



TECHNICAL REPORT 1

**A METHOD FOR ESTIMATING THE
OFF-SITE RISKS FROM BULK
STORAGE OF LIQUEFIED OXYGEN**

REVISION 2: 2018

British Compressed Gases Association

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PREFACE

The British Compressed Gases Association (BCGA) was established in 1971, formed out of the British Acetylene Association, which existed since 1901. BCGA members include gas producers, suppliers of gas handling equipment and users operating in the compressed gas field.

The main objectives of the Association are to further technology, to enhance safe practice, and to prioritise environmental protection in the supply and use of industrial gases, and we produce a host of publications to this end. BCGA also provides advice and makes representations on behalf of its Members to regulatory bodies, including the UK Government.

Policy is determined by a Council elected from Member Companies, with detailed technical studies being undertaken by a Technical Committee and its specialist Sub-Committees appointed for this purpose.

BCGA makes strenuous efforts to ensure the accuracy and current relevance of its publications, which are intended for use by technically competent persons. However this does not remove the need for technical and managerial judgement in practical situations. Nor do they confer any immunity or exemption from relevant legal requirements, including by-laws.

For the assistance of users, references are given, either in the text or Appendices, to publications such as British, European and International Standards and Codes of Practice, and current legislation that may be applicable but no representation or warranty can be given that these references are complete or current.

BCGA publications are reviewed, and revised if necessary, at five-yearly intervals, or sooner where the need is recognised. Readers are advised to check the Association's website to ensure that the copy in their possession is the current version.

This document has been prepared by BCGA Technical Sub-Committee 6. This document replaces BCGA Technical Report 1, Revision 1: 2013. It was approved for publication at BCGA Technical Committee 158. This document was first published on 08/10/2018. For comments on this document contact the Association via the website www.bcgaco.uk.

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* Throughout this publication the numbers in brackets refer to references in Section 7. Documents referenced are the edition current at the time of publication, unless otherwise stated.

FOREWORD

This revision of Technical Report 1 was prepared under the guidance of BCGA TSC6.

No technical changes have been introduced in this revision. The reason for the revision was to update the structure and formatting of the document to align this document with other BCGA publications.

TERMINOLOGY AND DEFINITIONS

May	Indicates an option available to the user of this Technical Report.
Shall	Indicates a mandatory requirement for compliance with this Technical Report and may also indicate a mandatory requirement within UK law.
Should	Indicates a preferred requirement but is not mandatory for compliance with this Technical Report.

TECHNICAL REPORT 1

A METHOD FOR ESTIMATING THE OFF-SITE RISKS FROM BULK STORAGE OF LIQUEFIED OXYGEN

A REPORT BY THE BCGA / HSE / SRD WORKING GROUP.

SUMMARY

This document summarises the conclusions reached by a joint British Compressed Gases Association (BCGA) / Health and Safety Executive (HSE) working group. It describes:

- the hazards from exposure to oxygen enriched air;
- if so exposed, the chance of being seriously injured;
- a method for determining the evaporation rate of liquid oxygen and the dispersion of oxygen vapour in the atmosphere; and
- the chance of a large spill occurring.

On the basis of the data included in this document it should be possible for site operators to produce an assessment of the offsite risks from a specific storage facility for liquid oxygen. The basis for the more relevant technical assumptions are detailed in the appendices.

1. INTRODUCTION

Oxygen is a basic constituent of air (about 21 % v/v) and is essential for supporting animal life. It is also a necessary component for all normal combustion processes and the intensity of a flame can be controlled by the proportion of oxygen mixed with fuel.

Liquefied oxygen (LOX) is commonly obtained by the liquefaction of air and the subsequent distillation of its components.

LOX is a cold liquid with a specific gravity of 1.2 which, if released to the atmosphere, boils to form a cold oxygen vapour at about -180°C . LOX is maintained in its liquid form by evaporative cooling at a temperature consistent with the storage vessel operating pressure, or it may be maintained temporarily as a liquid through the use of thermal insulation.

2. THE CONSEQUENCES OF OXYGEN ENRICHMENT

For the purposes of general risk estimation it is only those instances where oxygen is inadvertently released into the atmosphere which are considered, i.e. the cases of special test chambers operating with between 50 % to 100 % oxygen, and those commonly recognised hazards of working in confined spaces, are not included. Thus, it is the consequences of enriching the existing oxygen in the open air that are described here. Other considerations

are applicable for onsite and working conditions, and the conclusions of this Report are not intended to be applied in these circumstances.

2.1 Increased intensity fires

The way in which common materials burn in the air is well known, but when the oxygen concentration is increased materials will burn more rapidly. The burning rate, ease of ignition, and fire spread exhibit a non-linear rate of increase with increasing oxygen concentration. Some materials which do not readily combust in air, may combust vigorously at elevated oxygen levels. In general, these effects are slight at 25 % oxygen, significant at 40 % oxygen, and reach their maximum at about 50 % oxygen. Above this level the increases in effect due to further enrichment are hardly detectable. Thus, increased oxygen concentration is only a secondary hazard as there also needs to be a fuel supply and a source of ignition before the hazard is realised.

For the general public the fuel most likely to be sufficiently close to them to cause injury is their flammable clothing. Other common materials, e.g. curtains and upholstery, will also exhibit enhanced burning characteristics in oxygen enriched atmospheres. However, in general it is possible for individuals to remove themselves from areas of immediate danger. This can be seen from a number of incidents which have been reported (1). Thus for this assessment method it is only those persons who have their clothing ignited who are considered to be likely to be injured.

This fire hazard exists in normal day-to-day life, and it is only that proportion which is directly attributable to the increased effects from oxygen enrichment that are assessed.

The most frequent sources of ignition which cause clothing fires resulting in personal injury are smoking materials. The ability of people to react to either prevent the ignition source setting their clothing alight, or their ability to quickly extinguish the fire before it spreads significantly, will depend not only on the speed of their own reflex actions, but also on the degree to which the burning characteristics have been enhanced by the increased oxygen concentration.

Details of the relevant burning rate, reaction times, etc., and the supporting evidence are given in Appendices 1 and 3.

2.2 Physiological effects

Sustained breathing of pure oxygen at ambient temperatures for several hours can produce mild adverse effects but is not injurious, besides which such conditions do not result from the inadvertent spillage of LOX.

Oxygen vapour evaporating from a pool of LOX will be very cold, about $-183\text{ }^{\circ}\text{C}$, and as it mixes with the surrounding air the enriched cloud gradually warms up, disperses and the “oxygen enrichment” is diluted.

This cold cloud of enriched air could envelop people who were not expecting to be exposed to “cold” and were not suitably protected by clothing. There could be injury from the effects of cold if the exposed person did not, or was unable to, remove themselves from the cold oxygen enriched atmosphere. Under normal United Kingdom weather conditions the cooling of the ambient air changes the relative humidity, and condensing water mist can be seen; this provides an obvious indication

of the area to avoid. The speed of the wind (or the rate of ventilation) has an effect upon the rate of cooling of the exposed person, and the correlation of “effective temperature” with wind speed and actual temperature has been used to determine the hazard. Details are given in Appendix 2.

Cold clouds which have an “effective temperature” of -40 °C can only be experienced within a cloud having a significant fire hazard due to oxygen concentrations of 40 % or greater. This can be seen in the details in the Example Results, Appendix 5.

3. THE CHANCE OF BEING INJURED

From the various enhanced burning rates, fire spread in oxygen enriched atmospheres, and the human reaction times, detailed in Appendix 3, the chance of being injured has been estimated as shown in Table 1.

1.	Oxygen concentration (%)	25	30	35	40	
2.	Ignition time for typical clothing (seconds)	20	10	7.5	0	
3.	% of persons unable to prevent ignition of clothing.	5	75	90	100	
4.	Proportion of ignitions causing fatal or serious injury.	0.1	0.2	0.44	0.98	
5.	Line 3 x Line 4 % of persons injured.	0.5	15	40	98	
6.	Probability that ignition source exists (%)	a) At work	2	2	2	2
		b) Away from work	4	4	4	4
7.	Probability of fatal or serious injury (%)	a) At work	0.01	0.3	0.8	2.0
		b) Away from work	0.02	0.6	1.6	3.9

Table 1: Estimation of the chance of being injured.

NOTES:

1. Line 2 is an estimate of the time taken to ignite typical clothing, and each value is about 2 seconds faster than known ignition times for new dry denim overalls. For details refer to Appendix 1.
2. Line 3 is an estimate of the inability of persons to prevent the ignition. It is presumed that 5 % of the population cannot react within 20 seconds, and that none of the population react faster than 5 seconds. Refer to Appendix 3.
3. Line 4 is an estimate of the proportion of those ignitions which do occur, which then result in fatal or serious injury. This too is dependent on the enhanced burning rate and the individuals reaction times. For details refer to Appendix 3.
4. Line 5 is the estimate of the proportion of a population who is exposed to:
 - (i) oxygen enriched air, and
 - (ii) an ignition source in contact with their clothing – would then be injured.

5. Line 6 is an enhanced estimate of the number of persons who may be smoking at any one instance. This is deliberately over-estimated to compensate for not specifying other sources of ignition. Refer to Appendix 3.

6. Line 7 is the overall estimate of the instantaneous probability of being fatally or seriously injured if exposed to an oxygen enriched atmosphere.

It is recognised that smoking a cigarette has a definite duration after which the exposure to the increased fire hazard is removed and, therefore, the total number of fatal or serious injuries will need to take into account the duration of the exposure to the oxygen enriched atmosphere. Also the delaying effect of the enriched atmosphere penetrating into a building, the reduction in ignition sources resulting from warnings sent out as a result of an emergency plan and the operation of emergency isolation valves need to be considered. For these purposes it is assumed that after 30 minutes it would be practicable to have issued sufficient warnings that further ignition sources were not generated and there would not be any further increase in casualties; and that for domestic dwellings having an air change rate of 2 air changes / hour the internal oxygen concentration would only reach 30 % after 30 minutes continuous exposure to 35 % oxygen outside the building. The various factors are given in detail in Appendix 3.

4. THE DISPERSION OF OXYGEN VAPOUR

For the extent of the hazard range to be estimated it is necessary to postulate the size and type of spillage of LOX that could occur. For general risk assessment purposes to establish the hazard to persons outside the plant area it is usual to ignore the more minor releases which have limited hazard ranges.

Total failure of the largest liquid line connected to the storage vessel, or total failure of integrity of the storage vessel, can be used to calculate the release rate of LOX. Then depending on the individual plant design the evaporation rate can be estimated taking into account bunding, ground conditions, and process storage conditions. For this purpose HSE use the SPILL programme developed by SRD (2).

Once this 'source term' has been established it is then possible to estimate the dispersion of the oxygen vapour in the atmosphere. For this type of assessment the distances to oxygen concentrations of 40 %, 35 %, 30 % and 25 % and temperatures of -40 °C and 0 °C for the dispersing mixture are considered relevant, and are estimated for typical and least favourable weather conditions. For this purpose HSE use the computer models developed by SRD for dense gas dispersion; DENZ (3) for instantaneous releases, and CRUNCH (4) for continuous releases.

5. THE PROBABILITY OF THE FAILURE EVENT

When considering the estimated hazard ranges, it is necessary to also consider the probability of the failure event which causes these hazards. As previously described the more frequent small leakages with only short, and in general on-site hazard ranges are not assessed, only the more major sources of leakage being considered. The overall probability

of serious leakage will depend upon specific features of the installation, but the following values are indicative of the generic integrity of the equipment.

Serious leakage from pipe work failure has generally been found to occur with a probability of about 1×10^{-5} per year per section, e.g. say a 3 m (10 feet) length, and less serious leakage from each flange connection at about 2.5×10^{-3} per year per flange (5).

Storage vessels are fabricated in one of two ways, either on site, or in a fabrication shop.

The basic design of LOX vessels is to have an inner tank constructed from a material suitable for cryogenic temperatures inside an outer tank of carbon steel with insulation, and/or a vacuum, in the interspace. The probability of serious failure of pressure vessels generally has historically been found in *A survey of defects in pressure vessels built to high standards of construction* (6) to be about 2.4×10^{-3} per vessel year, and for vessels built to high standards about 4×10^{-5} per vessel year. Provided that it can be shown that shop fabricated LOX vessels have been designed, constructed and maintained to the same high standards, then a failure probability of the order of 10^{-5} per vessel year may be used if only failure modes appropriate to LOX vessels are considered.

There are not sufficient of the larger site fabricated vessels to establish a realistic historical failure probability. If it is demonstrated that the vessels are designed, fabricated, inspected and maintained to high standards, then it is considered that the failure rate may be lower than 10^{-5} per vessel year. Thus for risk assessment purposes, the storage vessel should be verified for design, construction and maintenance, i.e. maximum and minimum pressure and temperature and maximum load that the supports could safely sustain, etc., as described in Appendix 4. Provided that the vessel is kept within these limits by adequate operational controls or safety devices, then the probability of vessel failure is assessed to be so low that it is not necessary to estimate the consequences of vessel failure in great depth.

6. EXAMPLES OF RELEASES AND THEIR RANGE OF HAZARD

The following examples have been chosen as being typical of the larger size of the more common range of installation.

- i) Failure of 50 mm (2 inch) diameter NB pipe under 15 bar pressure.
- ii) Failure of 135 tonne shop fabricated vessel.
- iii) Failure of a 150 mm (6 inch) diameter NB pipe under 1.25 bar pressure with the leakage into a concrete bunded area.
- iv) Failure of a 150 mm (6 inch) diameter NB pipe under 1.25 bar pressure with no containment of the leakage.

6.1 Pipe – diameter 50 mm

This is typical of pipework sizes associated with Vacuum Insulated Evaporators (VIE) which can operate at pressures of 15 bar gauge.

Using a “flashing liquid” fluid flow formula the release rate from a full bore pipe failure has been calculated to be 32 kg/s which could persist for other 30 minutes dependent upon the initial vessel inventory.

As a result of flashing and pressurised release, it is estimated that 17 kg/s will immediately contribute to a vapour cloud, the remaining 15 kg/s is liquid which falls to the ground and evaporates.

Spill calculations indicate that within 30 seconds the evaporation rate is equal to the liquid fallout rate and, therefore, the oxygen cloud source can be considered to be a continuous release at 32 kg/s.

Because there is turbulence associated with pressurised releases an estimate of the initial entrainment of air into the cloud has been made which results in the initial cloud having an oxygen concentration less than 40 %.

The distances for dispersion to lower concentrations are given in Table 4, CRUNCH calculations, refer to Section 6.4.

6.2 Storage vessel – 135 tonne

This is typical of the larger shop fabricated vessel in which LOX is kept at pressures up to 15 bar gauge.

If the contents are suddenly, almost instantaneously, released there would be flash vaporisation and a pressure-driven expansion phase during which a large cloud would form.

The violence of this pressure-driven expansion will entrain air into the cloud which would result in an initial dilution before the cloud was further diluted during dispersion.

Various values can be adduced for the “entrainment factor” and three examples have been selected for a sensitivity analysis (refer to Appendix 5 for further details).

It would appear that there is not a significant difference between the distances to lower concentrations calculated by DENZ for the various different initial conditions. Refer to Table 2.

Air entrainment factor	% Oxygen concentration in cloud	
	Peak	Average
x 5	81.0	32.8
x 10	53.5	27.3
x 15.6	42.4	25.0

Table 2: DENZ calculations (based on Gaussian distribution).

The distances calculated by DENZ for a 135 tonne release for peak oxygen concentrations of 30 % and 25 % under Category D weather conditions and 6 m/s wind speed are shown in Table 3:

Air entrainment factor	Distance to peak oxygen concentrations of:	
	30 %	25 %
x 5	550 m	700 m
x 10	545 m	720 m
x 15.6	487 m	724 m

Table 3: DENZ calculations – 135 tonne release.

6.3 Pipe – diameter 150 mm

This is typical of pipework sizes associated with the large capacity, low pressure storage vessels. With a typical hydrostatic head of 11 m LOX liquid flow through a 150 mm (6 inch) diameter orifice has been calculated to be 245 kg/s initially. This decreases as the hydrostatic head decreases, and for typical stock levels of 1000 tonne releases could continue for over two hours if not controlled. Using the SPILL programme the evaporation of oxygen has been calculated for the total release of 1000 tonne.

It is found that both banded and unbanded releases have an initial high rate of vaporisation during the first 60 seconds which can be treated as a 13 tonne instantaneous release for dispersion purposes.

During the first 15 minutes the subsequent evaporation rates can be considered to be steady at 40 kg/s for the banded case and 240 kg/s for the unbanded case.

The distances calculated by DENZ for a 13 tonne release for X10 air entrainment under Category D weather conditions, and 6 m/s wind speed to peak oxygen concentrations of 40 %, 35 % and 25 % are 150 m, 190 m and 310 m respectively.

The distances to various concentrations from the continuous releases are given in Table 4, CRUNCH calculations, refer to Section 6.4.

6.4 CRUNCH calculations

Release Rate kg/s	Distance in metres to:				
	40 %	30 %	25 %	-40 °C	0 °C
240	82	96	120	62	100
40	28	32	40	21	30
32	- *	6	47 *	- *	30

Table 4: CRUNCH calculations.

For Category D weather conditions and 6 m/second windspeed the CRUNCH programme calculates the dispersion distance, as shown in Table 4.

* The 32 kg/s release includes air entrained which dilutes the initial release to less than 40 % and above -40 °C. The increased mass requires further distances for dispersion to lower concentrations than the undiluted 40 kg/s release.

7. REFERENCES

Document Number	Title
1. ORDIN, Paul M.	Mishaps with oxygen in NASA operations. NASA, Lewis Research Center. November 1971.
2. SHAW, P. and BRISCOE, F.	Evaporation from spills of hazardous liquids on land and water. Safety and Reliability Directorate Report SRD R 100, May 1978.
3. FRYER, L.S. and KAISER, G.D.	DENZ – A computer code for the calculation of the dispersion of dense toxic or explosive gases in the atmosphere. Safety and Reliability Directorate Report SRD R 152, July 1979.
4. JAGGER, S.F.	Development of CRUNCH: A dispersion model for continuous releases of denser-than-air vapour into the atmosphere. Safety and Reliability Directorate Report SRD R 229, January 1983.
5. United States Nuclear Regulatory Commission	USNRC; Reactor safety study. Report WASH – 1400 (NUREG – 75/ 014) Appendix III, Table 111.2.1. October 1975.
6. SMITH, T.A. and WARWICK, W.A.	Survey of defects in pressure vessels built to high standards of construction. Trans of ASME, PVP-PB-032, December 1978. Also published as “A survey of defects in pressure vessels in the UK for the period 1962 to 1978 and its relevance to nuclear primary circuits”. Safety and Reliability Directorate Report SRD R 203, December 1981.

Further information can be obtained from:

UK Legislation	www.legislation.gov.uk
Health and Safety Executive (HSE)	www.hse.gov.uk
British Compressed Gases Association (BCGA)	www.bcg.co.uk

THE EFFECT OF OXYGEN ENRICHMENT ON THE BURNING CHARACTERISTICS OF CLOTH MATERIALS

Various papers on burning characteristics (refer to list of references) were reviewed and particular attention was paid to those dealing with the properties of clothing or cloth materials. Whilst it is recognised that oxygen enrichment will affect the burning characteristics of all flammable (and some otherwise non-flammable) substances it is considered that clothing is the only “fuel” which, being continuously in such close proximity to people, would enable a measurable change of hazard to be determined.

There were several references specifically related to clothing, and some of the work by various military establishments had been initiated following incidents. Whilst recognising that different fabrics have different properties it has been possible to utilise various aspects of each work to establish an average value or trend for “clothing” for:

- i) Ease of ignition.
- ii) Rate of burning.
- iii) Surface spread of fire.

Ease of ignition

Figure A.1.1 illustrates the variation for the complete ignition of different types of clothing materials by either a lighted match or a burning cigarette.

Figure A.1.2 illustrates the variation in the time taken for an electric igniter to produce flame on a fabric. The ignition time values for curve “b” are not typical for ambient conditions as the experiments were conducted at pressures below 1 atmosphere to simulate high altitudes. However, the values are comparable with ignition times determined at various pressures in pure oxygen, Figure A.1.3, and the shape reinforces the trend indicated in curve “a”.

The values in Table A1.1 have been selected to be representative of ignition times at various oxygen concentrations:

21 % (25 %)	20 seconds
30 %	10 seconds
35 %	7.5 seconds
40 %	5 seconds

Table A1.1

Whilst these ignition times are smaller than those illustrated they have been selected as being realistic values which are also convenient for later analysis.

Rate of burning

The time to 50 % destruction of overalls is illustrated in Figure A.1.4 and this indicates a significant increase in rate of burning with increased oxygen concentration. Other work illustrated in Figure A.1.5 shows a different relationship between 25 % and 35 % oxygen concentrations. However, a marked increase is indicated at higher oxygen concentrations. It has not been necessary for later analysis to ascribe any absolute values to this property. However, it is a significant trend and relative values have been estimated and are displayed in Table A1.2.

21 % (25 %)	1 unit
30 %	1.25 units
35 %	1.75 units
40 %	3 units

Table A1.2

Surface spread of flame

One of the more dramatic effects of combustion of cloth in oxygen enriched atmospheres is the very rapid spread of fire by a “flash” propagating through the fine threads of the surface nap. At higher oxygen concentrations this flash fire is also capable of igniting the main bulk of the material. This effect is illustrated in Figure A.1.6. This property is relevant to the later analysis of injuries, but it has not been necessary for it to be quantified.

REFERENCES

Document Number	Title
1. JOHNSON, J.E. and WOODS, F.J.	Flammability in unusual atmospheres. Part 1, Preliminary studies of materials in hyperbaric atmospheres containing oxygen, nitrogen, and/or helium. NRL Report 6470 (AD 644 556). October 1996.
2. COLEMAN, E.H.	Effects of compressed and oxygen-enriched air on the flammability of fabrics. British Welding Journal, September 1959.
3. HILADO, Carlos J.	Flammability handbook for plastics (2 nd Edition). Technomic Publishing Co. 1974
4. DENISON, D.M. <i>et al.</i>	Problem of fire in oxygen-rich surroundings. Nature Volume 218, 22 nd June 1968.

5. WILK, I.J. Ranges due to increased flammability of material in oxygen enriched atmospheres. Journal of Chemical Education, Volume 45, No. 7, July 1968.
6. BALDWIN, R. Flame merging in multiple fires. Combustion and flame. Volume 12, August 1968.
7. THOMAS, P.H. On the development of urban fires from multiple ignitions. Fire research station note No. 699, February 1968.
8. National Fire Protection Association No. 53M USA. Manual on fire hazards in oxygen enriched atmospheres. 1974.
9. BALDWIN, W.J. and HOLIBER, J.A. Too much oxygen. National Safety News, September 1957.
10. DENISON, D.M. and TONKINS, W.I. Further studies upon the human aspects of fire in artificial gas environments. RAF Institute of Aviation Medicine, Ministry of Defence, September 1967.
11. CHIANTA, M.A. and STOLL, A.M. Effects of oxygen-enriched atmospheres on the burning rate of fabrics, Phase 2. US Naval Air Development Centre, Johnsville, June 1964.
12. DENISON, D.M., ERNSING J. and CRESSWELL A.W. The fire risks to man of oxygen rich gas environments. RAF Institute of Aviation Medicine, Ministry of Defence, 1965.
13. DENISON, D.M. An assessment of the fire risks of the oxygen enrichment experiments. RAF Institute of Aviation Medicine, Ministry of Defence, January 1965

Figure A.1.1

DELAY IN COMPLETE IGNITION OF VARIOUS MATERIALS (9)

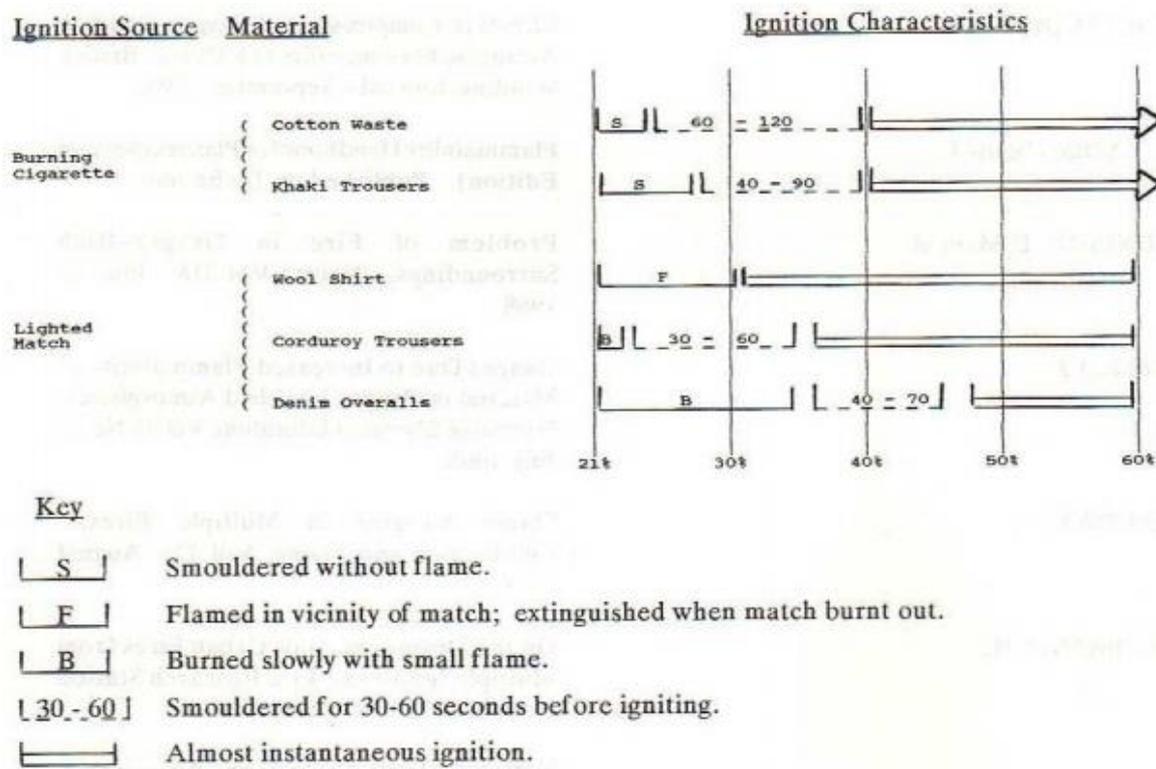


Figure A.1.2

TIME TO IGNITE CERTAIN MATERIALS (10) (11)

- a) Figure 4 from Reference 10.
New dry denim overalls.
- b) Figure 2 from Reference 11.
5 oz/yd cotton at 4.6 psi absolute.

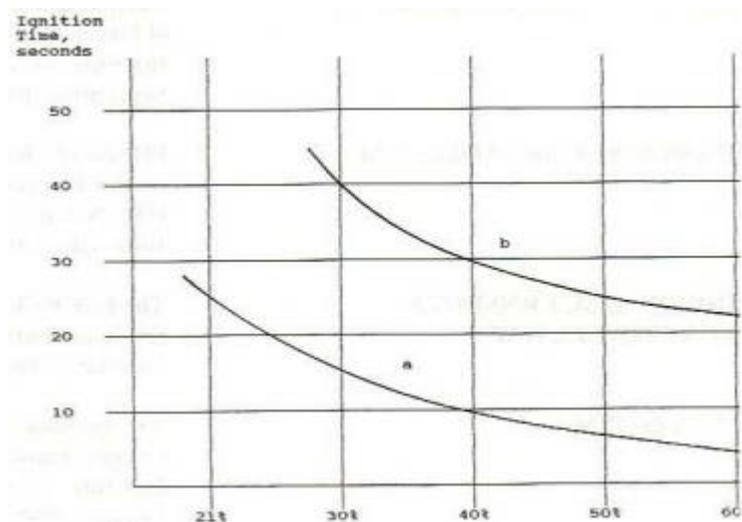


Figure A.1.3

THE RELATIONSHIP BETWEEN IGNITION TIME AND OXYGEN PRESSURE FOR NEW OVERALLS IN PURE OXYGEN ATMOSPHERES (10).

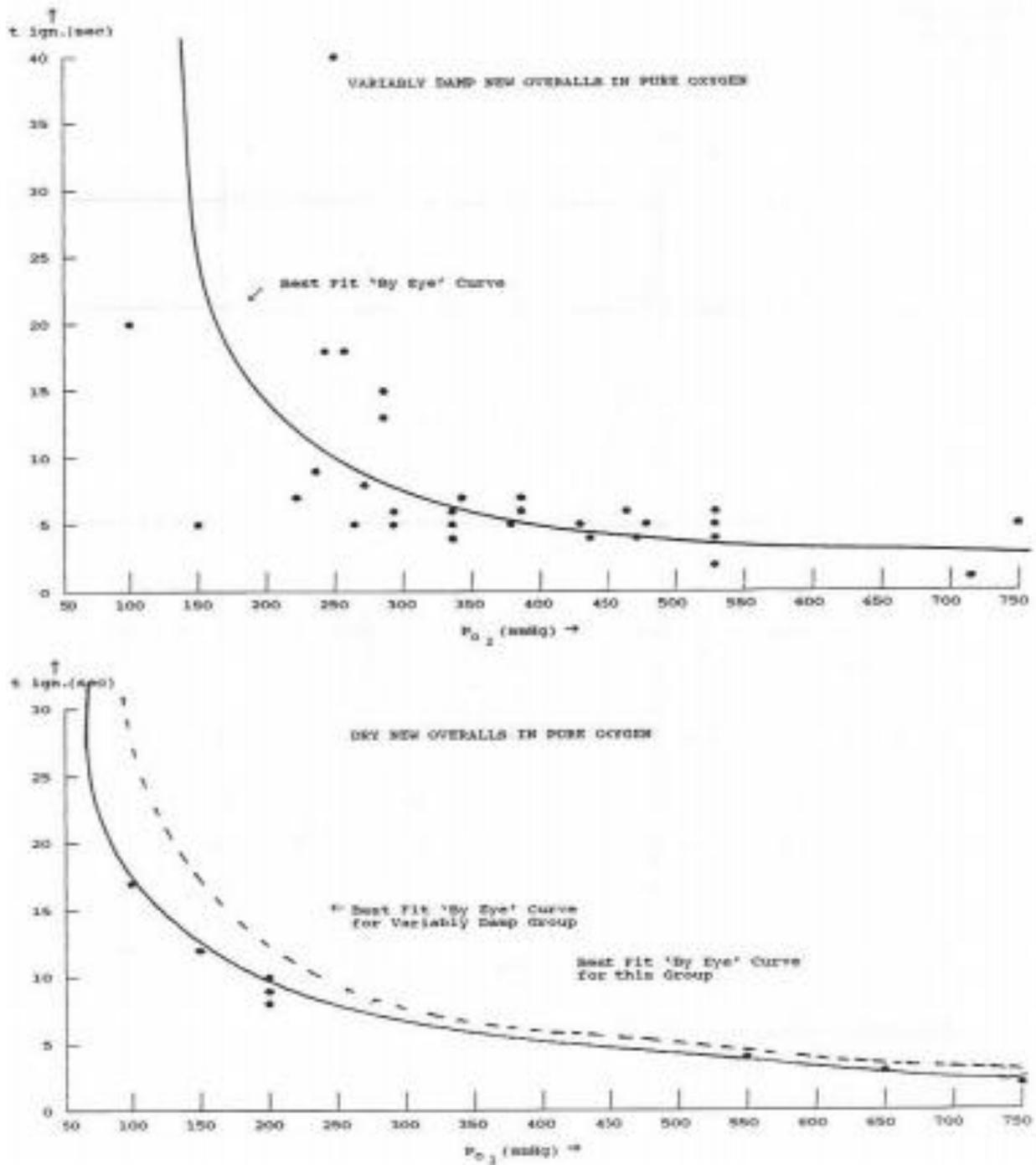
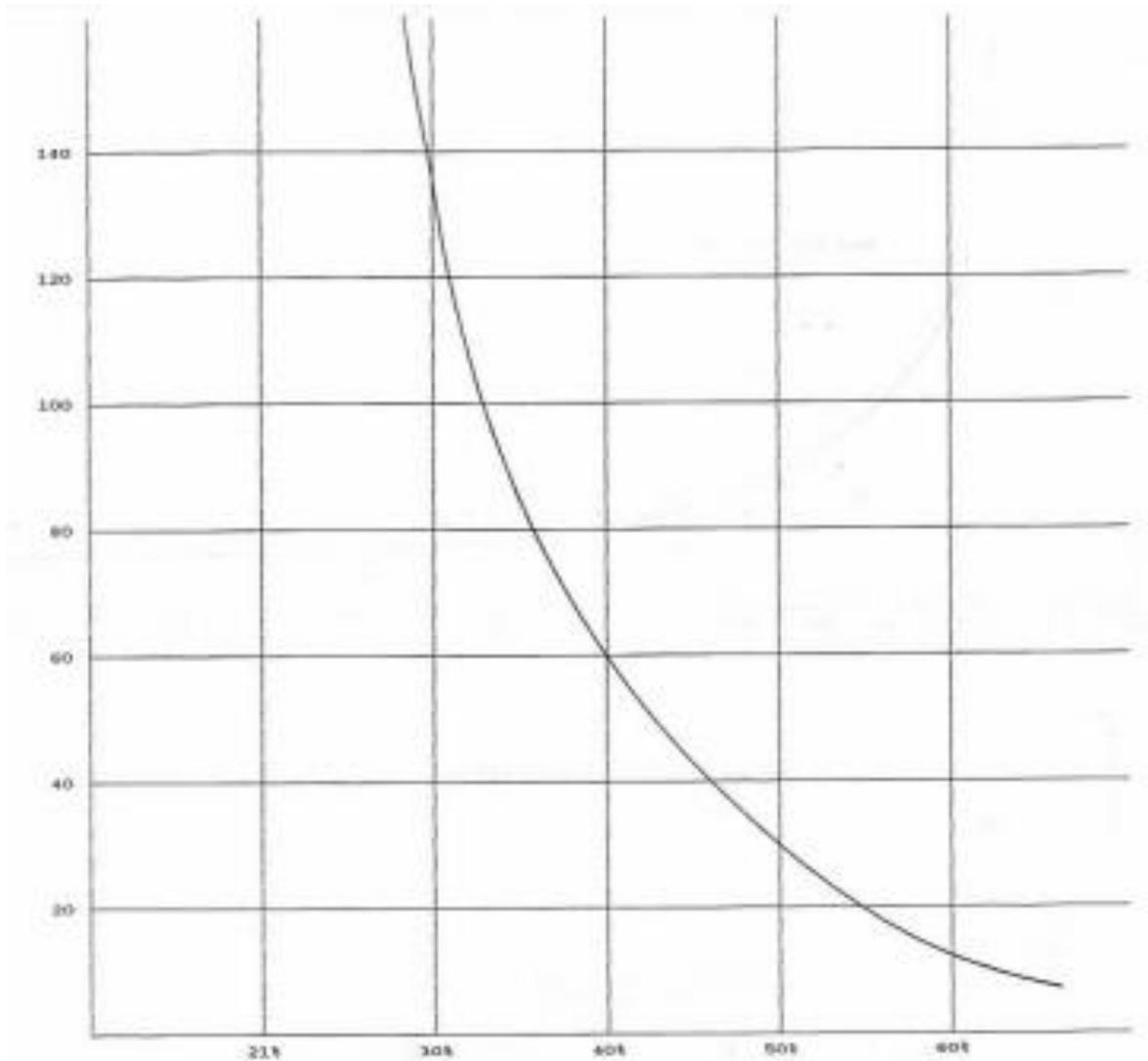


Figure A.1.4

TIME TO BURN (50 % DESTRUCTION) DENIM OVERALLS

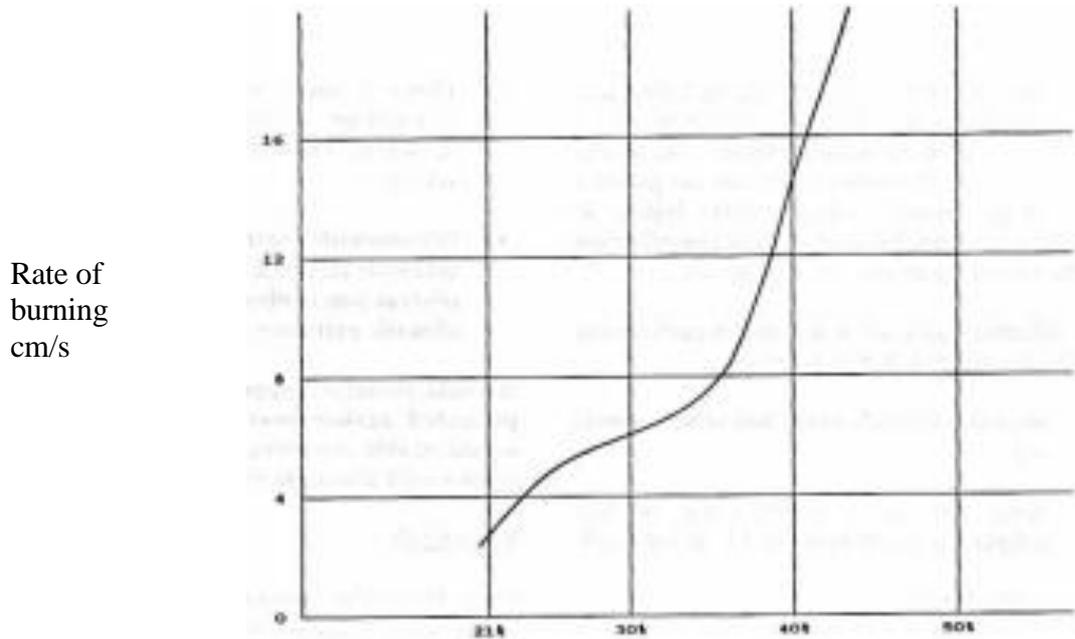
Time to 50 %
destruction,
seconds



Extract from Figure 11 in Reference 10.

Figure A.1.5.

BURNING RATE OF WHITE COTTON



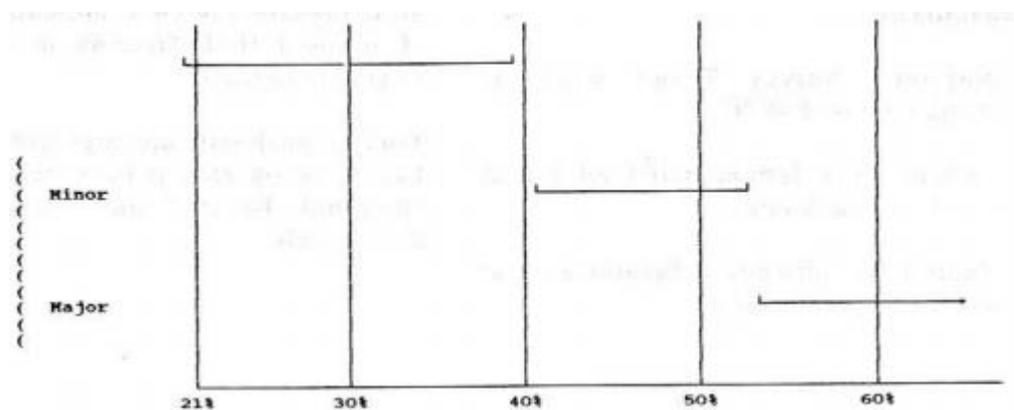
Extract from Figure 1 in Reference 2.
9.6 oz/yd cotton.

Figure A.1.6.

FLASH FIRE CHARACTERISTICS OF NEW DRY DENIM OVERALLS

No flash fire

Flash fire with
other sites ignited



Extracts from Figure 7 in Reference 10.

POTENTIAL FOR LOW TEMPERATURES AND WIND CHILL TO CAUSE INJURY

Physical contact with liquid oxygen, being at a temperature about $-183\text{ }^{\circ}\text{C}$, is recognised as a cause of immediate serious injury. As liquid spillage is unlikely to extend outside the process or storage areas, contact with liquid is considered to not be a significant contribution to the risks to persons outside the site.

The effects of air made cold by oxygen enrichment can be considered in two parts:

- i) Those due entirely to the low temperature, and
- ii) those due to a combination of low temperature and wind speed; Wind Chill.

Low temperature

The basic concern in this instance is not the cooling of the body by heat loss from the skin surface (which is the same as a “no-wind” Wind Chill effect – refer to text below), but more the direct effect on breathing and the possibility of shock induced injury. There is little experimental data available and consequently this aspect is assessed on the basis of medical opinions. It is relevant to note:

- i) Antarctic Survey Teams work at temperatures of $-40\text{ }^{\circ}\text{C}$.
- ii) Such teams are fully prepared and clothed for these conditions.
- iii) There is no difficulty in breathing air at $-40\text{ }^{\circ}\text{C}$ when seated or at rest.
- iv) There is some anecdotal evidence that discomfort increases with increased breathing rates associated with physical activity.
- v) Persons with respiratory disorders could be seriously affected, and cold induced airway obstruction is observed under the normal climatic extremes that occur in the UK.

It would, therefore, appear that a healthy person protected against heat loss through the skin would be able to survive and remove themselves from a cold atmosphere.

Wind chill

Data from the diagrams and tables in the References relating to wind chill (Figures A.2.1, A.2.2 and A.2.3) has been combined and represented in Figure A.2.4.

It is apparent that above an “equivalent temperature” of about $-30\text{ }^{\circ}\text{C}$, or an air temperature of about $-5\text{ }^{\circ}\text{C}$ for any wind speed, there is little danger to properly clothed persons. With only moderate wind speeds an air temperature of $-40\text{ }^{\circ}\text{C}$ presents great danger of exposed flesh freezing in a short time (1 minute or less).

For later analysis temperatures of $0\text{ }^{\circ}\text{C}$ and $-40\text{ }^{\circ}\text{C}$ have been selected as being representative of “minimal hazard” and “severe hazard” respectively.

REFERENCES

Document Number	Title
1. BURTON, A.C. and EDHOLM, O.G.	Man in a cold environment – physiological and pathological effects of exposure to low temperatures. Hafner Publishing Co. 1995.
2. COBLE, D.F.	The effects of cold – frostbite and hypothermia. Professional Safety <u>24</u> (2) pp 15 – 18. 1979.
3. DEAL, E.C., McFADDEN, E.R., INGRAM, R.H. and JAEGER, J.J.	Effects of atropine on potentiation of exercise – induced bronchospasm by cold air. J. Applied Physiology <u>45</u> pp 238 – 243. 1978.
4. Federation of Industrial Mutual Accident Insurance Associations.	Hazards due to low temperature during work in cold storage warehouses. Arbeitsmedizin. ASP 1/75 <u>10</u> (1) pp 19 and 20. 1975 (In German).
5. GENA SOTO, J.M. <i>et al.</i>	Hazards of exposure to cold. Seguranca 14 (56) pp 6 – 13. 1978. (In Portuguese).
6. HARTUNG, G.H., MYHRE, L.G. and NUNNELEY, S.A.	Physiological effects of cold air inhalation. Aviation, Space and Environmental Medicine 51 (6) pp 591 – 594. 1980.
7. Netherlands Labour Inspectorate Leaflet P No. 142	Work in cold storage plant. 1977. (In Dutch).
8. Private communication expressing medical opinions from:	
8.1 GREENBERG, Dr M.	Health and Safety Executive Employment Medical Advisory Service.
8.2 HARRISON, Dr M.H.	RAF Institute of Aviation Medicine.
8.3 JOHNSON, C.J.H.	Medical Officer to the British Antarctic Survey.
9. Private communication from KUEHN, A.L.	Defence and Civil Institute of Environmental Medicine, Ontario.

Figure A.2.1

WIND CHILL CHART (2)

m/s	Estimated wind speed mph	ACTUAL THERMOMETER READING °F											
		50	40	30	20	10	0	-10	-20	-30	-40	-50	-60
		EQUIVALENT TEMPERATURE °F											
0	Calm	50	40	30	20	10	0	-10	-20	-30	-40	-50	-60
2.2	5	48	37	27	16	6	-5	-15	-26	-36	-47	-57	-68
4.5	10	40	28	16	4	-9	-21	-33	-46	-58	-70	-83	-95
6.7	15	36	22	9	-5	-18	-36	-45	-58	-72	-85	-99	-112
8.9	20	32	18	4	-10	-25	-39	-53	-67	-82	-96	-110	-124
11.2	25	50	16	0	-15	-29	-44	-59	-74	-88	-104	-118	-133
13.4	30	28	13	-2	-18	-33	-48	-63	-79	-94	-109	-125	-140
15.6	35	27	11	-4	-20	-35	-49	-67	-82	-98	-113	-129	-145
17.9	40	6	10	-6	-21	-37	-53	-69	-85	-100	-116	-132	-148
Wind speeds greater than 40 mph have little additional effect		Little danger for properly clothed person				Increasing danger				Great danger (Exposed flesh may freeze within 30 seconds)			
DANGER FROM FREEZING OF EXPOSED FLESH													

Figure A.2.2

EQUIVALENT TEMPERATURE GRAPH (5)

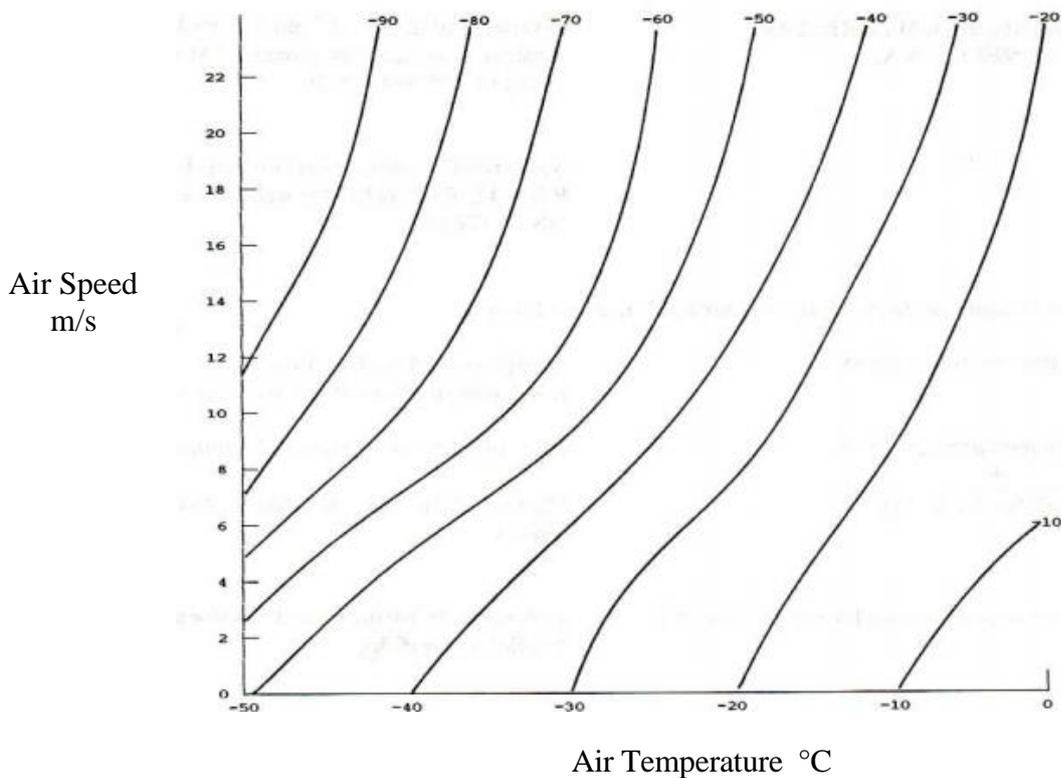


Figure A.2.3.

RELATIONSHIP BETWEEN WINDSPEED AND AMBIENT TEMPERATURE TO CAUSE FREEZING OF EXPOSED FLESH OF LIGHTLY DRESSED PERSONNEL (9).

Reference: Defence and Civil Institute of Environmental Medicine, Ontario.

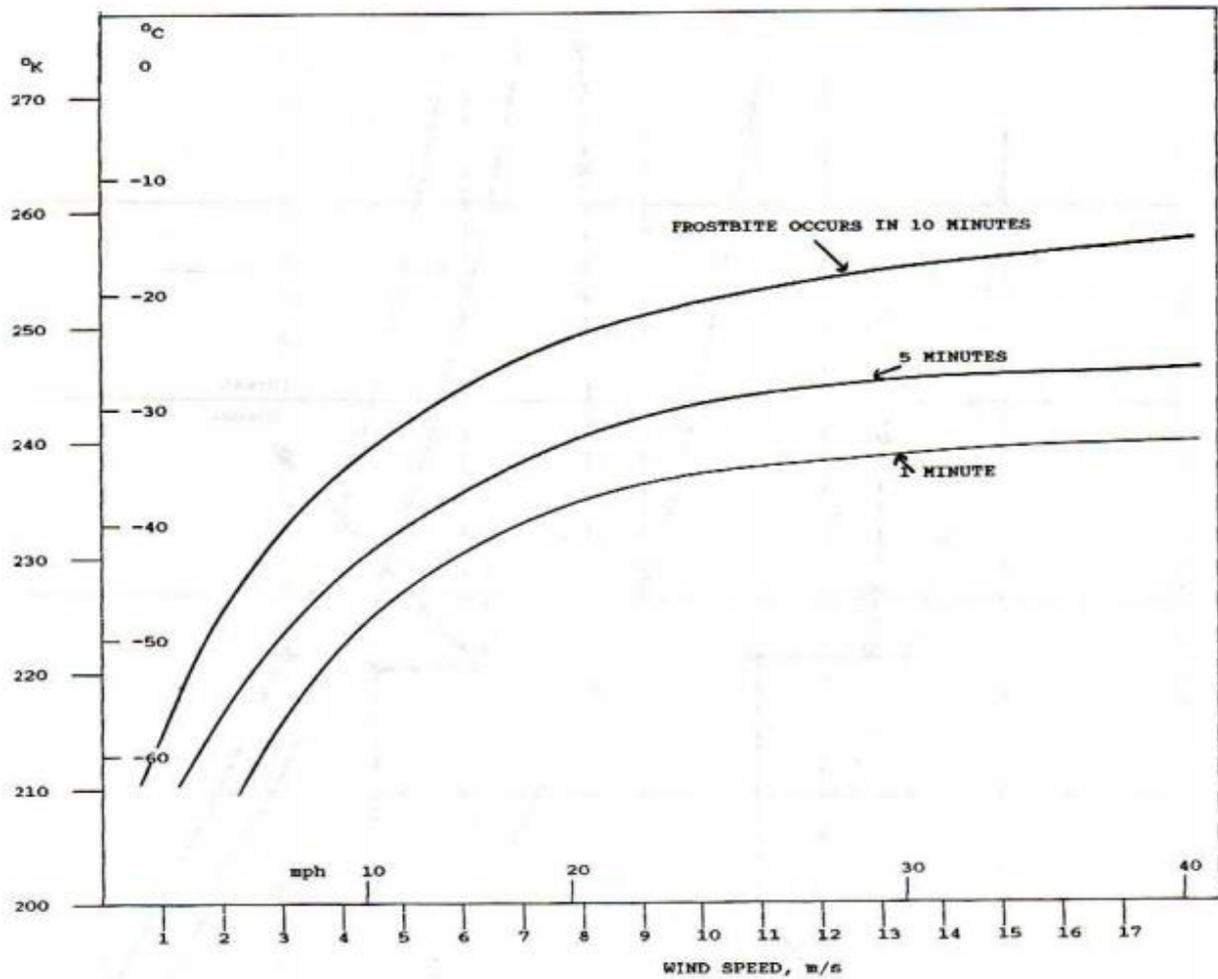
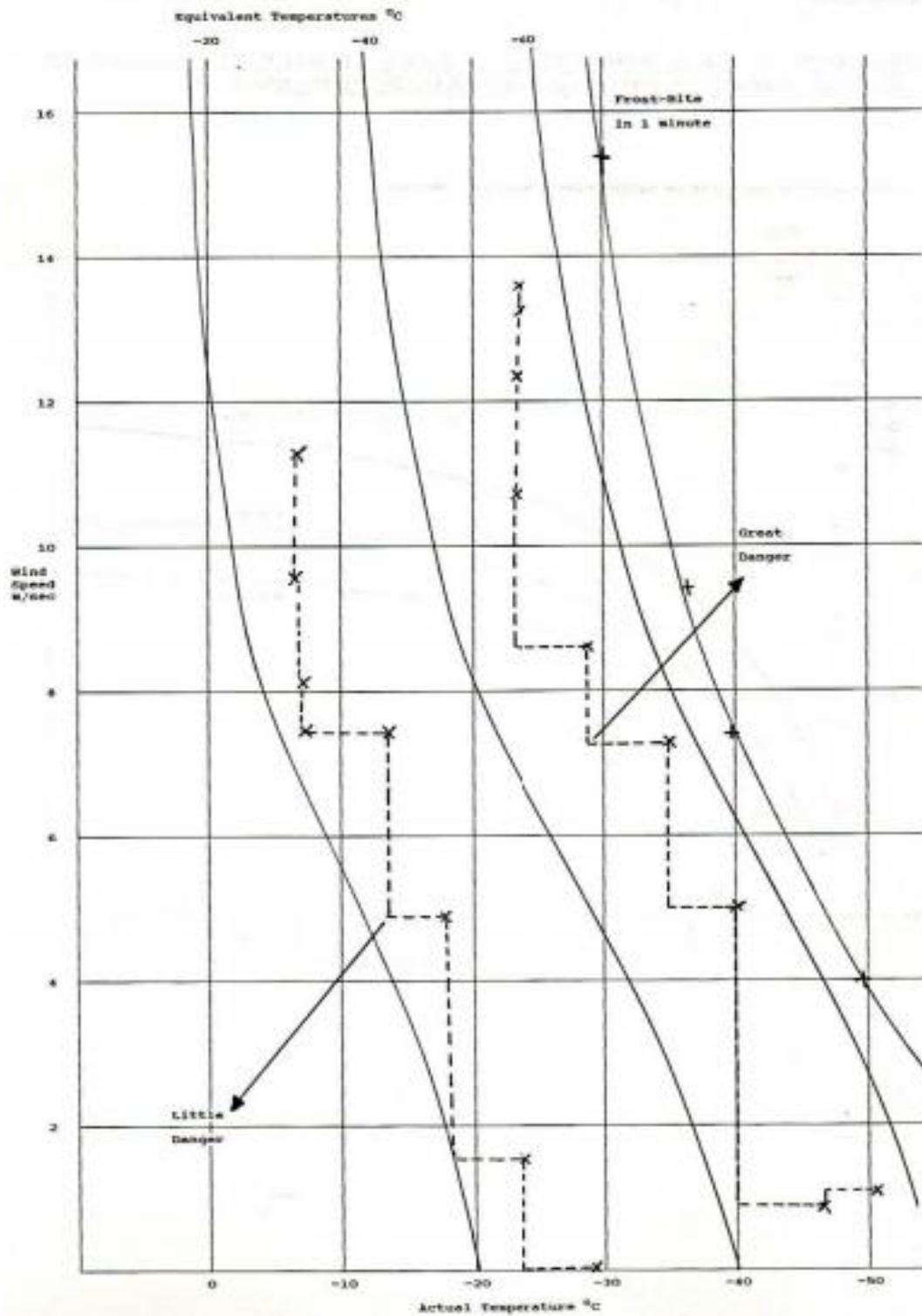


Figure A.2.4

WIND CHILL AND COLD HAZARDS



THE FACTORS AFFECTING THE NUMBERS OF CASUALTIES

When compared for the ability to cause fatal or serious injury the effects of burns appear to be more severe than the effects of cold for any given enrichment. However, the burns casualties will be limited to that proportion of the exposed population involved with an ignition source, whereas the whole of the population will be exposed to the cold, but only the susceptible will suffer from the effects of cold. For all the dispersion conditions examined in this example, see Appendix 5, it has been found that the “effective temperature” in an oxygen enriched atmosphere is above $-40\text{ }^{\circ}\text{C}$ when the oxygen concentration is 40 %. Thus, for the purposes of risk assessment it is assumed that a conservative assessment of casualties from fire encompasses the potential for casualties from cold.

As described in Appendix 1, the hazard being evaluated is the increase in casualties from burns which can be directly related to increased oxygen concentrations. The selection of clothing fires as being the only type of fire which would increase the casualties is based upon:

- i) Clothing is the source of fuel which is close to a person, and it is not easy to remove burning clothing.
- ii) The combustible materials in the household, other than clothing, will also exhibit enhanced burning characteristics. However, in general, it is possible to escape from the vicinity of such fires.
- iii) Flames which are fuel controlled, e.g. pilot lights, gas burners, wick burners, coal-fires, etc., in oxygen enriched atmospheres tend to burn more brightly, but with a smaller flame size.
- iv) Oxygen enrichment enhances combustion thus reducing smoke.
- v) Home Office fire statistics (1) indicate that smoking materials and cookers are the cause of the larger proportions of household fires.

Thus, it is upon the potential for persons who are smoking, or using matches, to ignite their clothing that this assessment concentrates. There are mitigating actions to reduce this potential, for example, the ability of a person to extinguish or brush off their clothes, a dropped burning match. Also, it is possible that although ignited, the clothing can be extinguished before injury results. Such reactions are assessable, and the ability of a person to make a manual response to an unexpected emergency has been quoted (2) as being between 5 and 20 seconds.

Taking these two values as the limits of the range of reaction times it has been assumed that:

5 % of the population are incapable of making any reaction, i.e. babies or disabled.

95 % of the population can react within 20 seconds.

80% of the population can react within 15 seconds.

25 % of the population can react within 10 seconds.

10 % of the population can react within 7.5 seconds.

This is shown graphically in Figure A.3.1. It is the converse that is important for assessment, i.e. those that are unable to take any mitigating action, and this can also be related to the typical ignition times for differing oxygen concentrations. Refer to Table A3.1.

Oxygen concentration	25	30	35	40
Ignition time, seconds	20	10	7.5	5
% of population unable to prevent ignition	5	75	90	100

Table A3.1

Even if ignition does occur there is still the possibility of taking action to extinguish or contain the fire before serious injury occurs, and this can be related to reaction times, and also to a probability that the ignited clothing, even if not extinguished, will not cause serious injury.

For the purpose of this assessment it is assumed that an additional time period equal in duration to the ignition period can be allowed for the possibility of a person reacting to minimise the effects of the fire. Thus, for the chosen oxygen concentrations, refer to Table A3.2.

Oxygen concentration %	25	30	35	40
Ignition time, seconds	20	10	7.5	5
% of population able to prevent ignition	95	25	10	Nil
Extinguishing time, seconds	20	10	7.5	5
Total time for reaction, seconds	40	20	15	10
% Population able to react	95 *	95	80	25
% Population who will be injured seriously because they cannot react at all	0 *	5	20	75
% Population ignited and able to react	5 *	70	70	25

Table A3.2

* With an additional period of 20 seconds, it is possible that another person will react.

The ability to react to prevent the effects of an ignition becomes less significant as the speed of propagation of the fire across the clothing increases. It has been assumed for this assessment that despite the ability to react, 10 % of ignitions at ambient conditions result in serious injuries, and that this value for the number of serious injuries in other oxygen concentrations is approximately proportional to the square of the linear burning rate. Thus, referring to Table A3.3:

Oxygen concentration %	25	30	35	40
Relative burning rate	1	1.25	1.75	3
Proportion of ignitions resulting in serious injuries %	10	15.6	30	90
% Population ignited and able to react	5	70	70	25
% of population seriously injured:				
a) Reacted but still injured	0.5	10	20	23
b) Unable to react at all	0	5	20	75
Total:	0.5	15	40	98
Thus ignitions which occur, i.e. %	5	75	90	100
The proportion that result in injury is:	0.1	0.2	0.44	0.98

Table A3.3

The proportion of the population who are actually at risk is limited to those who are smoking, playing with matches, or in close contact with a source of sparks.

An approximation of the patterns of smoking which have been observed (3) shows that smoking occupies about 5 % of the time at work and 10 % of the time away from work (including time asleep) based upon a 7.5 minute duration for smoking one cigarette.

In 1975 about 62 % men and 43 % women were smokers (4); allowing for the decrease in popularity of smoking in recent years, including the population under 16 who whilst not smoking may be playing with matches, and allowing for other causes of ignition or injury, it has been estimated that 40 % of the population can be considered to be “smokers”. Relating this to the proportion of time during which these activities are indulged gives the proportion of total population who may be at risk at any instance, i.e. 2 % whilst at work, 4 % whilst elsewhere or sleeping.

Obviously, if a population is exposed to oxygen enrichment and no ignitions occur immediately there is still the chance that someone may “light-up”. Using the 7.5 minute period as a discreet interval then the number of injuries would be increased by a factor equal to the number of intervals in the duration of the exposure, e.g.

Oxygen concentration %	25	30	35	40
Proportion of vulnerable population seriously injured %	0.5	15	40	98
Probability of ignition source being present (away from work) %	4	4	4	4
Initial probability of fatal or serious injury %	0.02	0.6	1.6	3.9
Probability after enrichment durations of:				
7.5 minutes	0.04	1.2	3.2	7.8
15 minutes	0.06	1.8	4.8	11.7
30 minutes	0.10	3.0	8.0	19.5

Table A3.4

There is also the mitigating effect of delayed enrichment of the atmosphere inside a building, and the reduction of ignition sources resulting from warnings issued as part of an Emergency Plan. On the basis that emergency action to stop or minimise the release can be taken within 30 minutes, and warnings to prevent more sources of ignition are given, then it is reasonable to presume that there need be no additional casualties after 30 minutes.

Within that time period there is a beneficial effect of delayed enrichment within buildings. Using the simple mixing theory formula:

$$C = C_0 (1 - \exp^{-Xt})$$

Then, for typical air changes (X) of 2 changes per hour for houses and 4 changes per hour for work premises, after time (t), and continuous outside enrichment levels (C₀), internal concentrations are displayed in Table A3.5.

Thus, whilst the probability of serious or fatal injury for a population outside for 30 minutes in 35 % oxygen is about 8 %, if the same population is inside a house then this probability is reduced to about 0.8 %. Similarly, an outside working population in 40 % oxygen for 7.5 minutes would have their probability of injury reduced from 4 % to about 0.6 % if they were inside a factory building.

For later analysis oxygen concentrations of 30 %, 35 % and 40 % have been selected as being representative of “hazard”, “severe hazard”, and “extreme hazard” respectively.

Oxygen concentration %	30	35	40
C for X = 2 after t =			
2 minutes	21.4	21.5	21.7
8 minutes	23.0	24.3	25.3
26 minutes	26.2	29.4	32.0
C for X = 4 after t =			
2 minutes	1.2	3.2	7.8
8 minutes	1.8	4.8	11.7
26 minutes	3.0	8.0	19.5

Table A3.5

REACTION TIMES

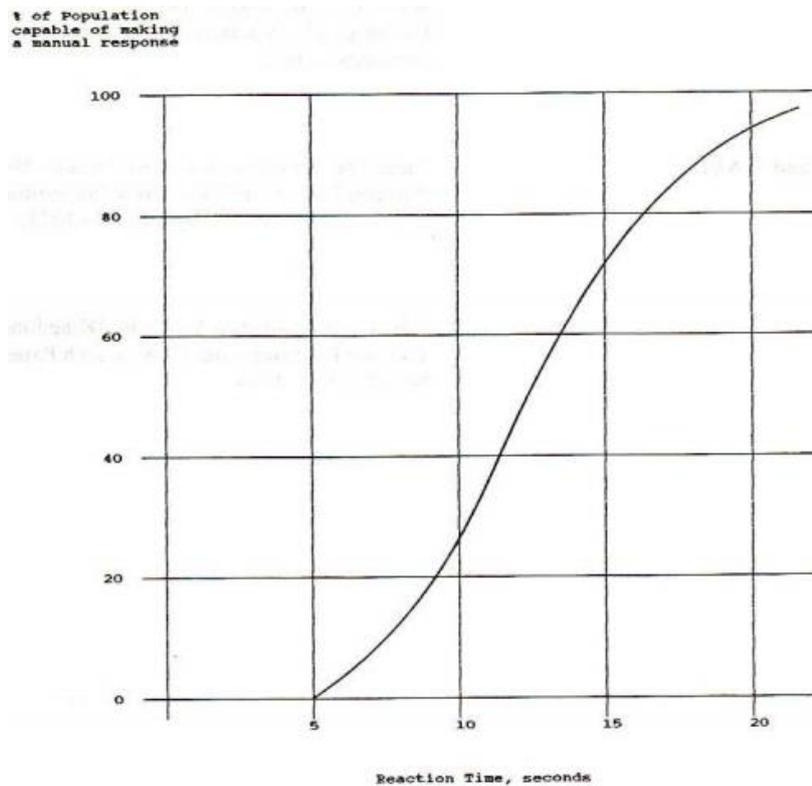


Figure A.3.1

REFERENCES.

Document Number	Title
1. Her Majesty's Stationary Office (HMSO)	Home Office, Fire Statistics, published annually.
2. DENISON, D.M. and TONKINS, W.I.	Further studies upon the human aspects of fire in artificial gas environments. RAF Institute of Aviation and Medicine, Ministry of Defence, September 1967.
3. MEADE, T.W. and WALD.	Cigarette smoking patterns during the working day. British Journal of Prevention and Social Medicine 31 pp 25 – 99. 1977.
4. LEE, P.N.	Statistics of smoking in the United Kingdom. Tobacco Research Council, Research Paper No. 1, 7 th Edition. 1976.

PRINCIPLES FOR VALIDATION OF STORAGE TANK DESIGN

The following principles were specified in a “*Statement of Intent*” issued by the British Compressed Gases Association dated 5th August 1981.

BCGA intend to carry out the following actions:

Prepare design summaries of existing “*large liquid oxygen storage tanks*”, and obtain the approval of a Recognised Inspection Authority to those summaries.

The design summary is to include validation of the following values:

- Maximum and minimum design pressures.
- Maximum and minimum design temperatures.
- Maximum liquid level.
- Support Design for the maximum liquid level.

The summary shall also include details of pressure safety valves, vacuum valves and level controls fitted to ensure the above values are not exceeded.

For the purposes of this statement the following definitions are applicable:

Definitions:

Large liquid oxygen storage tanks	Those of greater than 135 tonne net capacity per unit.
Recognised Inspection Authority	An independent body having such practical and theoretical knowledge and actual experience of the type of tank that will enable them to detect defects or weaknesses and to assess their importance in relation to the strength and function of the tank. Certain members of the Council of Independent Inspecting Authorities (CIIA) are capable of fulfilling this function.
Support Design	Provides a numerical value of the maximum load the vessel and its supports can safely sustain.

RELEASE RATE CALCULATIONS AND DISPERSION ESTIMATIONS

This Appendix details the calculations and estimations made for selection of the example cases used in Section 6 of the main text. There are three basic cases for release:

Case A - Pipework release from hydrostatic head only.

Case B - Pipework release from a pressurised system.

Case C - Instantaneous release of vessel contents.

Within these cases there are a series of other choices of conditions, e.g. for evaporation estimations:

- i) releases into bunded areas,
- ii) releases onto areas with no containment,

and also type of surface, concrete or moist soil, and for dispersion estimations a combination of weather stability characteristic and wind speed.

Pipework releases

Case A i)

A full 1000 tonne flat-bottomed vessel located in a bund discharges through a 150 mm (6 inch) nozzle under a hydrostatic head of initially 11 metres. The bund is 1 metre high and has 110 % of the volume of the vessel.

From the information given, the initial leak rate is 245 kg s^{-1} falling linearly to zero in 2.27 hours, after which time the entire contents of the vessel have been released. The leak rate at t seconds after the spill starts is $0.0300 (8165 - t) \text{ kg s}^{-1}$ (refer to Annex 1). The bund has a radius of 17.5 m.

The radius of the pool and total mass evaporated as functions of time have been calculated using SPILL (1).

The pool reaches the edge of the bund after 40 s (concrete surface) or 38 s (wet soil). At the same time, the maximum evaporation rates of 260 kg s^{-1} (concrete) and 193 kg s^{-1} (soil) are attained.

Subsequent computed evaporation rates agree well with simple application of equation 30 of (1); the rate of evaporation falls off as $t^{-0.5}$. After 8165 s, when the release finishes, the total mass evaporated is 138 tonne (concrete) or 100 tonne (soil). The whole pool takes 5 – 4 days (concrete) or 10 – 6 days (soil) to evaporate.

Case A ii)

This is the same as Case A i), but without the bund.

Use of the SPILL code indicates that a maximum evaporation rate of 327 kg s^{-1} is attained in each case, after 72 s (concrete) or 102 s (soil). However, the code then predicts that the depth of the pool falls to zero with its maximum radius 26 m after 124 s (concrete) or 33 m after 153 s (soil). This causes the calculation to stop automatically, so SPILL cannot be used to complete this calculation.

The unrealistic conclusion that the pool completely disappears arises because the simple model used in SPILL for heat transfer and fluid flow within the spilt liquid is unsuitable for very shallow pools (less than about 10 mm deep).

The real evaporation rate probably fluctuates around and fairly close to the spill rate, while the pool remains shallow with an area adjusted to give that rate of evaporation.

Case B i)

In this case a 135 tonne vessel pressurised at 15 bar above atmospheric pressure is discharged through a 50 mm (2 inch) diameter pipe. It is in a bund 1 m high with 110 % of the vessels volume.

As the liquid flows down the pressure gradient in the pipe and issues from the end, some fraction of it flashes into vapour; this fraction is calculated to be 26 % of a total flow rate of 32 kg s^{-1} for the given conditions (refer to Annex 2). The flow rate remains steady for 70 minutes until the vessel is empty. In addition, because of unsteady two-phase flow, some liquid will issue as an aerosol of fine droplets; this is assumed following convention, to be a further 26 %. Thus, 52 % of the oxygen released, or 17 kg s^{-1} appears as vapour promptly and the balance, 15 kg s^{-1} is available to form a pool. In this case the radius of the bund is 6.43 m.

It should be noted that the speed of discharge exceeds 13 ms^{-1} , and so the liquid may be projected outside the bund. In this case the pool evaporation rates would be those estimated for the unbundled Case, B ii) below.

The results of a SPILL calculation for a steady rate of discharge of 15 kg s^{-1} show that the evaporation rate rises to a maximum of 21 kg s^{-1} in each case, after 21 s (concrete) or 28 s (soil) and that the pool never reaches the bund. The pool depth drops to zero, terminating the calculation, after 24 s (concrete) or 38 s (soil). The result is unrealistic for the same reasons as in Case A ii), and a better estimate is probably that the evaporation rate fluctuates around 15 kg s^{-1} until either the bund is reached, or the discharge stops after 70 minutes. If the bund is reached, the evaporation rate will fall off as $t^{-0.5}$ as in example A i).

The total rate of production of oxygen gas is the prompt emission rate, 17 kg s^{-1} plus that from evaporation.

Case B ii)

This is the same as Case B i), except that there is no bund. As the bund was not reached in the SPILL calculations on Case B i), the code would give the same results in this case, and thus an evaporation rate fluctuating about 15 kg s^{-1} over 70 minutes is estimated for this case. Again this has to be added to the 17 kg s^{-1} of gas formed promptly on emission.

Vessel releases

Instantaneous release by catastrophic vessel failure of 135 tonne. This inventory was chosen as there are very few pressurised storages exceeding this capacity. Some calculations have also been carried out for releases of 100 tonne and 150 tonne to illustrate the sensitivity of hazard range to inventory.

Catastrophic failure of ambient pressure storage was not considered because there are relatively few of these large refrigerated storage tanks, and these can be considered individually if necessary.

Selected oxygen concentrations for dispersion calculations

The oxygen concentrations selected for the dispersion study were 25, 30, 35 and 40 % v/v. It is necessary to express these concentrations as a contaminant concentration in air in order to use the SRD codes DENZ (2) and CRUNCH (3), i.e. a concentration of “excess oxygen” in kg m^{-3} . The derivation of the appropriate excess oxygen concentrations is given in Annex 3.

As there may be effects due to exposure to low temperature, the ranges at which the cloud temperature is less than $-40 \text{ }^\circ\text{C}$ and $0 \text{ }^\circ\text{C}$ are also given.

Source terms

In order to use the DENZ (2) and CRUNCH (3) codes it is necessary to specify the “source term”, i.e. the cloud density, volume and temperature after any momentum associated with the original release has been dissipated, during which process air will be entrained from the surroundings. The source terms for pressurised and refrigerated releases are considered separately.

i) Instantaneous pressurised releases

Two assumptions have been made regarding air entrainment during the pressure-driven expansion phase of cloud formation.

Both assumptions are based on reports of clouds formed by catastrophic releases of liquid ammonia. The first is simply that the mass of air entrained is ten times the mass of stored liquefied gas. The second is based on the premise that the air entrainment will be related to the violence of the flash vaporisation occurring during the expansion phase. The volume of air entrained is taken to be sixty times the flash vapour volume. For oxygen stored at 15 bar ($-145 \text{ }^\circ\text{C}$) the flash fraction is 26 % and the air entrainment is about five times the mass of stored liquefied gas. (For comparison, chlorine, ammonia and propane stored at $20 \text{ }^\circ\text{C}$ have flash fractions of 16 %, 17 % and 31 % respectively). In the case of a low boiling point material such as oxygen, the flash volume is low simply because of the low temperature and so the total amount of air entrained will be less than

for a flashing liquid with a similar flash fraction, but boiling point nearer to ambient temperature.

At the moment there is insufficient evidence to confirm these assumptions for the general case of any liquefied gas under pressure. Other factors, such as storage pressure, may be relevant. In this work a storage pressure of 15 bar has been assumed, but the storage pressure in vacuum insulated equipment is not constant. The pressure and temperature gradually increase following a delivery of LOX until a further delivery of colder material is received. A pressure at the high end of the range of pressures experienced has been selected.

The use of two air entrainment assumptions in this report is intended to indicate the sensitivity of the results to the air entrainment assumption. It will be found that the hazard range is not sensitive, but the width of the cloud (and, therefore, the total area affected) is more sensitive.

The method for calculation of the source term cloud temperature and density is given in Appendix 5, Annex 4.

ii) Continuous pressurised releases

In the case of a flashing flow release from pipework part of the flash vaporisation occurs inside the equipment and the remainder on release to the atmosphere. The air entrained has been assumed to be ten times the mass of released liquefied gas.

iii) Refrigerated releases

The rapid vaporisation in the first minute or so following a refrigerated spill onto land has been modelled as a quasi-instantaneous release using DENZ. Two assumptions were made regarding air entrainment. Firstly, that the turbulence produced by the rapid vaporisation produces a similar degree of entrainment to the pressure release, i.e. ten times the mass of liquefied gas vaporised. Secondly, that no air is entrained. The latter assumption was incompatible with running the DENZ code at low wind speeds.

The steady-state vaporisation from a pool of spilled liquid oxygen was modelled using CRUNCH. The source cloud was assumed to be formed from oxygen only, i.e. no air entrainment.

Dispersion estimations

i) Weather conditions

The hazard ranges have been estimated for weather Category D, wind speed 3 ms⁻¹ and 6 ms⁻¹ and Category F wind speed 2 ms⁻¹. Category D conditions may be considered to represent “average” conditions and Category F “worst case” conditions for atmospheric dispersal.

ii) Continuous releases

The hazard ranges to the selected oxygen concentrations predicted by CRUNCH are summarised in Table 2. The predicted hazard range for a neutrally buoyant material is given, for comparison, using the method of Bryant (4).

It should be noted that as a precursor to the ongoing vaporisation from a banded refrigerated spill, at 40 kgs^{-1} , there is a more rapid vaporisation modelled by a 13 tonne instantaneous release.

iii) Instantaneous releases

The dispersion ranges to 25 % volume oxygen and areas affected by greater oxygen concentrations in the event of catastrophic pressurised releases of 100, 110, 135 and 150 tonne LOX are summarised, for the three selected sets of weather conditions in Table 2. These results are based on a source term assuming air entrainment of ten times the mass of oxygen released. Also given are the dispersion ranges and areas to 25 % volume oxygen for a 13 tonne instantaneous release, which has been taken to model the rapid boil-off in the first 100 seconds of a cryogenic spill into a bund from a 150 mm (6 inch) nozzle failure. This case has been studied for a source term similar to a pressurised release (i.e. air entrained equal to ten times the mass of oxygen vaporised) and for no initial air entrainment.

In the latter case the code would not function for low wind speeds. The total area affected by concentrations greater than 25 % volume oxygen was the same for each case, in weather Category D, wind speed 6 ms^{-1} .

The dispersion of 135 tonne and 13 tonne releases to concentrations greater than 25 % is summarised in Table 3. Also given is the maximum duration of oxygen concentrations exceeding 25 % volume at any point in the passage of the cloud.

The effect of varying the initial air entrainment in the source term for instantaneous pressurised releases has also been considered, for the 135 tonne case. The downwind dispersion ranges to 25 % and 30 % volume oxygen and total areas affected to greater than these concentrations, are given in Table 4. The downwind hazard range is not sensitive to the air entrainment assumption. The width of the plume and, therefore, the total area affected, is somewhat more sensitive although to a limited extent for risk assessment purposes.

REFERENCES

Document Number	Title
1. SHAW, P. and BRISCOE, F.	Evaporation from spills of hazardous liquids on land and water. Safety and Reliability Directorate Report SRD R 100, May 1978.
2. FRYER, L.S. and KAISER, G.D.	DENZ – A computer code for the calculation of the dispersion of dense toxic or explosive gases in the atmosphere. Safety and Reliability Directorate Report SRD R 152, July 1979.
3. JAGGER, S.F.	Development of CRUNCH: A dispersion model for continuous releases of denser-than-air vapour into the atmosphere. Safety and Reliability Directorate Report SRD R 229, January 1983.
4. BRYANT, P.M.	Methods of estimation of the dispersion of windborne material and data to assist in their application. AHSB (RP) R 42. 1964.

ANNEX 1

CASE A – LEAK RATE CALCULATION

1000 tonne flat bottomed vessel discharging through a 150 mm (6 inch) diameter nozzle, with initial hydrostatic head 11 m. The liquid flow release rate is given by:

$$G = CA [2\rho_L (P_1 - P_2)]^{0.5}$$

where

$$G = \text{Leak rate, kgs}^{-1}$$

$$C = \text{Coefficient of discharge, 0.8 assumed}$$

$$A = \text{Leak area} = 1.82 \times 10^{-2} \text{ m}^2$$

$$\rho_L = \text{Liquid density} = 1140 \text{ kgm}^{-3} \text{ at } -183 \text{ }^\circ\text{C}$$

$$P_1 - P_2 = \text{Driving pressure}$$

$$= z \rho_L g$$

where

$$z = \text{Liquid head, m}$$

$$g = 9.81 \text{ ms}^{-2}$$

giving

$$G = 0.8A \rho_L (2gz)^{0.5}$$

The initial leak rate, for $z = 11 \text{ m}$, is 244 kgs^{-1} .

For a level change dz the mass lost from the vessel is $(-)\ dz \cdot \rho_L \cdot x$, where x is the vessel cross sectional area (79.7 m^2).

The time taken for the level to change by dz is dt :

$$\text{giving } dt = \frac{\text{Mass loss}}{\text{Leak rate}}$$

$$= \frac{-X}{0.8A2g^{0.5}} \frac{dz}{z^{0.5}}$$

and producing the relationship between time in seconds and level change in m:

$$t = 2472 (z_1^{0.5} - z_2^{0.5})$$

The time taken for the vessel to empty completely ($z_1 = 11 \text{ m}$, $z_2 = 0$) is about 137 minutes.

As both leak rate and time are a function of $(z)^{0.5}$ a linear relationship between leak rate and time exists:

$$G = 0.03 (8165 - t) \text{ kgs}^{-1}$$

ANNEX 2

CASE B – LEAK RATE CALCULATION

The flashing flow release occurring from a 50 mm (2 inch) diameter pipe failure associated with a vessel containing liquid oxygen at 15 barg was estimated using a program for a programmable calculator compiled by Dr M Considine, SRD. This uses the equation:

$$G = CA [2\rho_m (P_1 - P_c)]^{0.5}$$

where

G	=	Leak rate, kgs ⁻¹
C	=	Coefficient of discharge, 0.8 assumed
A	=	Leak area, m ²
ρ_m	=	Mean density of liquid and gas mixture, allowing for the vapour fraction formed in pressure reduction from upstream temperature T_1 to choke temperature T_c . The choke temperature is determined for the fluid vapour pressure equal to P_c .
P_c / P_1	=	Critical pressure ratio, $P_c =$ Choke pressure
P_1	=	Upstream pressure, Nm ⁻²

The following inputs were used:

Liquid Density	1.14 (1140 kgm ⁻³)
Upstream Pressure	220.5 psig (15 barg)
Ratio of Specific Heats	1.4
Choke Pressure P_c was	109.6 psig
Molecular Weight	32
Upstream Temperature	-145 °C (for vapour pressure 15 barg)
Choke Temperature	-156 °C
Latent Heat	50.9 cal g ⁻¹ (value at -183 °C)
Liquid Specific Heat	0.41 cal g ⁻¹ K ⁻¹

For these conditions a leak rate of 32 kgs⁻¹ was estimated. The flash fraction at the release point is about 8 %. However, on release, further flashing results in the total flash fraction being about 26 %, i.e. the release is calculated to be about 8.3 kgs⁻¹ vapour, remainder liquid. However, the violence of this process will produce an aerosol of vapour and fine liquid droplets, much of which will be dispersed downwind rather than forming a pool. This process cannot be modelled at the present time, a common assumption is that an amount of liquid equal to the flash fraction is entrained as droplets and subsequently vaporises.

ANNEX 3

OXYGEN CONCENTRATIONS IN OXYGEN-AIR MIXTURES EXPRESSED AS EXCESS OXYGEN, WT/VOL

In order to use the DENZ program for oxygen-air mixtures, it is necessary to specify the desired hazard level concentrations as concentration of excess oxygen, i.e. the concentration of oxygen above that normally present in air, in kgm^{-3} .

The normal concentration of oxygen in air is 21 % v/v, 23.1 % w/w.

The selected hazard levels are 25 %, 30 %, 35 % and 40 % v/v.

A temperature of 15 °C is assumed.

	Density of nitrogen at 15 °C	=	$\frac{28}{22.4} \times \frac{273}{288}$	=	1.185 kgm^{-3}
	Density of oxygen at 15 °C	=	$\frac{32}{22.4} \times \frac{273}{288}$	=	1.354 kgm^{-3}
	Volume of 1 kg mol at 15 °C	=	$22.4 \times \frac{273}{288}$	=	23.63 m^3
For normal air	21 % vol O ₂ , vol O ₂	=	0.21×23.63	=	4.96 m^3 , mass 6.72 kg
	79 % vol N ₂ , vol N ₂	=	0.79×23.63	=	18.67 m^3 , mass 22.12 kg
	Oxygen concentration	=	$6.72 / 23.62$	=	0.284 kg m^{-3}
For 25 % vol O ₂	Mass of O ₂ in 1 kg mol mixture	=	$0.25 \times 23.63 \times 1.354$	=	8.0 kg
	Oxygen concentration.	=	$8.0 / 23.63$	=	0.338 kgm^{-3}
	Excess oxygen concentration over normal air	=	$0.338 - 0.284$	=	0.054 kg m^{-3}

However, the cloud may not have reached ambient temperature at the required concentration. For example, at 0 °C.

Volume of 1 kg mol	=	22.4 m ³
21 % vol O ₂ mass of O ₂	=	6.72 kg
25 % vol O ₂ mass of O ₂	=	8.0 kg
Excess O ₂ concentration	=	$(8 - 6.72) / 22.4 = 0.057 \text{ kg m}^{-3}$

As the cloud will be seen to have usually reached 0 °C by this stage, this difference due to density change is negligible.

By similar calculation the excess oxygen concentration is found for other concentrations and the following values have been used:

% O₂ v/v	Excess O₂ kgm⁻³
25	0.054
30	0.118
35	0.19
40	0.26

ANNEX 4

DISPERSION SOURCE TERMS

1. Instantaneous pressurised releases

a) Flash fraction

Flash fraction for pressurised storage at 15 bar (-145 °C).

$$= 1 - \exp \left[-\frac{C}{L} (T_a - T_b) \right]$$

where	C	=	Liquid heat capacity, 0.41 cal g ⁻¹ K ⁻¹
	L	=	Latent heat, 50.9 cal g ⁻¹ at -183 °C
	T _a	=	-145 °C
	T _b	=	Oxygen boiling point, -183 °C

$$\text{Flash fraction} = 0.26$$

i.e. for 100 tonne stored, 26 tonne flash vaporised, 74 tonne liquid at -183 °C.

b) Air entrainment – heat balance

A common assumption made when using DENZ is that the initial air entrainment is ten times the mass of released material, i.e. in the 100 tonne oxygen example, 1000 tonne air.

The final cloud temperature is obtained from a heat balance:

$$= M_A C_A (T_A - T) = M_L L + M_G C_G (T - T_G)$$

Where:	M _A	=	Mass of air, 10 ⁶ kg
	C _A	=	Specific heat of air, 0.245 kcal kg ⁻¹ K ⁻¹
	T _A	=	Ambient air temperature, 288 K assumed
	M _L	=	Mass of oxygen remaining as liquid after flash, 74 x 10 ³ kg
	L	=	Latent heat of vaporisation, 50.9 kcal kg ⁻¹
	M _G	=	Mass of oxygen flash vaporised, 26 x 10 ³ kg
	C _G	=	Oxygen vapour specific heat, 0.22 kcal kg ⁻¹ K ⁻¹
	T _G	=	Vapour temperature after flash, i.e. normal boiling point, 90 K

The heat balance is solved for the final cloud temperature, T, which in this case is 262.2 K.

c) Cloud density

$$\begin{aligned} \text{Oxygen density at 262 K} &= \frac{32}{22.4} \times \frac{273}{262} &= 1.488 \text{ kg m}^{-3} \\ \text{Air density at 262 K} &= 1.2928 \times \frac{273}{262} &= 1.347 \text{ kg m}^{-3} \\ \text{Total cloud volume} &= \frac{100 \times 10^3}{1.488} + \frac{1100 \times 10^3}{1.347} &= 8.1 \times 10^5 \text{ m}^3 \\ \text{Mean cloud density} &= \frac{1100 \times 10^3}{8.1 \times 10^5} &= 1.36 \text{ kg m}^{-3} \end{aligned}$$

This mean cloud density and temperature will apply for any mass of oxygen released where the air entrainment factor is ten in mass terms.

d) Varying air entrainment

The sensitivity of the dispersion results to the initial air entrainment assumption has also been considered. The cloud parameters have, therefore, been calculated for different initial air entrainment, as follows.

In some work on flash vaporising liquids stored at ambient temperature (e.g. Reference 5), the initial air entrainment has been taken to be 63 times the volume of flash vapour. This is based on the premise that the air entrainment is a function of the violence of the flash vaporisation, but its extension to refrigerated materials has not been validated by observations of releases. This assumption would yield:

$$\begin{aligned} \text{Flash volume of 1 kg mol oxygen (at boiling point)} &= 22.4 \times \frac{90}{273} &= 7.38 \text{ m}^3 \\ \text{Vapour density} &= 32 / 7.38 &= 4.333 \text{ kg m}^{-3} \\ \text{Flash volume} &= 0.23 \text{ m}^3 \text{ kg}^{-1} \\ \text{Flash fraction} &= 0.26, \text{ i.e. flash volume} &= 0.06 \text{ m}^3 \text{ (kg stored oxygen)}^{-1} \\ \text{Air entrained} &= 63 \times 0.06 &= 3.77 \text{ m}^3 \text{ (kg stored oxygen)}^{-1} \\ &= 4.6 \text{ kg ambient air (kg stored oxygen)}^{-1} \end{aligned}$$

i.e. an air entrainment factor of about 5 in mass terms rather than 10. This gives a cloud with initial temperature 241 K and density 1.48 kg m⁻³.

2. Rapid cryogenic releases

Two assumptions have been made for the rapid vaporisation in the early stages following a refrigerated spill, when vaporisation rates are high:

- (i) Turbulence produced by rapid vaporisation sufficient to produce similar degree of air entrainment to pressurised release base case.
- (ii) No air entrainment, giving a cloud of oxygen only initially, at 90 K, cloud density 4.33 kg m^{-3} , with cloud base area set equal to the bund area.

3. Continuous pressurised releases

The only case considered was the release arising from failure of a 50 mm (2 inch) diameter pipe, associated with a vessel at 15 bar. The degree of air entrainment assumed is as in the base case shown in Annex 4, 2. (i). The total volumetric release rate, including entrained air, is then $260 \text{ m}^3 \text{ s}^{-1}$.

4. Continuous vaporisation from refrigerated releases

Two cases have been considered:

A long term release of 40 kgs^{-1} vaporising from a banded spill, and a continuous release at 240 kgs^{-1} from an unbanded release, both following failure of a 150 mm (6 inch) diameter nozzle on a large refrigerated storage vessel. In each case the source density is 4.33 kgm^{-3} at 90 K (no initial air entrainment).

TABLE 1

DISPERSION RANGES FOR CONTINUOUS RELEASES IN VARIOUS WEATHER CONDITIONS

Approximate ranges in metres

Oxygen Concentration % v/v		CRUNCH			BRYANT	
1. Cryogenic spill from a 150 mm (6 inch) nozzle failure						
Evaporation rate (kgs ⁻¹)		D (3 ms ⁻¹)	D (6 ms ⁻¹)	F (2 ms ⁻¹)	D	F
	40 %	40	28	65		
40 (bunded spill)	30 %	48	32	74		
	25 %	60	40	86	115	450
	-40 °C, 0 °C	30, 45	21, 30	53, 73		
	40 %	146	82	227		
240 (unbunded spill)	30 %	170	96	320		
	25 %	215	120	390	320	1300
	-40 °C, 0 °C	110, 181	62, 100	220, 316		
2. Pressurised release from a 50 mm (2 inch) pipe failure						
Release rate		D (3 ms ⁻¹)	D (6 ms ⁻¹)	F (2 ms ⁻¹)	D	F
	40 %	-	-	-		
32 kgs ⁻¹	30 %	20	6	55		
	25 %	92	47	240	100	380
	0 °C	67	30	170		

TABLE 2

DISPERSION RANGES FOR INSTANTANEOUS RELEASES

1. Assuming instantaneous entrainment of a mass of air equal to ten times the mass of oxygen released. This produces a source cloud at about $-10\text{ }^{\circ}\text{C}$, with a density about 1.1 times that of air and with mean oxygen concentration about 30 % wt (27.3 % volume). Hazard ranges are quoted for 25 % volume oxygen (0.053 kgm^{-3} excess oxygen).

Oxygen (tonne)	Weather conditions	Downwind hazard range (m)	Upwind hazard range (m)	Total area affected to greater than hazard level (m^2)
100	D, 3 ms^{-1}	709	96	0.38×10^6
	D, 6 ms^{-1}	649	63	0.22×10^6
	F, 2 ms^{-1}	984	177	0.91×10^6
110	D, 3 ms^{-1}	737	100	0.41×10^6
	D, 6 ms^{-1}	665	65	0.23×10^6
	F, 2 ms^{-1}	1015	185	0.97×10^6
135	D, 3 ms^{-1}	793	110	0.48×10^6
	D, 6 ms^{-1}	729	70	0.27×10^6
	F, 2 ms^{-1}	1122	204	1.10×10^6
150	D, 3 ms^{-1}	820	115	0.51×10^6
	D, 6 ms^{-1}	767	72	0.30×10^6
	F, 2 ms^{-1}	1170	213	1.30×10^6
13	D, 3 ms^{-1}	326	41	0.08×10^6
	D, 6 ms^{-1}	311	32	0.05×10^6
	F, 2 ms^{-1}	433	74	0.18×10^6

2. Assuming no air entrainment initially, instantaneous boil-off from a cryogenic spill, oxygen temperature $-183\text{ }^{\circ}\text{C}$, density 3.54 times that of air. Cloud base area set to bund area, $8.8 \times 10^2\text{ m}^2$.

Oxygen (tonne)	Weather conditions	Downwind hazard range (m)	Upwind hazard range (m)	Total area affected (m^2)
13	D, 3 ms^{-1}		(Model not valid)	
	D, 6 ms^{-1}	209	85	0.05×10^6
	F, 2 ms^{-1}		(Model not valid)	

TABLE 3

**DISPERSION OF 13 TONNE AND 135 TONNE INSTANTANEOUS LIQUID OXYGEN
RELEASES TO VARIOUS CONCENTRATIONS**

Release (tonne)	Weather conditions (Category, wind speed ms ⁻¹)	25 % Range (m)	25 % Area (km ²)	30 % Range (m)	30 % Area (km ²)	35 % Range (m)	35 % Area (km ²)	40 % Range (m)	40 % Area (km ²)	Maximum duration (minutes)
135	D3	790	0.47	600	0.25	475	0.14	400	0.09	8.2
135	D6	720	0.27	545	0.15	445	0.09	355	0.05	~2
135	F2	1115	1.12	865	0.61	675	0.35	575	0.21	29
13	D3	325	0.08			195	0.023	165	0.015	3.7
13	D6	310	0.05			190	0.014	150	0.009	~1
13	F2	433	0.18			275	0.052	230	0.032	15

NOTES:

1. Source term assumes air entrainment is ten times mass of oxygen released.
2. Oxygen concentrations (25, 30, 35, 40 %) are total O₂, % volume.
3. Ranges are downwind ranges in metres (upwind ranges not quoted).
4. Areas are total exposed areas, i.e. upwind + downwind area, km² (i.e. m x 10⁻⁶).

Maximum duration quoted is maximum cloud passage time at any point downwind exposed to concentrations greater than 25 % volume total O₂



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