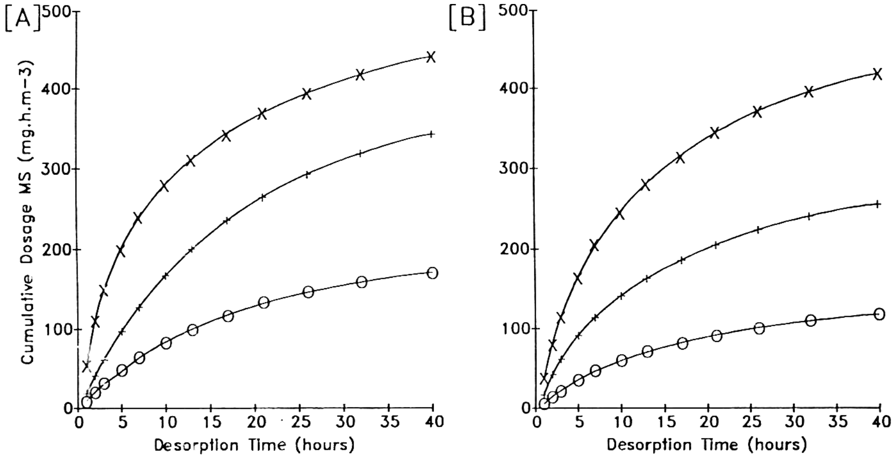

Fig. 1. Cumulative desorption of MS from [A] Alkyd vehicles and [B] PUP vehicles after winter weathering—experimental data and SAAM fits. The unbroken lines are the SAAM fits. Weathering time: (×) 1.5 h, (+) 2.25 h, and (○) 3.0 h.

of P_l for each level of IC calculated. P_l was regressed on IC and the following relationship was established:

$$P_l = 5.2IC + 1.7 \qquad (2)$$

3.1 MS desorption after weathering

The MS desorption data from vehicles exposed to the weather for various periods of time were fitted using CONSAM to the developed empirical model (eq. 1) as shown in Fig. 1. Values of P_l calculated with eq. (1) are given in Table 1. Values of IC_w, the contamination level after weathering, are also detailed in Table 1 and were calculated from eq. (2).

TABLE 1

Derived values of P_l, level of residual contamination (IC_w) and removal efficiencies (RE) for MS after weathering under winter conditions for alkyd and polyurethane coated vehicles

Paint type	Weathering time (hours)	P_l (S.D.)[a]	IC_w (g)	RE[b] (%)
Alkyd	1.5	540 (9.5)	104	18
Alkyd	2.25	396 (1.1)	75.6	41
Alkyd	3.0	197 (4.3)	37.6	70
PUP	1.5	487 (8.5)	93.1	27
PUP	2.25	306 (3.0)	58.5	54
PUP	3.0	141 (4.7)	26.8	79

[a] Standard deviation.

[b] Mass of MS applied by spraying ($IC_0 = 127.5$ g).

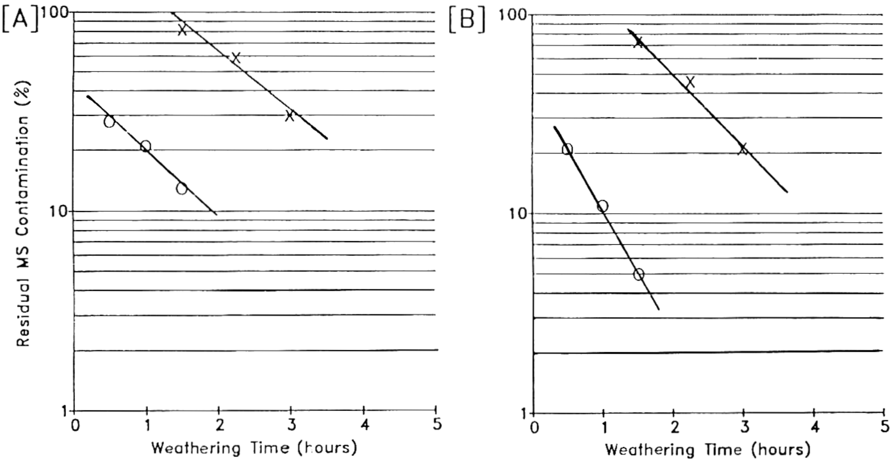

Fig. 2. Plot of percentage residual MS contamination vs. weathering time for winter (×) and summer (○) months for [A] Alkyd vehicles and [B] PUP vehicles.

It is clear that weathering during winter months is not effective in removing MS contamination from the vehicles under examination. Removal efficiencies ranged from 18% to 70% for alkyd coated vehicles and 27% to 79% for polyurethane coated vehicles. The removal efficiencies for winter weathering are shown graphically in Fig. 2 and are also compared with data previously obtained from summer weathering [2]. The residual contamination levels after winter weathering are such that the hazard from many toxic chemicals would remain well above the minimum risk value of 3%. The consequence is that active means of decontamination or clean-up should be sought during winter months.

The polyurethane coating was designed to be extremely resistant to penetration by toxic chemicals and the greater removal efficiency for vehicles with such coatings may be attributed to the chemical hardness of the paint. That the removal efficiencies for the polyurethane systems are only some 10% greater than for alkyd systems may be ascribed to the penetration of MS into cracks and crevices and into other absorbent materials on the vehicles. Desorption from such design artifacts tends to negate the chemical hardness of the polyurethane paint.

3.2 Active clean-up process

Of the two decontamination procedures investigated, one relies upon physical removal, the other upon chemical destruction. In the former, treatment with a hot water and detergent pre-wash removes liquid contamination and any dirt, oil and grease which may have absorbed contamination. This is followed by application of steam at 150 °C which evaporates remaining liquid agent, accelerates the evaporation of absorbed contamination and contributes to destruction of contamination through hydrolysis.

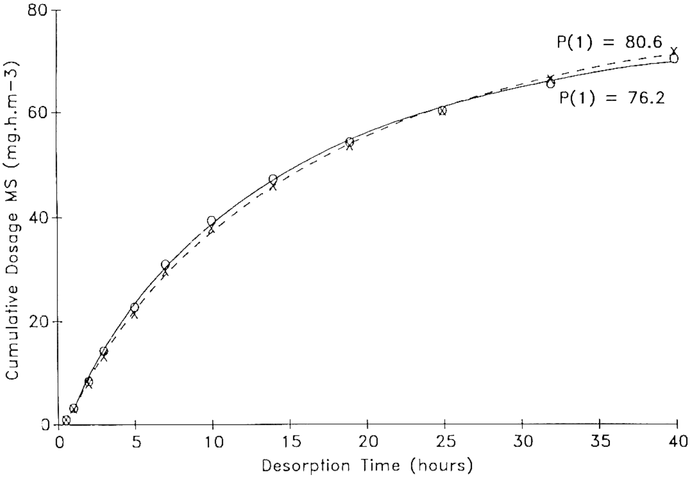

Fig. 3. Cumulative desorption of MS from vehicles after clean-up with a detergent pre-wash and steam at 150 °C—experimental data and SAAM fits. The solid and dotted lines are the SAAM fits, (○) PUP landrover, and (×) Alkyd vehicles.

Figure 3 depicts the desorption of MS from vehicles following treatment with detergent pre-wash and steam at 150 °C. The derived values of P_1, level of residual contamination (IC_w) and removal efficiencies (*RE*) for MS are detailed in Table 2.

The *RE* for MS on both vehicles is approximately 80% which is similar to that obtained by weathering during winter months for polyurethane vehicles and some 10% better than alkyd vehicles. There is little difference between the

TABLE 2

Derived values of P_1, level of residual contamination (IC_w) and removal efficiencies (*RE*) for MS after decontamination with detergent/steam or C8 emulsion/steam for alkyd and polyurethane coated vehicles

Paint type	Decontamination process	P_1 (S.D.)[a]	IC_w[b] (g)	*RE* (%)
Alkyd	Detergent steam	80.6 (2.7)	15.2	81
Alkyd	C8 emulsion steam	22.7 (0.5)	4.04	95
PUP	Detergent steam	76.2 (2.1)	14.3	82
PUP	C8 emulsion steam	20.1 (0.5)	3.42	96

[a] Standard deviation.

[b] Mass of MS applied by spraying ($IC_0 = 80$ g).

two types of paint system which indicates that the residual contamination is not associated with the paint systems but rather with common absorbing micro features.

3.3 Chemical decontamination process

The chemical decontamination procedure involves a pre-wash, as described above, followed by application of C8 emulsion, an active decontaminant which has been designed to extract extremely toxic contamination from absorbent surfaces into the emulsion where a combination of oxidation and hydrolysis ensures decomposition.

Finally the emulsion is removed by application of steam at 150 °C. The disadvantages of the system are the deleterious effects on some materials and possible problems associated with using chlorinated hydrocarbon solvents.

Figure 4 depicts the desorption of MS from vehicles following decontamination with C8 and steam at 150 °C. The derived values of P_1, level of residual contamination (IC_w) and removal efficiencies (RE) for MS are given in Table 2. RE for both types of painted surface is 95–96% with little difference between the two types of surface. As with the physical removal system the residual contamination is associated with micro design features of the vehicles.

Furthermore, the residual amounts of MS after decontamination with C8 are 4% and 5% for PUP and Alkyd vehicles. If we extrapolate the data depicted in Fig. 2 for summer weathering from these levels, then a level of 3% residual contamination would be reached 0.5 to 1 hour after completion of the decontamination process i.e. 1 to 1.5 hours after contamination. In this regard the C8 process must be regarded as more effective than summer weathering.

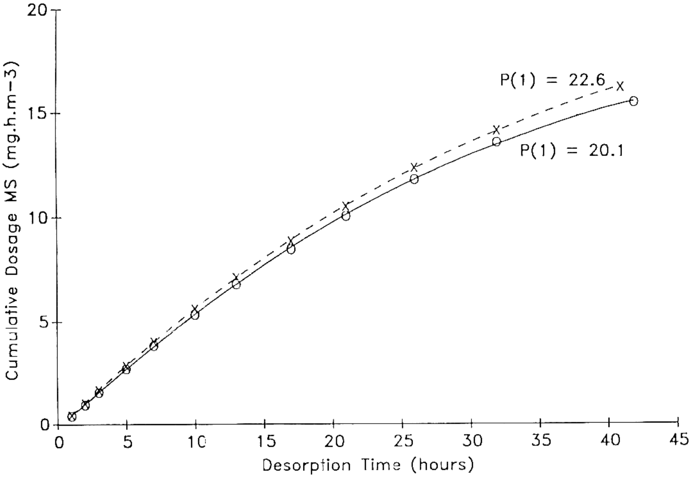

Fig. 4. Cumulative desorption of MS from vehicles after decontamination with C8 emulsion and steam at 150 °C—experimental data and SAAM fits. The solid and dotted lines are the SAAM fits, (○) PUP landrover, and (×) Alkyd landrover.

Decontamination with the C8 process therefore is necessary to eliminate vapour hazard in cooler climates or in winter conditions similar to those in S.E. Australia.

4. Conclusions

With summer weathering a level of 3% residual contamination would be achieved by weathering for 2–4 hours depending on paint type. This would be sufficient to reduce the hazard to below the minimum risk value for most chemicals. Weathering during the winter would not be sufficient to reduce the vapour hazard to minimum risk levels.

The physical removal system, while more effective than winter weathering, also did not reduce the residual vapour hazard to below the minimum risk value.

The C8 emulsion system is much more effective than either the physical removal system or winter weathering in removing contamination. The C8 process also must be regarded as more efficient in combination with weathering than summer weathering alone. It is necessary to eliminate vapour hazard in cooler climates or in winter conditions similar to those in S.E. Australia.

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Letter to the Editor

The assessment of major hazards: The lethal toxicity of chlorine

This is a belated and brief response to the comments on our paper on the crosschecking of our model of the toxicity of chlorine to man [1, 2] from accounts of gas warfare in the First World War [3] by Griffiths and Fryer [4] and by Marshall [5], the delay being occasioned by the retirement of one of us and the extended absence of the other on public business.

At the time when we did our work there was a wide range of estimates of the lethal concentration of chlorine to man. One value which was frequently quoted as the LC_{50} for a 30-minute exposure was 30 ppm. Our own estimate was considerably greater and towards the upper end of the range of quoted values. We had already stated that the value was unlikely to be much higher than that which we had adopted and in our third paper took it as read that the question to be decided was whether the value should be lower.

Our model was cast in the form of a probit equation, which has two parameters, the intercept and the slope. The intercept determines the LC_{50} for a given exposure period. We described our work as a crosscheck on our model. Our concern was in fact to crosscheck the LC_{50}, but we did not make this clear. We agree with Marshall that our work does not give a crosscheck on the slope. For a given LC_{50}, there is a family of probits of different slopes which will give rather similar results in the type of crosscheck with which the paper was concerned.

The chlorine gas clouds behaved as a dense gas. We gave some of the eyewitness evidence for this. We used, however, a passive gas dispersion model, for the reasons given below. There was no doubt in our mind as to this distinction, but the critiques indicate that it seems to have caused some misunderstanding.

Our reasons for using a passive gas dispersion model were as follows. One was that there was no one clearly preferred dense gas dispersion model and we wished to avoid getting into the question of the merits of various models. Another was that the dense gas dispersion models did not appear to have been validated for infinite line sources. Another was that a passive gas dispersion model was expected to give a lower bound to the gas concentration so that the survivals would be for the concentrations estimated or *higher*. We half expected that others would check our results with a dense gas dispersion model and are glad that this has been done.

The results obtained by Griffiths and Fryer indicate, with the exception considered below, that, as expected, the gas concentrations given by the dense gas dispersion model are higher than those given by the passive gas dispersion model. This provides support for a higher lethal concentration.

The exception is the conditions where the top of the gas cloud is so low that it is near head height. Here Griffiths and Fryer's results for their first scenario, that with the lowest cloud height, show that the height of the gas cloud is below head height, taken as 1.7 m, as far as about 160 m from the source. They also quote results of a further run in which tuning of the inputs extends the distance at which the cloud remains below head height to 200–250 m. Further, these authors draw attention to the fact that in the Thorney Island and Maplin Sands trials there were considerable fluctuations in concentration over a vertical extent of about 2 m from the ground, quoting particularly results obtained at 100 m from the source.

We agree that this feature of a cloud near head height should be taken into account. At Hill 60 the men stood fast. The proportion exposed at distances of less than 200 m was taken as 13% and at 200 m as 25%. If the gas cloud was below head height to just beyond this latter distance, men at distances of 200 m or less would have been exposed to concentrations lower, and those at higher distances to concentrations higher, than we estimated. At Langemarck 15% of the men were taken as being at distances of less than 200 m and 50% at 200 m. Again for a gas cloud reaching head height just beyond 200 m, the effect would be to decrease the concentration at less than 200 m and to increase it beyond. In this case we believe that most of the men fled. Our results showed that an appreciable proportion of the toxic load was experienced at distances greater than 200 m.

With regard to a cloud near head height, we conclude that (a) the effect does introduce greater uncertainty into the interpretation of events, but that (b) on what we regard as the most probable scenarios the lower concentrations near the source are largely counterbalanced by the higher concentrations further from it.

In describing the gas attacks, we gave various quotations, and some paraphrases, trying to give as complete an account as we could, but did not intend thereby to endorse all the material.

On details of the Langemarck attack, we will mention just five: (a) the numbers exposed, (b) the state of the trenches, (c) the behaviour of the gas cloud, (d) the degree of flight and (e) the level of physical activity. Our estimates of the numbers exposed were based on figures supplied by the Army Historical Branch (AHB) [6] for the numbers in the front line trenches. This source also quotes the following concerning the Canadian dispositions: "On the 13th Battalion's front, 3 of its 4 companies were in the front line. Two platoons were in support positions 700 yards behind." The rest of the fourth company were further back still. In other words, at this stage of the war it seems to have been practice to put the majority of men in the forward area actually in the front line.

The trenches appear to have been rudimentary. The AHB give the following quotation concerning the state of trenches taken over by the Canadians at this time: "The front line consisted of unconnected lengths of untraversed trench usually but 2 ft deep.... cluttered with frail shelters. Apart from these the defensive works were four groups of shelter trenches for supporting platoons between 300 and 700 yards behind the front line." An account by McWilliams and Steel [7], which is concerned primarily with the Canadians, who had just taken over on the French right, and which we were not aware of at the time of writing, quotes to the same effect. We took it as read that the gas, being dense, would fill the trenches.

The gas cloud appears to have left part of Langemarck itself unaffected. The Algerians there put up a spirited resistance. Our reference to the cloud lifting at this point was simply a paraphrase of the German accounts. We noted it, but it plays no part in our treatment. Marshall draws attention to the fact that in a gas attack there were sometimes gaps in the cloud. The aerial photograph which he gives of an unidentified but later gas attack shows gaps in the cloud originating in gaps in the line source itself. Some such effect combined with topographical features seems a sufficient explanation.

On the question of whether the men held fast and were gassed in the trenches or fled, Marshall's arguments are essentially *a priori*. We quoted various eyewitness accounts to the effect that there was large-scale flight. Further evidence is given by McWilliams and Steel [7]. In addition to the sources which we quoted, they give accounts from some six additional witnesses, five of them Canadians, each with a separate reference, to the effect that men fled in large numbers.

In any event, our interest was primarily in the survivors and the degree of exposure which they suffered. We described a scenario in which men were exposed to a toxic load by retreating through the gas cloud. Despite this exposure a large and known number survived and were taken prisoner by the Germans. Even if our estimate of the number who survived and reached the Allied 'lines' is too high, the overall picture is of a large number of survivors despite exposure to high concentrations.

Our model of chlorine toxicity includes a factor for the level of physical activity. This factor is part of our original model and is based on the experimental relation between levels of activity and inhalation rate; it is not a value assumed in order to fit the gas warfare case. In a given case, however, it is necessary to decide what level of activity is to be assumed. We assumed a level of exertion slightly greater than unhurried walking, to allow for a degree of panic, and believe this is about right. As we stated, we initially assumed a higher level of activity.

With regard to the Wulverghem attack, there is doubt as to whether the release was one of chlorine only or of chlorine/phosgene mixture. We gave an analysis assuming it was chlorine only, but in view of the doubt about the gas and the further complicating factor that by this stage troops had respirators, we stated that this attack gave less information. We should perhaps have made it clearer that our conclusions were not based on this case.

Marshall also makes a number of points concerning the problems of determining injury relations in general and the assumptions underlying probits in particular. We agree with many of these points, but will not discuss them here. Suffice it to say that the difficulties in obtaining injury relations and the possibilities of their misuse are not sufficient reasons for abandoning the attempt to derive them.

The point of our paper was to try to determine whether there is any clue from chlorine gas attacks as to whether the lethal concentration of chlorine is towards the upper or lower end of the range of estimates then current. We said no more than that we regarded our preferred reconstruction, which accorded with our model of toxicity, as more probable than alternative ones. We have discussed above some of the principal criticisms and conclude that at least the thrust of the points made is not in the direction of a lower lethal concentration. The critiques made suggest, however, that further work of this nature would be unlikely to result in a consensus view.

F.P. LEES
R.M.J. WITHERS

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Book Reviews

Air Monitoring. Part 1: Contamination Assessment (19 min), *Part 2: Direct Reading Instrument* (27 min), by L. Detrick, Duxbury, MA distributed by Emergency Films, Plymouth, MA, $495 (two video tapes).

Recently a local chemical plant had an accident spewing semireacted chemicals into the environment. Thinking that "emergency" did not require Fire Department notification, they began cleaning on their own with the help of a cleanup firm. When the fire chief arrived several hours after the spill, he found a hot (contaminated) zone delineated, but no one had monitored the air quality inside the zone. Not a good step. This video cassette addresses that concern.

In the preface to the video film, the accompanying brochure states:

> "Before you take action at a hazardous emergency, you need to determine whether the air is contaminated, and if so, what the risks are. This (tape) is designed to provide training to emergency responders who carry out air sampling activities at hazardous material incidents."

According to the back of the video cassettes, the first video tape, entitled *Contamination Assessment*, provides fundamental lessons about atmospheric sampling under emergency response conditions including:

- Basic emergency response monitoring instruments
- Dangers and risks to the air monitoring team
- Decontamination for monitoring instruments
- When to carry out atmospheric sampling
- Role of personal air sampling devices
- Hazards of contaminated atmosphere
- Size-up for air monitoring
- Air monitoring priorities
- Interpreting readings

Monitoring instruments demonstrated included:

- Combustible gas indicators
- Oxygen meters
- Detector (colorimetric) tubes
- Organic vapor analysis (survey) instruments
- Radiation detectors
- Toxic gas detectors

- Dust monitors
- Personal air samplers, such as used in work place monitoring
- Passive dosimeters

Once the trainer had shown the various types of instruments, he then discussed the need for sampling and the order of use (i.e. radiation first, then other components). Topics discussed were: instrument failure, second instrument verification, relativity of readings (i.e. versus calibration gas) and decontamination (of both personnel and monitoring instruments). A technique used to protect instruments from contamination during sampling, which I had not seen before, was to wrap them in plastic (or plastic bags) with the plastic, of course, not covering the detecting sensor and the admonition to be aware of the potential for some instruments to overheat.

The second video film, entitled *Direct Reacting Instruments*, provides, according to the jacket, fundamental lessons about atmospheric sampling equipment used in emergency response, explaining instrument capabilities, how they work, calibration checks, basic use and interpretation of readings from:

- Combustible gas detectors
- Reaction monitors
- Survey instruments: flame ionization detectors and photoionization detectors
- Detector tubes
- Oxygen meters

As a chemical engineer who has spent much time in the laboratory with analytical equipment, I was keenly interested in the video cassettes' description of how the instruments work. To say the least, I was pleased with their treatment of the topic. Their descriptions were simplistic, but scientifically correct coupled with a good demonstration. I asked our local hazardous material response team to view the tapes. They were quite complimentary, but want to acquire all the instruments shown on the tape. Unfortunately, the Battalion Chief pointed out the cost to obtain all the instruments shown in the video was well beyond the department's budget.

GARY F. BENNETT

Cryogenics Safety Manual, third edition, by British Cryogenics Council, published by Butterworth–Heinemann, Oxford, or 80 Montvale Avenue, Stoneham, MA, 1991, ISBN 0-7506-0225-2, 105 pp., £20/$54.95.

Cryogenic fluids are substances normally manufactured, stored, used, handled or processed at temperatures at or below minus 85 °C (188 K). In practice, they may be produced on the spot from chemicals of known purity, or purchased in large quantities in special liquid containers, pipelines, rail, road or tanker ships. Eleven cryogens are discussed ranging from very light (hydrogen and helium) to xenon.

Chapter 1 presents general safety requirements in making, using, and disposal of cryogenics. Four of the eleven have serious fire/explosion potential (namely, hydrogen, methane, ethane and ethylene), a reality which must be carefully controlled. All eleven have the ability to introduce serious contact hazards of skin and eyes. Safety control procedures for all include treatment of cryogenic burns, anoxia, precautions when working in confined spaces (including rescue and first-aid), appropriate warning signs, toxicity (low except in the case of carbon monoxide), thermal burns from the substances which are flammable, hypothermia, safety devices and instruments, with emergency control, toughness of materials which may be considerably reduced, overpressure and safety work permits.

Chapter 2 covers oxygen, nitrogen and argon. Oxygen is especially critical with respect to ignition or adding intensity to fire, and information such as the list which is provided deserves special attention in this regard. Oil-lubricated compressors in nitrogen or oxygen-service should not be switched to compressing air without a thorough cleaning. It is also noted that ambient air will condense into liquid nitrogen, producing an unexpected hazard.

In Chapter 3, similar detailed treatment is given to natural gas, ethylene and ethane.

Chapter 4 deals with the high energy fuel, hydrogen, which when mixed with air or other oxidizers produces large amounts of energy. Small leaks have been known to ignite spontaneously (reverse of Joule–Thompson).

Chapter 5 on helium and other relatively rare gases, notes the specific properties of these cryogenics in detail.

This is an excellent volume, with many pictures, charts and tables. A well-organized index concludes the work. It is recommended to anyone making, using, shipping or storing any cryogen.

HOWARD H. FAWCETT

Principles of Environmental Toxicology, by S.F. Zakrzewaki, American Chemical Society, Washington, D.C., 1991, 240 pp. (hard cover), ISBN 0-8412-2125-1, $59.95; (paperback) ISBN 0-8412-2170-7, $44.95.

As the title indicates, this book is slanted toward the environment. None the less, the first five chapters do provide the essentials for an elementary course in toxicology. Various pharmacological concepts are reviewed, while metabolism of xenobiotics, factors that influence toxicity, and chemical carcinogenesis and mutagenesis are also covered. Over half of the book is devoted to environmental concerns, including different types of pollution and corresponding controls.

A chapter on occupational toxicology reviews the most frequent types of toxicity noted in working populations. The final chapter discusses the regulatory agencies, with emphasis on the role of the EPA and mention of OSHA. Three appendices are added, two of which really should have been included with the main chapters. The index is fairly comprehensive.

Overall, this appears to be useful, both for a first exposure to toxicology and for study of the interactions between the environment and various types of pollutants.

ELIZABETH K. WEISBURGER

Environmental Risk: Identification and Management, by A.R. Wilson, Lewis Publishers, Chelsea, MI, 1991, ISBN 0-87371-388-5, 400 pp., plus index, $69.95.

The author states in the Introduction that this book will attempt to provide uniform methodology for the identification, measurement and reporting of environmental risks, and furnish definitions of various types of environmental risk assessments, in addition to a management program for control of such risks.

In Part I, The Context of Environmental Risk Management, the topics covered include: basic concepts and terminology; environmental regulations; professional liability and response; risk management policy; an inventory system for environmental risks; control mechanisms; analysis of potential targets and risk sources; cost models and estimation; and management decision-making. Sample worksheets for many situations are given; as well as tables on persistence of various organic compounds, toxicity ratings and checklists for environmental compliance.

Part II, Environmental Risk Investigation, treats the numerous factors that must be examined, including historic land use, sampling and the statistical concepts, geography, topography, hydrology, laboratory selection and certification, and finally, how to combine all these into a risk assessment.

The coverage of all topics is very thorough. Most enlightening is the chapter on regulatory aspects; after reading this volume, one may be reluctant to purchase any piece of land, for the problems go with the purchaser. Overall, this appears to be a valuable addition to the literature of risk assessment.

ELIZABETH K. WEISBURGER

Introduction to Occupational Epidemiology, by S. Hernberg, Lewis Publishers, Chelsea, MI, 1991, ISBN 0-87371-636-1, 223 pp., $59.95.

This introductory book by an occupational physician who is the director of the Finnish Institute of Occupational Health, provides a good background of the subject, definitions of terms, and a discussion on the place of epidemiology in science. There are numerous examples of how various aspects of epidemiological studies are conducted. Exposure–effect and exposure–response relationships are covered briefly, while exposure data and measures of exposure, collection of data, and proxies for exposure data and job-exposure matrices are mentioned in another chapter. Other chapters discuss such topics as validity, precision, biases, specific problems, how to plan a study, and guidelines for interpreting epidemiologic studies.

For a chemist concerned with exposure, the book would have been more useful if exposure effects, dose–response relationships and exposure data for specific compounds, such as carcinogens, had been discussed in one chapter rather than spread over several chapters. The design of the book is somewhat unusual for key phrases are highlighted or set apart from the text. For some, this may be disturbing; for others, it may be useful. None the less, for those needing fundamental information about epidemiologic terms and procedures, this would be a useful book.

ELIZABETH K. WEISBURGER

Chemical Safety Data Sheets: Vol. 4b Toxic Chemicals, Royal Society of Chemistry, Cambridge, UK, 1991, ISBN 0-85186-321-3, 350 pp., £49.95.

This book contains hazard data on 78 toxic substances, from which an informal assessment of the hazard can be made and the necessary control measures devised. Using this book, the hazardous properties of the referred to substances can be identified and quantified.

The book covers (as noted in the title) chemicals whose names begin with the letters M to Z. It starts with magnesium phosphate and ends with zinc phosphate. This volume is just one of a series of books being put out by the Royal Society of Chemistry.

For each chemical the data given include:

- Identifiers-synonym, CAS No., UN No.
- Threshold limit values - from several countries
- Physical properties
- Packaging and transportation-instruction, storage

- Manufacture–how done
- Use
- Hazards-chemical, biological, carcinogenicity, mutagenicity, and reproductive hazards
- First-aid
- Handling and storage
- Disposal
- Fire precautions
- References

GARY F. BENNETT

Successful Management of the Analytical Laboratory, by O.I. Milner, Lewis Publishers, Chelsea, MI, 1992, ISBN 0-87371-438-5, 155 pp. plus index, $39.95.

This slim book is written in an easily read style. Discussed are such obvious topics as the role and function of the analytical laboratory, how to organize and staff the laboratory, the place of employee safety and health programs, sampling, quality performance and control, waste disposal, and training, and continued education. In addition, various aspects of the actual management functions of the laboratory supervisor are covered and illustrated by case reports on how various situations were handled. These chapters emphasize the need for communication with employees. Useful statistical tests are explained, together with information on budgeting and cost control, as well as information management. Most of the material covered in this book would also be valuable for managers of other types of chemical laboratories.

ELIZABETH K. WEISBURGER

Bargaining with Uncertainty: Decision-making in Public Health, Technological Safety, and Environmental Quality, by Merrie G. Klapp, Auburn House, Greenwood Publishing Group, Inc., Westport, CT, 1992, ISBN 0-86569-046-4, 168 pp., $42.95.

In this book, Merrie G. Klapp discusses how changes are brought about in regulatory decisions in public health, technological safety and environmental quality. She examines the power citizens have to challenge these decisions and asserts that scientific uncertainty is their greatest defense. Only when there is a degree of uncertainty in the scientific evidence produced by experts can decisions be overturned. This uncertainty results from a significant range of risk estimates by different scientists based on diverse reasonable assumptions about the data, parameters, models and extrapolations used to calculate the risk. Professor Klapp suggests that regulatory decisions can be changed, but only under certain conditions:

(1) citizens or industrialists must organize a protest against the decision, and

(2) the legislature or courts must take scientific uncertainty into account and intercede to constrain the regulatory agency by shifting the burden of proof of existing harm or safety.

Additionally, through the examining of case studies, Klapp demonstrates that the United States is the exception and not the rule to this use of scientific uncertainty. In Britain and France, scientific uncertainty is kept secret and never used as a bargaining tool in changing decisions. Scientists remain behind the scenes and do not make public the evidence of uncertainties in scientific information. Public reports concerning regulatory decisions are released as undisputed fact.

W. MICHELE SIMMONS and CURTIS C. TRAVIS

Journal of Hazardous Materials, 32 (1992) 125–127
Elsevier Science Publishers B.V., Amsterdam

Announcements

Managing Hazardous Air Pollutants, Second International Conference, July 13–15, 1993, The Capital Hilton, Washington, DC, USA

Aims and Scope

Worldwide focus on clean air issues has intensified tremendously in recent years. Concern over hazardous air pollutants has raised questions about the health and environmental impact of industrial activity, including electric power production, and has motivated nations to develop strategies for managing these substances.

In the United States, the Clean Air Act Amendments of 1990 listed 189 pollutant categories for possible control. This legislation, along with economic, environmental, and political attention worldwide, had led to an upsurge in research aimed at developing understanding about the sources, impacts, and control of hazardous air emissions.

This conference will highlight the state of the art in the management of airborne trace pollutants, focusing on key issues of common interest to utilities, industry, and government. It will cover the following topics:

- What are the sources of pollutants? In particular, what do electric utilities emit?
- Can we accurately measure amissions?
- What health and environmental risks may these substances pose?
- What are the existing and emerging technologies for controlling emissions?

The conference will provide an opportunity for discussion and information exchange among representatives of electric utilities, industry, government agencies, equipment suppliers, consulting firms, and research and academic institutions. The first conference drew people representing 13 nations and succeeded in establishing an ongoing forum for exchange of ideas and technical information.

Who should attend

- Utility managers, engineers, and plant operators
- Environmental scientists, managers, and engineers
- Equipment suppliers
- Consulting engineers and architect/engineers

- Goverment agency managers and staff

Call for papers

Deadline: October 1, 1992

Abstracts should convey in 150 words maximum the essence of the intended paper, indicating clearly the contribution it will make to the subject. Mail abstracts to: Winston Chow, Conference Chairman, EPRI, 3412 Hillview Avenue, Palo Alto, CA 94304, Fax(415)855-2041; or Lori Lehmann, Conference Program Coordinator, Decision Focus, Inc., 650 Castro Street, Suite 300, Mountain View, CA 94041-2055.

Selected papers

Notification: December 1, 1992
Paper due: April 1, 1993

Presenters of selected papers will be notified of acceptance by December 1, 1992. Unless otherwise indicated, the first author listed on the abstract will be presumed to be the presenter. Presentations are limited to 20–30 minutes, followed by a short question-and-answer period. Plan to use only 35-mm slides or viewgraphs (projector, overhead projector, and audiovisual technician will be provided). Speakers must provide a master of their paper by April 1, 1993, so that preprints can be prepared. The lenght should not exceed 15 pages, including illustrations. Certain papers may be selected for the poster session on Tuesday evening, July 13, 1993, in conjunction with an EPRI-hosted reception with exhibits.

Conference topics

General
- Keynote Address
- Regulatory Update, United States
- Legislation/Regulatory Trends, International

Emissions Sources, Measurements, and Quantities
- Data Sources
- Field Measurements
- Stream Compositions
- Chemical Sampling and Analytical Methods
- Data Quality and Accuracy of representation

Atmospheric Fate
- Emission Inventories
- Ambient and Deposition Characterization
- Chemical Transformation

- Simulation Techniques

Health and Environmental Information

- Health Effects Studies, Results, and Interpretation
- Ecological Effects Studies, Results, and Interpretation
- System characterization Models

Risk Analysis

- Exposure Assessment
- Multimedia Pathways
- Dose–Response Formulations
- Uncertainty Analysis
- Risk Analysis Models

Control Strategies and Applicable Technologies

- Strategies for Reducing Pollutant Load
- Available Environmental Control Technologies: Their Capabilities, Limitations, and Applications

Emerging Information, Technologies, and Tools

- Innovative Process Technologies
- New/Improved Modeling Developments
- Novel Approaches for Managing Hazardous Air Pollutants
- Other Innovative Research, Ideas, and R&D Needs

SUBMISSION OF PAPERS

Submission of a manuscript implies that it is not under consideration for publication elsewhere and further that, with the exception of review papers, original work not previously published is being presented.

Papers should be submitted to Dr. G.F. Bennett, Department of Chemical Engineering, University of Toledo, 2801 W. Bancroft Street, Toledo, OH 43606, U.S.A. or Dr. R.E. Britter, Department of Engineering, University of Cambridge, Cambridge CB2 1PZ, Great Britain or Dr. J. Mewis, Department of Chemical Engineering, Katholieke Universiteit Leuven, de Croylaan 46, B-3030 Leuven (Heverlee), Belgium. Authors in the Far East should submit papers to Dr. T. Yoshida, Chemical Engineering Laboratory, Department of Mechanical Engineering, Faculty of Engineering, Hosei University, 7-2 Kajino-cho 3-chome, Koganei-shi, Tokyo 184, Japan.

MANUSCRIPT PREPARATION

Three copies of the manuscript should be submitted in double-spaced typing on pages of uniform size with a wide margin on the left. The top copy should bear the name and the full postal address of the person to whom the proofs are to be sent. A summary of 100–200 words is required.

References should be numbered consecutively throughout the text and collected together in a reference list at the end of the paper. Journal titles should be abbreviated. The abbreviated title should be followed by the volume number, year (in parentheses), and page number.

ILLUSTRATIONS

Line drawings should be in a form suitable for reproduction, drawn in Indian ink on drawing paper. They should preferably all require the same degree of reduction, and should be submitted on paper of the same size as, or smaller than, the main text, to prevent damage in transit. Photographs should be submitted as clear black-and-white prints on glossy paper. Each illustration must be clearly numbered. Colour illustrations can be reproduced at the author's expense.

Legends to the illustrations must be submitted in a separate list.

All tables and illustrations should be numbered consecutively and separately throughout the paper.

LANGUAGE

The principal language of the journal is English, but papers in French and German will be published.

PROOFS

Authors will receive page proofs, which they are requested to correct and return as soon as possible. No new material may be inserted in the text at the time of proofreading.

REPRINTS

A total of 50 reprints of each paper will be supplied free of charge to the principal author. Additional copies can be ordered at prices shown on the reprint order form which accompanies the proofs.

A pamphlet containing detailed instructions on the preparation of manuscripts for JOURNAL OF HAZARDOUS MATERIALS may be obtained from the publishers.

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