
Technical guidance on hazard analysis
for onshore carbon capture installations
and onshore pipelines

TECHNICAL GUIDANCE ON HAZARD ANALYSIS FOR ONSHORE
CARBON CAPTURE INSTALLATIONS AND ONSHORE PIPELINES

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This publication has been produced as a result of work carried out within the Technical Team of the EI, funded by the EI's Technical Partners. The EI's Technical Work Programme provides industry with cost-effective, value-adding knowledge on key current and future issues affecting those operating in the energy sector, both in the UK and internationally.

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FOREWORD

In 2006, the Department of Business, Enterprise & Regulatory Reform (formerly the DTi) asked the Health & Safety Executive (HSE) to determine if there were any health and safety concerns relating to the deployment of large scale carbon capture and storage (CCS) technology in the UK.

The HSE carried out a significant review on all aspects of the carbon capture and storage chain, from the various capture technologies through to the injection points on the offshore platforms. It identified a number of areas which it believed merited greater attention.

These concerns can be split into two broad subject areas:

1. Modelling the dispersion of any leak of carbon dioxide appropriately.
2. Ensuring good practice from industrial gases, chemicals and energy sectors is fed into the UK CCS industry.

Modelling the dispersion of any leak of carbon dioxide appropriately

The HSE was concerned that the commercial models available to model gas dispersion were not validated for carbon dioxide (which has particular thermodynamic properties). As a result, any dispersion modelling using these commercial models may not be accurate and without any validation of the models, it would be impossible to use them with any confidence.

Ensuring good practice from industrial gases, chemicals and energy sectors is fed into the UK CCS industry

The properties of carbon dioxide affect the choice of materials and plant design. Although many of these issues are well understood by the industrial gases sector, they are not necessarily standard practice. For example, certain elastomers are commonly used in seals in the power generation and oil and gas industry, but cannot be used for carbon dioxide as they explode when rapidly depressurised.

In response to the concerns raised by the HSE, the Energy Institute (EI) formed an industry group to work with the HSE to resolve the issues raised. The work forms two separate documents:

1. Guidance on hazard analysis for carbon dioxide in onshore CCS installations and pipelines.
2. Information on current practices in the industrial gases sector to inform the decision making and plant design and specification in the CCS industry.

The document is intended for guidance only and is intended to improve the industry's knowledge, to assist developers and operators to carry out hazard analysis, procure and manage their plant safely. While care has been taken to ensure the accuracy and relevance of its contents, this document is not and does not purport to be comprehensive or to contain all information that readers may require. Accordingly, the EI, its sponsoring companies, section writers and the working group members listed in the Acknowledgements (together 'the contributors'), cannot accept any responsibility for any inaccuracy or omission or action taken, or not taken, on the basis of this information. The EI and the contributors do make any representation or warranty in respect of the information contained in this document and shall not be liable to any person for any loss or damage which may arise from the use of any of the information contained herein.

Any comments or suggestions for improvements on this publication should be sent to the Technical Department, Energy Institute, 61 New Cavendish Street, London, W1G 7AR
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The project was coordinated by Isabelle McKenzie, CCS Technical Manager, Energy Institute.

1 INTRODUCTION

Who is Technical guidance on hazard analysis for onshore carbon capture installations and onshore pipelines for?

This publication provides information for:

- Health and safety practitioners who carry out hazard analysis of onshore carbon capture and storage (CCS) installations and pipelines.
- Modellers who carry out modelling for carbon dioxide dispersion for high pressure systems.
- Project engineers and managers who procure new CCS installations and pipelines.
- Engineering designers involved in the design of CCS installations.

What does this publication cover?

This publication provides information on:

- Hazard and risk analysis for carbon dioxide systems.
- Failure frequency data sources that could be used for carbon dioxide systems.
- Detailed guidance on the methods for using commercially available dispersion models within the hazard analysis.
- Fatal area predictions using SLOT/SLOD data and dispersion modelling.
- Gaps and uncertainties in modelling carbon dioxide systems.
- An overview of dispersion modelling fundamentals.
- Information on how previous incidents with carbon dioxide have affected industry practice.

Why the need for this publication?

This publication has been prepared to:

- Provide guidance on the methodology for carrying out hazard analysis of onshore CCS installations and pipelines.
- Communicate methods and sources of information required for hazard analysis to an audience that may not be familiar with modelling carbon dioxide.
- Communicate uncertainties in modelling of carbon dioxide.

What does this publication not cover?

- This publication does not cover offshore installations, where the dispersion modelling techniques would be different due to the use of other source terms. Source terms define the characteristics of a CO₂ release.
- This guidance should not be used for low/reduced momentum dispersion scenarios without expert guidance.
- This publication investigates hazard analysis with regard to carbon dioxide. We recommend that companies carry out full hazard analysis of installations and pipelines

- to include other possible hazards, e.g. impurities within the gas stream specific to the project, or other materials stored on site, to give comprehensive hazard analysis.
- In certain cases, the analysis contained in this publication should be combined with further modelling work, using different techniques to deal with particular topographical issues within any dispersion area. It may be useful to consider computational fluid dynamic (CFD) modelling, which may be suitable for confined or constrained areas.

Where can I find further information?

Further sources of information are listed in the References.

2 HAZARD AND RISK ANALYSIS OF CARBON DIOXIDE SYSTEMS

2.1 NEED FOR HAZARD ANALYSIS

The IChemE (Jones) definition for hazard analysis is the identification of a hazard, the analysis of the mechanisms by which these undesired events could occur and (usually) the estimation of the extent, magnitude and the likelihood of any harmful effects.

Losses from a hazard can often be caused by a responsible organisation or individuals failing to use available knowledge to prevent an incident, rather than a total lack of knowledge. Hazard analysis makes an important contribution to system safety by making an organisation aware of the hazards; to allow it to apply its knowledge in order to manage safety, or to enable it to seek outside help if the hazard is beyond its expertise or experience.

Various techniques are available for hazard analysis of the risks that may be associated with any particular process or operation. All seek to answer the following questions (in progression):

1. What undesirable events can happen?
2. How frequently can they happen?
3. What are the consequences?
4. Is the risk from the process or operation acceptable?
5. What can be done to avoid or reduce the likelihood of the events and/or reduce the consequences?

Hazard identification methods (e.g. 'What if?', 'How can?', 'Hazard and operability study (HAZOP)') are required to answer the first question. With relevant frequency data, questions two and three are answered by quantitative risk assessment (QRA) methods, the appropriateness of which (for carbon dioxide) is discussed later in this document. The final questions involve an iterative procedure until a defined acceptable risk level for the process is obtained.

The work process to be carried out for the hazard analysis of a CCS system is summarised in Figure 1. The risk measures, data sources and analysis techniques indicated are discussed in more detail in the following sections.

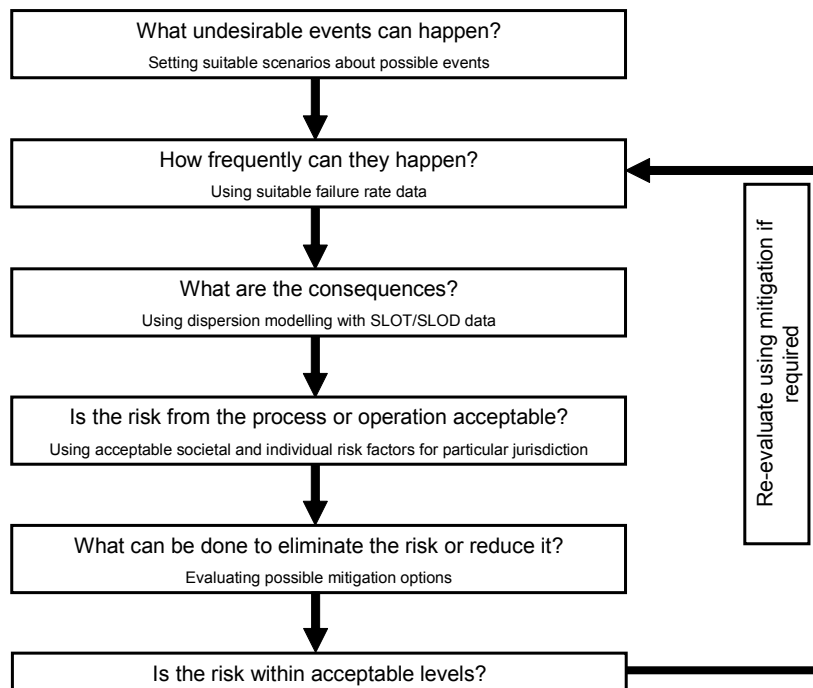


Figure 1 Flow diagram of basic hazard analysis process, which is also relevant for a CCS installation

2.2 WHAT MIGHT HAPPEN?

Setting scenarios that reflect the range of loss of containment issues that might occur is crucial to evaluating the hazard. A loss of containment incident on a carbon dioxide processing or transportation plant (including pipelines) may result in the release of a gas cloud or an uncontrollable release of energy. Harm can be caused by the ingestion of the gas, low temperatures in the vicinity of the release or the effects of the physical blast. Damage to adjacent equipment, structures (such as buildings) and the environment need also to be considered where appropriate, especially if collateral damage produces further knock-on results such as fires or explosions, release of stored material, or missiles (blast fragments). Failures may range from small, transient leaks through to large scale vessel or pipe ruptures, and the potential consequences may vary from inconsequential or reversible health effects through to fatal or serious injury, and major economic effects from the damage caused.

2.2.1 Failure cases

Suitable hazard identification techniques and information from known incidents should be used to identify possible loss of containment events that need to be looked into for further detailed analysis.

In order to determine the risks from an accidental loss of containment of carbon dioxide, various failure cases for the processes involved will need to be considered, release scenarios determined and release and dispersion modelling carried out to evaluate the consequences.

Classical hazard analysis of chemical processes would aim to cover the whole range of hazardous events to obtain a model for the total risk from the process being considered, whereas studies to determine the worst case events need only model the consequences of the perceived largest failure cases. Either way, the use of appropriate commercial computer codes to model release cases and obtain dispersion results is undeniably the best way of carrying out the consequence calculations. If the total process risk is to be considered, the data being processed to obtain a result will generally be so large that only computer-aided mathematical calculations will be practical. A number of commercial dispersion modelling programmes combine risk calculations with consequence modelling for the addition of appropriate frequency, probability and physical data.

For worst case events (including, where required, estimation of frequency and maximum potential fatalities) hand or spreadsheet calculation from the consequence modelling is a practical alternative.

The concern is that failure to analyse the potentially large number of smaller events may result in overlooking the hazards to an individual or group of individuals (such as operators or itinerant workers) much closer to the process or pipeline transportation system.

Depending on the risk evaluation required, the failure cases may need to cover the whole range of possible events from small continuous releases (representing undetected or irremediable leaks from the processes) through to line ruptures or catastrophic failure of vessels where large but finite inventories of hazardous material could be released.

An intermediate case that could be of interest because of the particular physical properties of carbon dioxide, is a 'running crack', where an initial small failure in the pipe steadily propagates into an extensive crack running along the length of a section of line. One of the final scenarios from this type of failure might be a release equivalent in total flowrate to a line break but because it would be emanating from a 'line source' term, it would not necessarily have the impact of the corresponding full bore pipeline rupture. Alternatively a running crack may result in the equivalent of a full bore line rupture with carbon dioxide flowing from both sides of the resulting rupture.

2.2.1.1 Topography and impingement

Particular scenarios may need to be modelled due to project-specific characteristics. For example, where projects propose a pipeline route through any terrain which would affect the dispersion of the cloud such as a valley, or heavily urbanised areas, then additional modelling may be required to understand the dispersion of the cloud. In many cases, further modelling techniques such as CFD modelling (to evaluate the concentrations in the gaseous cloud) will be needed. In particular, we draw attention to any possible impingement near the source of the release (i.e. near the source term) which may reduce the cloud momentum and hence air entrainment into the cloud which will increase the resultant carbon dioxide concentration in the cloud. In pipeline corridors, impingement can occur if the release is downwards or if the object (such as a digger) that caused the failure impinges on the release. Impingement also occurs on capture and storage sites. Where any impingement occurs, additional modelling and analysis will be required to ensure that concentrations are modelled adequately.

This publication provides some example calculations of hypothetical rupture failure cases in high pressure carbon dioxide pipelines with appropriate mathematics using selected data to evaluate individual fatal accident risk.

2.2.1.2 Physical blast

A rupture may result in a physical blast close to the site caused by the expansion ratio of the

liquid to gas. The effect of the physical blast can be calculated using a TNT equivalent¹ or similar models.

2.3 UNDERSTANDING THE LIKELY FREQUENCY

2.3.1 Need for failure rate data

One result of risk being defined in mathematical terms of frequency or probability is the necessity of having (or being able to estimate) failure rate data for the cause of the undesired event. Ideally historical data for the exact causes of previous events would produce the most accurate future risk predictions. However, assembling such data in sufficient detail is notoriously difficult except in specialised industries or situations (e.g. the nuclear industry or aircraft crash investigation) where the value of such data to the owners or operators is clear. Recourse often has to be made to more generalised sources of data in order to carry out risk calculations.

Examples of data sources that could be pertinent to the separation, compression and transmission of carbon dioxide are given in 2.3.2.

Although such data may not represent the exact failure mechanisms likely to be encountered for carbon dioxide, the data can be adjusted to account for known variations in physical conditions, or, more easily, used to calculate bounding (or worst case) outcome likelihoods. Normally the criteria for acceptability of risk are defined in terms of orders of magnitude/bands of tolerability that are set conservatively. Thus generic data may be adequate to screen out which risks are likely to be unacceptable without further detailed consideration of avoidance, protection or mitigation (for which more accurate use of data may be required). Additionally, in the UK, the concept of having to demonstrate that the detrimental effects are being kept as low as reasonably practicable (ALARP) means that additional cost-effective improvements to reduce risk should never be ruled out irrespective of the originally calculated risk.

2.3.2 Introduction to failure frequency data sources

Failure rate data may be obtained in a number of ways:

- By sample testing - usually of mechanical or electrical components in a specific test environment.
- From plant experience - by companies from reliability based data collection, or by organisations collating and analysing industry or nationwide incident reports.
- From data banks and literature sources - much of the plant experience data and component information is reported in this way.
- By predictive techniques - appropriately combining component data on constituent parts of a complex system e.g. by using fault tree analysis.

¹ 'TNT equivalent' is a method of quantifying the energy released in explosions. The tonne of TNT is a unit of energy released in the detonation of one ton of TNT, approximately equal to 4,184 GJ.

Generally data for risk assessment will be from data banks and literature sources. However, there are potential drawbacks with their use in that much of the information may come from sources such as the nuclear, aerospace or defence industries where the necessary high quality of installation, maintenance and testing may mean that the data collected may be optimistic for other less-regulated industries or processes.

In addition, literature sources will inevitably be historical compilations and can suffer from being incomplete or out-of-date for modern applications. For example, Lees' *Loss Prevention in the Process Industries*² although currently published as the third edition in 2005 contains pipeline event and failure data references (Table 23.1) only up to the end of the 20th century. Lees' list of principal reliability data sources (Table A14.1) cites Davison³ as its source but this was published in 1994.

Published data considered appropriate as sources for QRA of carbon dioxide separation, compression and pipeline transmission systems are given in 2.3.3. However care will be required even in the use of such selective data because of the potential effects of differences between CCS systems and the source industries.

2.3.3 Example data sources for failure rate data

2.3.3.1 European Gas Pipeline Incident Data Group (EGIG)

EGIG is a cooperation of 12 major European gas transmission system operators and is the owner of an extensive database of pipeline incident information collected since 1970.

EGIG has maintained and expanded the European gas pipeline database. The transmission companies now collect data on more than 122 000 km of pipeline each year. The total exposure, which expresses the length of a pipeline and its period of operation, is 2,77 million km/yr.

The statistics of all incidents collected in the database give failure frequencies. The seventh report⁴ gives an overall incident frequency equal to 0,37 incidents per year per 1 000 km over the period 1970 to 2007. The five-year moving average, which represents the average incident frequency over the last reported five years, equals 0,14 per year per 1 000 km. This frequency is almost six times lower than that reported in the first years of the database. Failure frequencies have been reducing regularly year-by-year although the rate of change has fallen in recent years.

The reported major cause of incidents remains external interference (third party damage) (50 % of all incidents), followed by construction defects/material failures (16 %) and corrosion (15 %).

² Mannon S. (ed) *Lees' Loss prevention in the process industries* 3rd edition, 2005 (Elsevier Butterworth – Heinemann, Oxford UK).

³ Davidson J.(ed) *Reliability of mechanical systems* 1994 (IMechE, London UK).

⁴ Seventh report of the European Gas Pipeline Incident Data Group *Gas Pipeline Incidents 1970-2007* Published Dec 2008.

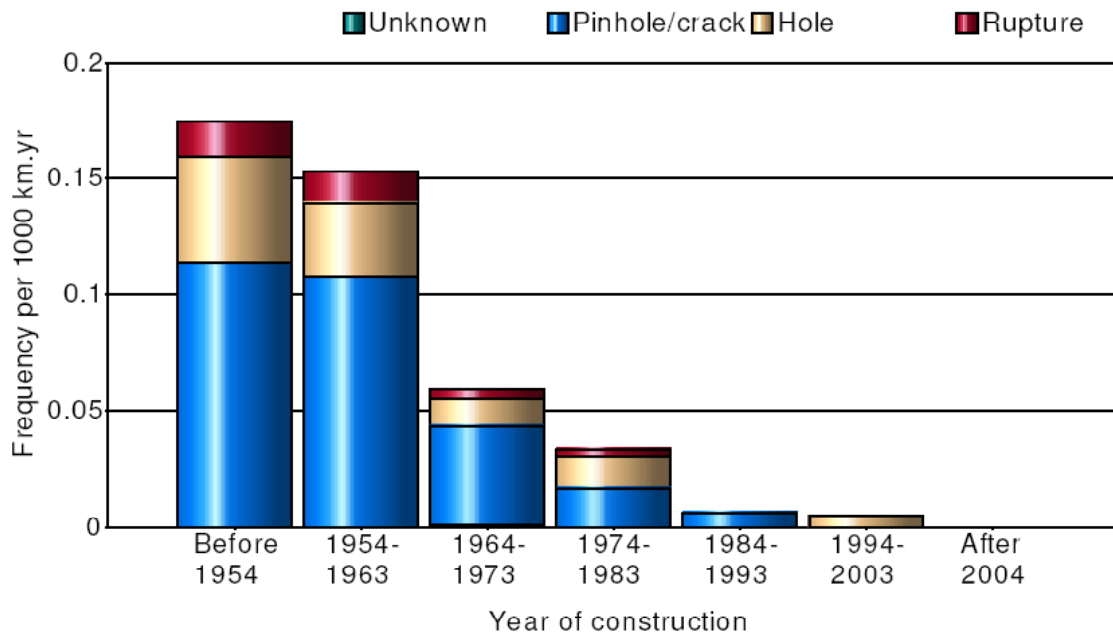


Figure 2 Effect of year of construction on likely failure

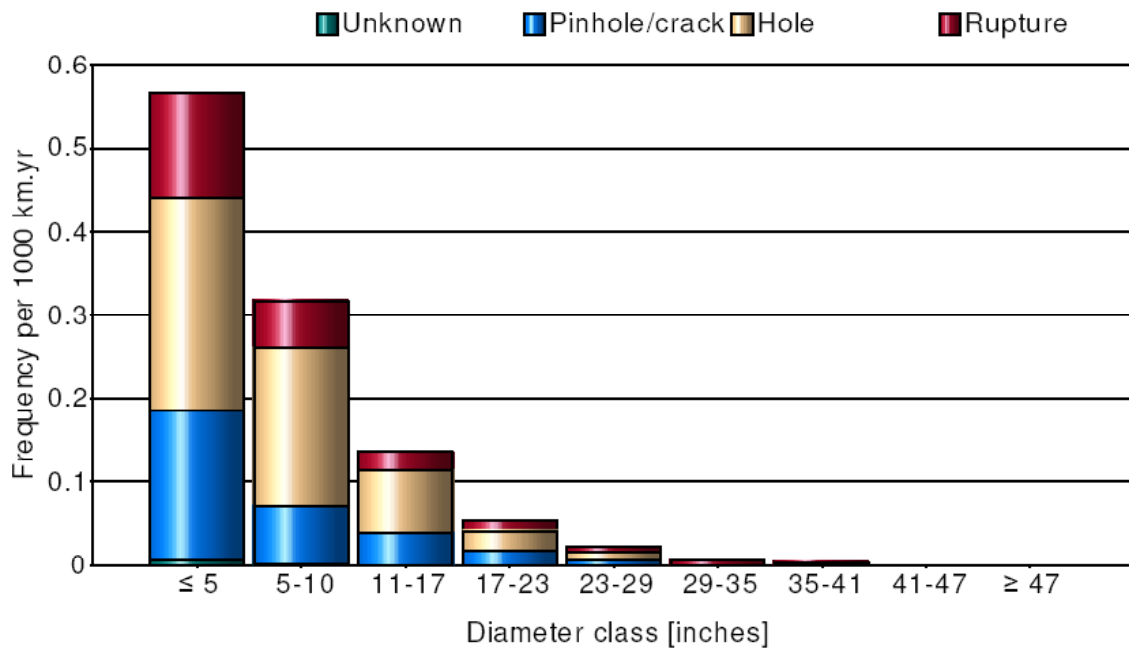


Figure 3 Impact of pipeline diameter on failure frequency and mode

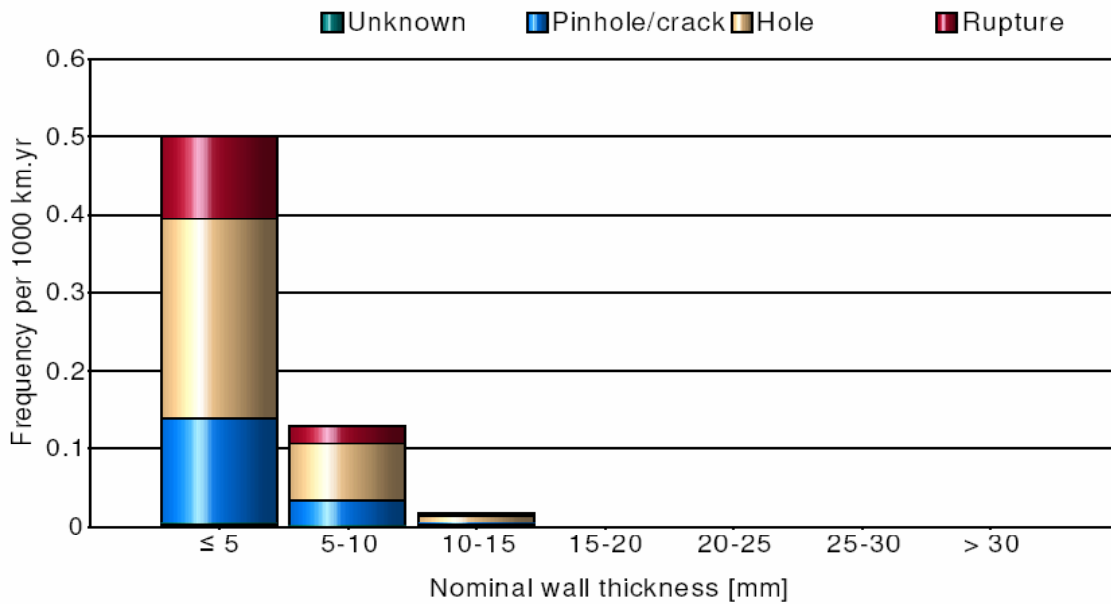


Figure 4 Impact of wall thickness on failure frequency and mode

2.3.3.2 UK Pipeline Operators Association (UKOPA)

UKOPA is an independent organisation which provides a formal, recognised forum for UK pipeline operators to discuss, establish and present a consistent view on strategic issues of mutual interest relating to the safe operation and maintenance of pipelines. One of UKOPA's primary aims is to influence the development of a consistent risk-based approach to land use in the vicinity of new and existing pipelines. A key factor in achieving this is the availability of a UK pipeline database containing failure data for all pipelines. UKOPA has launched a joint industry initiative to develop this database.

The latest UKOPA report⁵ presents collaborative pipeline and product loss incident data from onshore major accident hazard pipelines (MAHPs) operated by National Grid, Scotia Gas Network, Northern Gas Network, Wales and West Utilities, Shell UK, BP, Huntsman and E-ON UK, covering operating experience up to the end of 2006. The data presented cover reported incidents within the public domain on pipelines (i.e. not within a compound), where there was an unintentional loss of product from the pipeline. Unlike the Europe-wide EGIG, this UKOPA database contains extensive data on pipeline failures and on part-wall damage, allowing prediction of failure frequencies on pipelines for which inadequate failure data exist.

The overall failure frequency over the period 1962 to 2006 is 0,248 incidents per 1 000 km/year, whilst for the EGIG data in the previous section this figure was 0,263 incidents per 1 000km/year (covering the period from 1962 to 2004).

The failure frequency over the five-year period up to the end of 2006 is 0,028 incidents per 1 000 km/year, which remains unchanged from the figure in the previous report (covering the five-year period up to the end of 2004).

⁵ Document 07/0050 - UKOPA Pipeline Fault Database *Pipeline Product Loss Incidents (1962 - 2006)*

2.3.3.3 Conservation of Clean Air and Water in Europe (CONCAWE)

An extensive network of cross-country oil pipelines in Europe meets a large proportion of the need for transportation of petroleum products. For more than 30 years CONCAWE has been collecting facts and statistics on incidents and spills related to European cross-country pipelines.

At over 35 000 km the inventory covered currently includes the vast majority of petroleum pipelines in Europe, transporting around 800 million m³ per year of crude oil and oil products. The latest CONCAWE report⁶ covers the performance of these pipelines in 2006 and a full historical perspective since 1971. The performance over the whole 36 years is analysed in various ways, including gross and net spillage volumes, and spillage causes grouped into five main categories: mechanical failure, operational, corrosion, natural hazard and third party.

12 spillage incidents were reported in 2006, corresponding to 0,34 spillages per 1 000 km of line, slightly above the five-year average but well below the long-term running average of 0,56, which has been steadily decreasing over the years from a value of 1,2 in the mid-70s.

Half the incidents were related to mechanical failures, four incidents to third party activities and two to corrosion. Over the long term, third-party activities remain the main cause of spillage incidents.

2.3.3.4 Pipeline and Hazardous Material Administration (U.S. Department of Transport (DOT))

Statistics on pipeline incidents in the United States can be found at the Office of Pipeline Safety (OPS) within the U.S. Department of Transportation, Pipeline and Hazardous Materials Safety Administration.

Carbon dioxide pipeline failure data⁷ are contained within the hazardous liquid accident data, despite carbon dioxide being both a gas when released at ambient conditions and classed as non-hazardous under DOT regulations. These data are the only specifics related to transmission of compressed supercritical carbon dioxide. The carbon dioxide is used for enhanced oil recovery through a system of onshore pipelines over a network of approximately 5 000 km.

Det Norske Veritas (DNV) have analysed the data⁸, and report corrosion to be the major single cause of failure for carbon dioxide in the US system during 1986-2008. A separate analysis⁹ of the same data through to 2002 reported an incident rate of 0,33 per 1 000 km/year, which is higher than pipeline failure data reported from the US hydrocarbon pipeline transmission system. However, the authors caution on drawing conclusions from such a comparison because the carbon dioxide system sample size is small.

The data from all these sources are summarised in Table 1.

⁶ CONCAWE report no. 7/08 *Performance of European cross-country oil pipelines - statistical summary of reported spillages in 2006 and since 1971*.

⁷ Office of Pipeline Safety (OPS) within the U.S. Department of Transportation, Pipeline and Hazardous Materials Safety Administration (<http://ops.dot.gov/stats/IA98.htm>).

⁸ Johnson, K. et al *Mapping of potential HSE issues related to large-scale capture, transport and storage of CO₂* DNV report number 2008-1993, 2009 (Det Norsk Veritas, Horvik, Norway).

⁹ Gale, J. and Davidson, J. *Transmission of CO₂ - safety and economic considerations* Energy, 29, 2004: pp.1319-1328.

2.3.4 Overall summary of failure data

	EGIG	UKOPA	CONCAWE	US DoT
Overall	0,37	0,25	0,56	0,33
Latest five-year rolling average	0,14	0,028	0,34	NA*

*Evaluated data are for early period of operation only.
Reported failures of past five years indicate that rolling average will be higher than overall value given.

Table 1 Pipeline failure data summary (incidents per 1 000 km/year)

2.3.5 Plant equipment failure data

Lees' *Loss prevention in the process industries or Offshore reliability data handbook* 4th edition, (OREDA) contains references to plant equipment failure rate data from numerous sources. As previously discussed component data from such sources could be synthesised into appropriate plant failure data if the nature and size of the plant (process) were available.

A convenient (though dated) compilation of plant equipment leak data is given in Annex 8 of Cox, Lees and Ang¹⁰. In the publication, Cox is showing a case study on how to put together leak frequency and size data for a defined 'standard plant'. This deals specifically with the problem of estimating frequencies of ignition of flammable leaks for hazardous area classification. However it has relevance to QRA for the risks from loss of containment of any physical process such as for carbon dioxide where flammability is not an issue.

2.3.6 Selecting appropriate failure rate data for pipelines

Whilst there is a small body of failure rate data for carbon dioxide pipelines and a larger body of data for other pipelines, it is important to analyse the data and understand the likely failure modes for carbon dioxide versus other pipelines to ensure that appropriate comparisons are being drawn.

2.3.6.1 Third-party interference

For carbon dioxide pipelines, failure by third party interference is likely to be comparable with all pipeline types. European gas pipeline data indicate that, where pipelines are buried and are likely to follow similar pipeline routing, the likelihood of third party interference to carbon dioxide pipelines will be comparable in European countries. EGIG results show that the largest failure mechanism is third party interference. Likewise, US data, where carbon dioxide pipelines often run overground, may be a better comparison for developers who are developing over-ground networks.

¹⁰ Cox, Lees and Ang, *Classification of hazardous locations* published 1990 (Institution of Chemical Engineers, Rugby UK). *Offshore reliability data handbook* 4th Edition, (OREDA 2002), prepared by SINTEF and distributed by DNV.

2.3.6.2 Corrosion

Corrosion is a common failure mode for pipelines and is the largest single cause cited for US carbon dioxide pipelines. The applicability of corrosion data will depend on the design and operation of the pipeline. Corrosion risk can be mitigated through the rigorous control of moisture in the carbon dioxide stream, ensuring that there is no free water and insufficient dissolved water to reduce hydrate formation across the range of operating conditions within the pipeline. Control and inspection in the event of water ingress will be an important element in the operating procedures.

The design of the pipeline, such as the material selected and methods of construction, will have a direct bearing on the likelihood of failure through corrosion.

When screening projects in the early design phase, using a range of failure frequency data will allow an understanding of how design criteria and operating techniques may impact on the likelihood and severity of a failure.

2.3.6.3 Other failure modes

Other failure modes for pipelines can be designed out or considered specifically. The appropriate selection of seals and valves for carbon dioxide service - in particular the careful use of elastomers which are designed for carbon dioxide service and will not fail through explosive decompression - will mitigate against failure at valve locations, along with an appropriate maintenance regime. Impurities within the stream, including the range of likely impurities over normal and abnormal operating conditions must be included within the pipeline design considerations. Secondary effects of a failure should also be considered. These can include:

- Possible further brittle failure through local cold temperature effects.
- Ground movement giving rise to movement of the pipeline and/or displacement of its supports.
- Secondary damage to surrounding equipment from the effects of a rapidly cooling high pressure release.
- Movement of any debris during the initial moments of release.

2.3.7 Selecting appropriate failure rate data for plant

There are less data available for failure rates at plants, although existing data sources provide a valuable starting point. Further data gathering on carbon dioxide/CCS specific equipment failure rates (for equipment in service in CCS and other applications) should be gathered in a systematic way to improve failure rate estimations.

2.4 WHAT ARE THE CONSEQUENCES OF AN EVENT?

To understand the consequences of the event, it is necessary to model the dispersion of the carbon dioxide (giving the concentrations) combined with the lethality of those concentrations. The toxicological and asphyxiant hazards of carbon dioxide are discussed in *El Good plant design and operation for onshore carbon capture installations and onshore pipelines*. Carbon dioxide displaces air in confined areas (as it is heavier) and can settle in a particular area. In such instances it acts as an asphyxiant. Where there are continued sufficiently high concentrations of oxygen to support human life, high concentrations of carbon dioxide exhibit a toxicological impact. This second scenario can occur in high momentum releases.

The following sections continue with a discussion of release scenarios and the dispersion programmes available to model a compressed dense/supercritical fluid release, plus the specifics required to model carbon dioxide - which has markedly different physical properties from the gases for which the commercial codes were originally produced. This

publication then provides a review of the data that are needed to complete a hazard analysis with specifics on the dose-response relationship for probability of fatality from exposure to carbon dioxide.

In order to adequately discuss model inputs and outputs a common software baseline was used by the authors. Numerous software packages and codes are available, however referencing and considering modelling in a particular application enables detailed consideration to be given. The use, and referencing of, DNV PHAST¹¹ does not represent an endorsement of this system by the EI, and any modeller should refer to their software provider to discuss limitations and validity for use with carbon dioxide.

2.4.1 Introduction to commercial dispersion models

Although a large number of computer models exist to predict the results of accidental release of dense gases or fluids, only a small number have been evaluated as being suitable for general use and, in particular, for accuracy of result against feed test data obtained by experiment for dense gas releases. The American Center for Chemical Process Safety¹² has reported on 22 of the models (both public and proprietary), and tested the accuracy of 10 of these against selected field test data. PHAST, as a widely used proprietary package of predictive risk and consequence calculation programmes, was included in the evaluation and performed well against the measured data¹³. For this reason and its general availability, PHAST has been used to carry out the example calculations for the rupture cases used later in this publication (section 3.4).

However, the peculiar physical properties of compressed carbon dioxide mean that the versions of PHAST available at the time of drafting (version 6.53.1 and 6.54) can potentially produce run errors in the programmes due to an inability to always automatically generate appropriate source terms (the concept of a 'source term' is explained in section 3)¹⁴.

2.4.2 Recommended modelling techniques for carbon dioxide hazard analysis using commercially available models (excluding PHAST)

Most models allow source term data to be input directly into the model. This allows the user to place correct physical properties for carbon dioxide within the models and obtain dispersion modelling results.

The selection of the source term parameters used for dispersion modelling must be done with care and recommendations are given in Table 2 on bounding assumptions when carrying out screening calculations.

¹¹ PHAST is a hazard analysis computer package, applicable to all stages of design and operation across a range of process and chemical industry sectors. It is used to identify situations which present potential hazards to life, property or the environment.

¹² *Guidelines for Use of Vapor Cloud Dispersion Models* 2nd Edition 1996 (American Institute of Chemical Engineers, Center for Chemical Process Safety - New York, USA).

¹³ See Figure 8-3 in CCPS reference.

¹⁴ Witlox, H.W.M., Harper, M., and Oke, A. *Modelling of discharge and atmospheric dispersion for carbon dioxide releases* Mary Kay O'Connor Process Safety Center - 2008 International Symposium and World Conference on Safety of Oil and Gas Industry, Houston, October 2008 (also submitted for publication in *Journal of loss prevention*).

Table 2 Recommended source term assumptions

Source term component	Recommended modelling method	Notes
Initial flow rate	Use two-phase flashing flow models for the liquid flow rate ignoring solid formation.	
Solid formation and entrainment	All solid entrained and contributes to the cloud.	This is based on observations of liquid CO ₂ jets at about 15 barg on operational CO ₂ production facilities. When the pressure of the source reduces to a value close to the triple point, solid CO ₂ 'snow' will 'rain out' rather than remain entrained in the jet, but by this time a substantial amount of inventory may have been released and the mass emission rate will be relatively small. (These notes are designed to help screen modelling scenarios. Total solid entrainment into the cloud gives a conservative estimate (i.e. high) of mass flow in the cloud. It does not imply that all will become entrained and that there will be no solid carbon dioxide hazard at the site. Further work on solid entrainment and particularly in cases where the heat energy in the plume is reduced would improve modelling results.
Momentum jet velocity	Assume jet velocity does not exceed the sonic velocity	Care needs to be taken, some models use a 'pseudo velocity' as a calibration factor in the initial jet phase calculation. If in doubt consult the supplier of the model ¹⁵ .
Initial CO ₂ density	Use data available from various well known sources e.g. National Institute of Standards and Technology (NIST)	
Other data/ physical properties data (JT coefficient, Cp, Cv, Entropy, Enthalpy etc)	Use data available from various well known sources e.g. NIST.	

¹⁵ For choked flow the orifice speed (before atmospheric expansion) equals the sonic speed, while for the subsequent atmospheric expansion 'supersonic' flow may occur. As indicated, many models presume a 'pseudo velocity' as input to the dispersion model. It should be realised that it is more important that the near-field jet entrainment is predicted accurately (and therefore the concentrations in the near-field), rather than that the correct value of the post-expansion velocity is chosen.

2.4.3 Combination of dispersion modelling and SLOT/SLOD data to give fatal area predictions

Consequence modelling from the dispersion calculations involves determining the effect distances for any given level of harm which can be caused for each failure case. The effect distances may vary depending on the weather conditions and orientation of release as well as the release conditions defined in each failure case. Unless the worst case effect distance found for all calculated failure cases and release variables is small enough to determine that the risk is already tolerable (usually because of adequate separation of possible hazard sources from potentially exposed populations), further calculations are required. These calculations need to take into account the risk that each failure case can have on any local population, and should sum all the risks from the cases and conditions being considered in order to produce, as appropriate, either the individual or societal risk measures discussed in 2.5.3 and 2.5.5. Such calculations comprise the QRA, also discussed in 2.5.

The frequency for each failure case is required, and has to be estimated or obtained from sources such as those in 2.3. Additionally, population data for the potentially exposed area will be required. These data may need to be divided between day and night depending on whether the exposed population varies in this timescale. Unless the release mechanisms in the individual failure cases are independent of the weather conditions (i.e. they are directional through equipment orientation or extreme terrain effects), probability data on weather conditions and wind directions will also need to be obtained. Probability data or event trees may need to be constructed to account for possible measures in place as mitigations of the consequences of the cases considered (e.g. likelihood that release durations are restricted by activation of emergency shutoff valves (ESVs), or protection available to exposed populations by being indoors or through timely evacuation).

All of the above can be obtained straightforwardly by QRA analysts. However data for the level of harm to be considered (which in the case of a carbon dioxide release is the risk of death or irreversible serious injury) are more specialised, and are dependent on available toxicological research information.

Table 3 Exposure reactions to carbon dioxide

Concentration in air (% v/v)	Effect
1 %	Slight increase in breathing rate.
2 %	Breathing rate increases to 50 % above normal level. Prolonged exposure can cause headache, tiredness.
3 %	Breathing increases to twice normal rate and becomes laboured. Weak narcotic effect. Impaired hearing, headache, increase in blood pressure and pulse rate.
4-5 %	Breathing increases to approximately four times normal rate; symptoms of intoxication become evident and slight choking may be felt.
5-10 %	Characteristic sharp odour noticeable. Very laboured breathing, headache, visual impairment, and ringing in the ears. Judgment may be impaired, followed within minutes by loss of consciousness.
10-15%	Within a few minutes exposure, dizziness, drowsiness, severe muscle twitching, unconsciousness.
17-30%	Within one minute, loss of controlled and purposeful activity, unconsciousness, convulsions, coma, death.

Table 3¹⁶ shows reactions of the human body to various concentrations of carbon dioxide in air. However individuals will have varying responses to concentration levels and the duration of exposure, and there can be no discrete predictable point where all individuals will have an identical reaction to any given gas exposure. A more appropriate method is to use probability distribution mathematics on observed or experimental data for exposure of large populations to specific doses. This should result in a statistical model for assessing the dose-response relationship for a generalised typical population. The probability unit (Probit) method is a customary analysis technique used to obtain a generalised time-dependent relationship for any variable that has a probabilistic outcome that can be defined by a normal distribution. See Lees' or similar standard texts for detailed discussion on Probit¹⁷. The relationship would be of the form:

Probit = a + b log (dose) where a, b are constants characteristic of the gas (or any other agent).

HSE's specified level of toxicity (SLOT) and significant likelihood of death (SLOD) levels for carbon dioxide can be used to set the threshold and 50 % mortality levels of any exposed population for carbon dioxide. The HSE data are given in Table 4.

Table 4 SLOT and SLOD values for carbon dioxide

Exposure period (min)	CO ₂ concentration (%) producing:	
	SLOT	SLOD
0,5	11,5	15,3
1	10,5	14,0
10	7,9	10,5
30	6,8	9,2
60	6,3	8,4
120	5,5	7,7

The HSE paper *Assessment of the dangerous toxic load (DTL) for specified level of toxicity and significant likelihood of death (SLOD)*¹⁸ gives the DTL values for SLOT and SLOD from which the following Probit for fatality from exposure to carbon dioxide can be derived assuming that SLOT is equivalent (conservatively) to a 1 % probability of mortality in an exposed population.

$$Y = \ln C^8 \cdot t - 89.8$$

(Y is the Probit value, C is concentration of carbon dioxide in air in parts per million by volume, t is exposure time in minutes)

The Probit variable is normally distributed between 2 (zero probability) and 8 (100 % probability of outcome) with a mean value of 5, and a standard deviation of 1. The derived Probit for carbon dioxide gives the following probability results that fit the data for SLOT and SLOD.

¹⁶ Ref. *Air Products and Chemicals, Inc Safetygram-18 1993* and <http://www.ptil.no/getfile.php/PDF/Ptil%20CCS%202008.pdf> Table 6.1

¹⁷ Lees' (ibid) Chapter 9 Section 9.18.3

¹⁸ From <http://hse.gov.uk/hid/haztox.htm>

Table 5 Derived probability of fatality for carbon dioxide

Probit	Probability of fatality (%)	Concentration for one minute exposure (%)	Concentration for 10 minute exposure (%)	Concentration for 60 minute exposure (%)
7,85	99,75	20	15	12
6,06	85,5	16	12	9,5
5	50	14	10,5	8,4
3,76	11	12	9	7,2
2,67	1	10,5	7,9	6,3

Graphically, the Probit result is as shown in Figure 5.

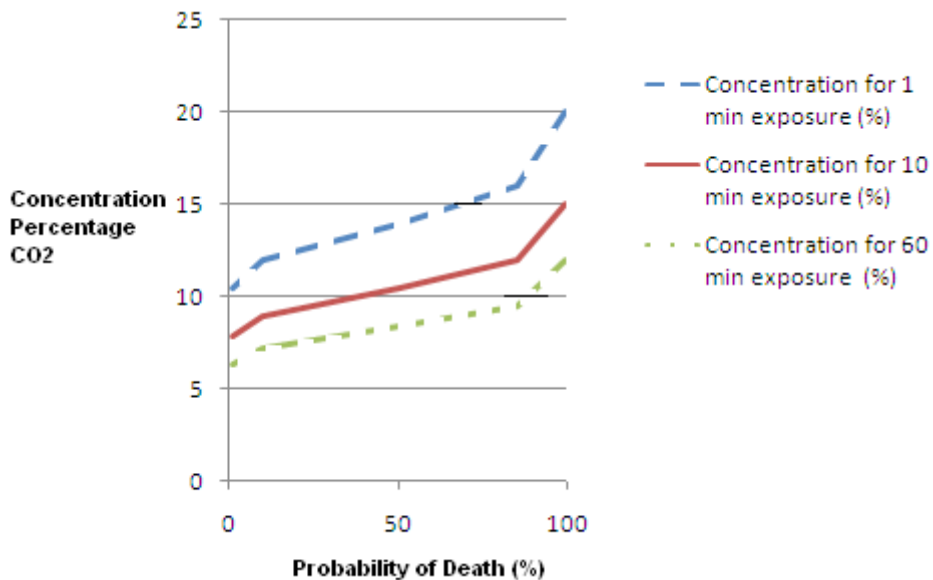


Figure 5 Carbon dioxide dose-fatality relationship

2.4.4 The impact of impurities on carbon dioxide consequence modelling

It is unlikely that CCS facilities will be processing or transporting pure carbon dioxide. This means that the impact of the impurities on the source term needs to be assessed. Of particular importance is the impact of the impurities on the predicted mass flow rate from any of the release scenarios. If the impurities are likely to reduce the mass flowrate then, for the purposes of risk assessment, they can be ignored unless the chosen risk criteria cannot be met.

In addition to the impact on the source term, impurities that may be toxic, such as hydrogen sulphide or carbon monoxide, could be present within a CCS facility or pipeline. It is imperative to check that such impurities do not constitute the 'defining' hazard in terms of consequence modelling from carbon dioxide-containing equipment.

2.5 IS THE RISK ACCEPTABLE?

Once a scenario is modelled and a percentage likelihood of fatality is calculated, it is necessary to determine if that risk is acceptable. This section discusses the issue of acceptable risk.

2.5.1 The concept of risk and its definition

It is first necessary to define risk, and important to differentiate risk from hazard since to the non-expert the terms are usually interchangeable. The following definitions are taken from the Institution of Chemical Engineers (Jones¹⁹), although others exist.

Hazard is a physical situation with a potential for human injury, damage to property, damage to the environment, or some combination of these.

Risk is the likelihood of a specified undesired event occurring within a specified period. It may either be a frequency (the number of specified events in a given period) or a probability (the chance of the specified event following a prior event). Mathematically, risk is a function combining both the failure events and the consequences of them.

Risk occurs in every human activity and is virtually impossible to eliminate without avoiding the activity completely. As a generality for industry, if the activity is to take place at all, the risk should be kept ALARP, and the remaining risk has to be at a level that is acceptable to workers, the public at large, and the appropriate regulatory authorities or internal standards of an organisation. These authorities will usually define the criteria for acceptability of any risk as well as policing compliance to manage the risk at the levels intended.

2.5.2 Introduction to the elements of risk

Some hazards by their nature result only in a risk to individuals (i.e. one person is affected at any one time). It can be appropriate to express the level of risk simply in terms of likelihood of death in a year. An example²⁰ of such measures would be:

Risk of being fatally struck by lightning in the UK (per year) is 1 in 10 000 000.

Comparison of levels of risk by this method is generally unsatisfactory not least because the likelihood of exposure of the affected population is never clear. Such measures can however be useful in establishing the tolerability criteria²¹ to be applied to risk since the example is a generally unavoidable (involuntary) risk taken without question by the general public.

¹⁹ Jones, D.A. (ed.) *Nomenclature for hazard and risk assessment in the process industries* 2nd edition 1992 (IChemE, Rugby, UK).

²⁰ Skelton, R., *Process safety analysis – an introduction* 1997 (IChemE, Rugby UK).

²¹ The basis for establishing risk criteria is not fully discussed here. General references on the subject such as Lees' *Loss prevention in the process industries* should be consulted.

Better measures of individual risk include statistics based on death (or serious injury) per unit of activity. This takes into consideration the exposure time of the individual to the hazardous activity. The UK chemical industry developed the statistic of fatal accident rate (FAR) that has been extended to cover a wide range of industrial and other activities. The FAR is the number of deaths expected per 100 million exposed hours (or more descriptively, the number of deaths expected in a workforce of 1 000 during a working lifetime). A commonly published example²² of this measure is:

FAR for the chemical and allied industries in 1987-1990 was 1,2.

Again there can be difficulty in using and comparing statistics on this basis. For this example the scope of the data source (the chemical and allied industries) is not disclosed, and the fact that the great proportion of fatal accidents within the chemical industry are not particularly related to the process hazards is not shown (trips, falls from heights and contact with objects predominate). The fact that the chemical industry (or its components) can show progressive improvements in the FAR over time due to safety management techniques, but the publication of such data in the literature lags far behind this reduction, also affects views on risk criteria acceptability.

QRA calculations for a particular hazardous process or activity can generally produce risk results expressed or illustrated in the following terms:

- individual risk;
- risk contours;
- societal risk, and
- fatality-number (F-N) curves.

All of these could be relevant to the hazard analysis of a carbon dioxide separation, compression and distribution system, and are detailed in the following sections.

2.5.3 Individual risk

The IChemE (Jones) definition for individual risk is the frequency at which an individual may be expected to sustain a given level of harm from specified hazards. Such a risk is location specific, and is also dependent on the fraction of time a person is likely to be at each hazard location in question. Assuming the 'level of harm' is defined as fatality, the individual risk is equivalent to the FAR term defined above except that it will usually be expressed as fatalities per year rather than per hour of exposure.

2.5.4 Risk contours

Visualisation of QRA calculation results for individual risk is often easier with the use of risk contours. These give the locus of location points with equal summed risk of harm from the specified hazards. At any given location the contour point could be considered as the individual risk to a person who is permanently (100 % of the time) located at that point. Risk contours are thus particularly useful in land planning cases where location of houses or communities in relation to potentially hazardous activities needs to be considered.

A hypothetical example²³ of the presentation of risk contours on a map is shown in Figure 6. Shown are the individual risk contours of 10^{-5} , 10^{-6} , 10^{-7} and 10^{-8} fatalities per year for a fictional proposed chemical plant site near a populated area.

²² Mannon S. (ed), Lees' *Loss prevention in the process industries* 3rd edition 2005 (Elsevier Butterworth – Heinemann, Oxford UK).

²³ Dutch *Purple Book* 1st ed.1999, *Guidelines for quantitative risk assessment* CPR18E (Sdu Uitgevers, Den Haag Netherlands).



Figure 6 Presentation of individual risk contours

2.5.5 Societal risk

The individual risk statistic shows the frequency of a given level of harm for a person or group of people within a specified period. It does not cover the magnitude of any single hazard realisation in terms of the total number of individuals affected. This is important for potential process related incidents which can cause death or injury to more than one person at a time, where a measure is needed to give the likelihood of events of different magnitudes. This is called societal risk. The public tolerance of societal risk is generally much lower than for the sum of equivalent individual risks. For example, in the UK around 3 000 people per year are killed in road accidents but this is generally not considered worth protesting, whereas a report of multiple deaths in a single accident on the railway is likely to result in calls for redress, even though statistically the individual risk of fatal injury on the railways is at least an order of magnitude lower than on the road.

The IChemE (Jones) definition for societal risk is the relationship between frequency and the number of people suffering a given level of harm in a given population from realisation of specified hazards.

This information, after calculation from individual pairs of event frequency (F) and number of persons suffering the given harm (N), can be presented as a histogram or cumulative histogram, but is more usually represented as an F/N curve.

2.5.6 FN curves

An FN curve depicts the FN pairs on a diagram where the frequency of events F causing N or more cases of the given harm is plotted against the number N. Usually the given level of harm is death, and the plot is on a logarithmic scale since there is likely to be a sharp fall

in the number of events that could cause a high number of fatalities when compared to the number (of smaller events) that might cause one death. Plots of the results of various alternative risk reduction strategies can easily be placed on the same graph, and by plotting a known tolerability limit on the diagram, decisions on the acceptability of the predicted risk may be made.

A hypothetical presentation²⁴ of a societal risk curve along with an illustrative tolerability limit is shown in Figure 7.

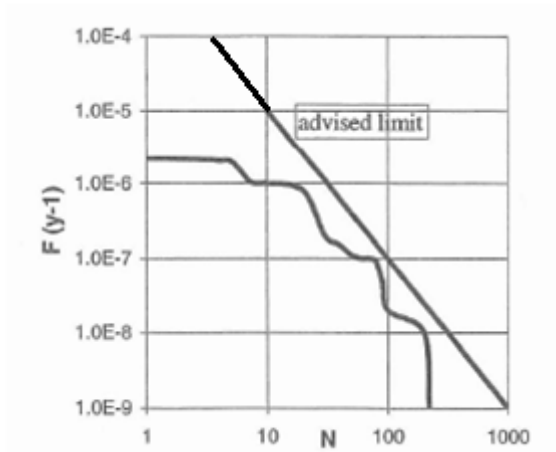


Figure 7 Presentation of the societal risk curve

2.6 WHAT CAN BE DONE TO ELIMINATE OR REDUCE RISK?

If risk levels are unacceptable, there are strategies which can be employed to reduce risks further. Reducing the frequency of an event and reducing the severity of an event can both be used to reduce overall risk. This section provides some suggestions of possible mitigation strategies.

2.6.1 Reducing frequency

By understanding possible causes of failure, it is possible to reduce the likely frequency of an event. For example through:

- Protecting against third party interference (e.g. thicker pipe or protective overburden at vulnerable pipeline locations – such as road crossings).
- Protecting against corrosive failure of equipment (e.g. designing appropriately for wet environments, moisture control, thicker materials, suitable inspection regimes).
- Protecting against blockages and other operation issues (e.g. appropriate design of blowdown vessels and vents to prevent blockages).
- Proactive prevention of leaks (e.g. inspection, test and maintenance, pigging onsite and pipeline walk-arounds for small leaks, quality assurance (QA) procedures, change management procedures for plant).

²⁴ Dutch *Purple Book* (ibid).

2.6.2 Reducing severity

Once an incident has occurred, the severity of that incident can be reduced by a number of mitigation strategies. Examples include:

- Appropriate staff training and procedures (e.g. emergency plans, confined space entry procedures, low temperature awareness).
- Reducing inventory released (e.g. crack arrestors, block valves, appropriate monitoring).
- Appropriate emergency plans (e.g. including how to inform local population of a potential hazard etc.).

2.7 SUMMARY OF HAZARD AND RISK ANALYSIS

Issue	Key points
What events might happen?	Suitable hazard identification techniques and information of known incidents should be used to identify scenarios that need to be modelled. Scenario setting should take into account topography, impingement, proximity to populations and the case by case assessment of whether additional detailed CFD modelling is required. Scenarios should also assess whether any impurities cause a hazard that has a more severe consequence than carbon dioxide alone.
Understanding the likely frequency	There are sources of failure rate data which could be applied to CCS installations and pipelines, but care must be taken when using these data because either sample sizes are small or data are from a comparable industry but not CCS. Examples of data given in this document are not exhaustive and other options should be explored. With the limited CCS related failure data, participants should ensure that suitable mechanical integrity programmes are set in place.
What are the consequences of an event?	The consequence of an event is the likely fatality rate at specified locations based on a time duration dose of carbon dioxide. Fatality probability can be calculated using probit functions for carbon dioxide combined with carbon dioxide concentrations calculated through dispersion modelling.
Is the risk acceptable?	Societal risks set a framework for understanding whether the risk is acceptable or not, as no activity is completely risk free. Risk levels should be discussed with health and safety regulators and company safety specialists.
What can be done to eliminate or reduce risk?	Mitigation strategies focus on reducing frequency of an event and/or reducing the severity of the event.

3 HAZARD ANALYSIS EXAMPLE

3.1 INTRODUCTION

This section describes the input and results for a small hazard modelling exercise. It is intended to provide an illustration of several techniques used to predict the consequences of dense phase carbon dioxide pipeline rupture. It also provides a basic guide to understanding the output from dispersion models.

3.2 DISPERSION MODELLING FUNDAMENTALS

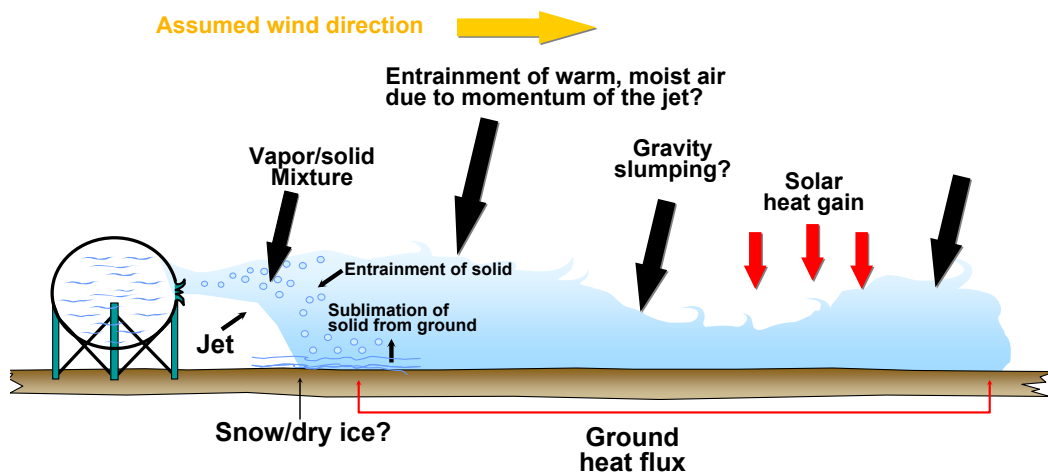


Figure 8 Overview of carbon dioxide cloud formation

At the initial point of release, carbon dioxide will be in a high velocity jet. This will be a mixture of gaseous carbon dioxide and some fine particles of solid carbon dioxide. The characteristics of the initial jet are known as the source terms. They comprise pressure, density, temperature and velocity, which are then used to calculate the mass flow rate and the initial jet momentum within the 'development zone', where the gas expands to atmospheric pressure.

The cloud contains a certain amount of momentum, related to the initial release velocity, which ensures that the cloud starts to move away from the point of release. As it moves, air is entrained into the carbon dioxide cloud, reducing the concentration. Some of the fine solid particles entrained in the cloud of carbon dioxide may 'rain out' onto the ground and form a pile of carbon dioxide 'snow'. Some of the solid will sublime in the cloud as it takes in heat from the surrounding area. The prevailing wind will also influence the movement of the cloud away from the release point.

As the initial cloud moves away from the release point, further carbon dioxide is released from the pipeline, adding to the cloud. Assuming the pipeline is isolated once a leak is detected, the flow rate from the pipeline decays over time as the inventory is used up. The total inventory released will depend on the pipeline (length, pressure, diameter) or

size of vessel and any mitigation in place. During this phase, the cloud is getting larger in overall length and diameter and air entrainment continues around the surface area of the cloud. Rain out of solid carbon dioxide increases as the release pressure approaches the solid formation pressure, which is approximately 7 barg.

Eventually, the flow rate from the release point decreases and then stops as the inventory pressure is exhausted. The cloud continues to move downwind, entraining air and eventually dispersing.

When modelling the dispersion of carbon dioxide, the models provide different views of the dispersion of the cloud, which when examined together give a representative picture of the cloud. In the hazard analysis example illustrated in this chapter, the snapshots give the following information:

1. The mass flow rate over time, demonstrating how the rate of flow of carbon dioxide decays.
2. The extent of the cloud, which shows for particular concentrations how far the cloud travels before it is finally dispersed. As an illustration, it gives no indication of the duration of that concentration.
3. The lethality of the cloud, which combines probit figures with the duration of exposure. This gives an indication of the impact on human health of the cloud at various distances from the release.

It is only by understanding the combination of information produced by dispersion models and combining them with a probit function that we can assess the likely impact of the scenario modelled.

3.3 CONDITIONS USED IN THE HAZARD ANALYSIS EXAMPLE

3.3.1 Assumed pipeline configuration

The pipeline modelled is assumed to be 54 km long, completely level and straight, and is assumed to suffer a full bore rupture at one end. The rupture occurs at a pig trap, such that the subsequent release is horizontally orientated, with pipeline centre-line 1 m above ground level^{25 26}.

- Three pipeline diameters are considered (mm values below are pipe bore diameters).
- Case 01 8" (203 mm);
 - Case 02 16" (406 mm), and
 - Case 03 28" (711 mm).

These cases have been chosen because they mirror work carried out by Mahgerefteh²⁷ on natural gas and carbon dioxide pipelines.

3.3.2 Assumed inventory

In each case, the pipeline is assumed to contain pure, dense phase (i.e. liquid) carbon dioxide at a pressure of 117 barg and temperature of 10 °C. Any ongoing flow in the pipeline, prior

²⁵ This is an extremely pessimistic scenario, under UK gas pipeline design, block valves must be placed every 16 km and therefore it is unlikely that a CO₂ pipeline would have an uninterrupted 54 km run.

²⁶ Full bore ruptures of large diameter pipelines are rare events according to the available failure rate data.

²⁷ *Pressurised CO₂ Pipeline Rupture* I.Chem.E. Symposium series No. 154, 2008.

to rupture, is ignored as it is considered negligible compared to the initial flow rates following full bore rupture.

3.3.3 Assumed weather conditions and terrain

Neutral stability atmospheric conditions are assumed, with an ambient air temperature of 10 °C, humidity 70 % and a wind speed of 5 m/s at a height of 10 m above ground. The wind direction is along the pipe axis, blowing in the same direction as the release.

It is assumed that the releases occur on a flat coastal plain with presumed surface roughness of 0,01 metre and presumed substrate temperature of 10 °C.

3.4 EXAMPLE RELEASE CALCULATIONS

3.4.1 Recommended modelling technique for carbon dioxide dispersion for specific loss of containment scenarios

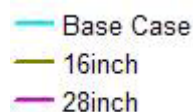
In modelling of releases from a supercritical pressure carbon dioxide pipeline such as the following examples, use of PHAST 6.53.1 or 6.54 (as available at the time of drafting) will generally result in correct predictions of the release flowrate down to the point where the pressure at the orifice reaches the triple point pressure at 5,1 bara, after which errors are likely to be introduced because the current physical data held by the programme will assume liquid being present rather than solid. Similarly, because of the physical property errors, the dispersion predictions will be less accurate if (as normal) solid is formed after release. Indications from reports of modellers' progress are that the effects of the errors resulting from incorrect physical properties are unlikely to be dramatic. An indication of the error could be found by comparison of PHAST 6.54 with PHAST 6.6 which more correctly includes the effects of solid formation; however 6.6 has not been released at time of drafting. Therefore until the release of PHAST 6.6, the user should take care when using PHAST 6.54 for carbon dioxide releases; see 2.4.2 and Annex B for details.

3.4.2 Discharge results

Discharge results have been obtained for the three cases in 3.3 using the DNV PHAST programme suite (version 6.54). The fluid flow characteristics of the release from a rupture at the end of a length of pipeline are included within PHAST as an option entitled 'long pipeline'.

The results shown in Figure 9 (discharge results for pipeline cases) are given as function of time since release, for expelled flow rate (kg/s), orifice pressure immediately prior to depressurisation to ambient (bar), total remaining pipe mass (kg), and solid mass fraction after depressurisation to ambient (kg/kg). Here the 'solid mass fraction' is evaluated and reported in PHAST 6.54 using 'liquid' properties.

The graph keys are:



 — Base Case

 — 16inch

 — 28inch

Where the base case refers to the 8" pipe diameter.

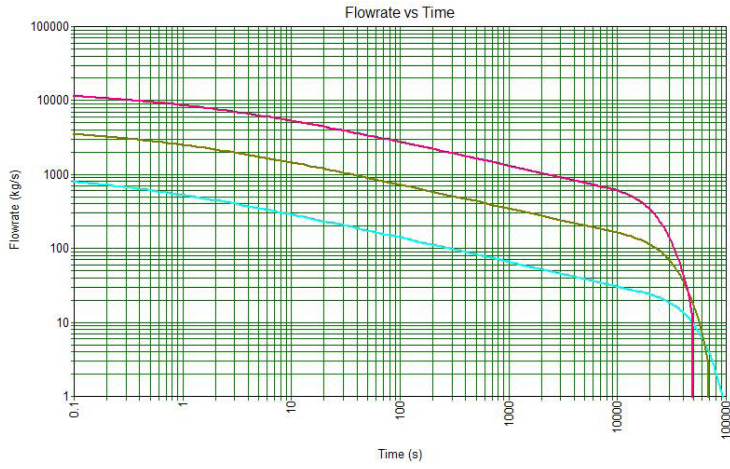


Figure 9a Mass flowrate released

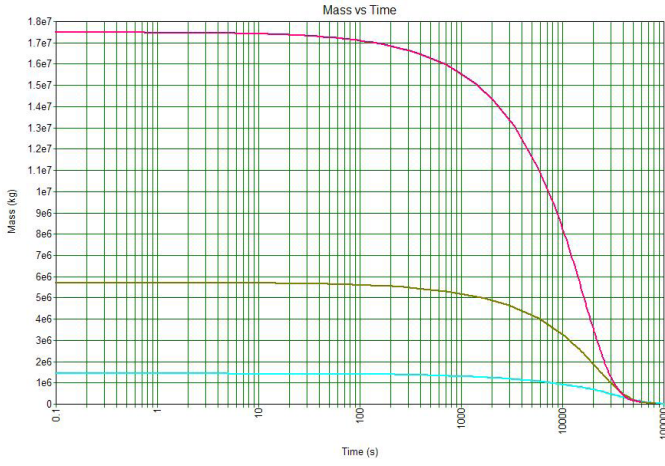


Figure 9b Total mass remaining in pipe

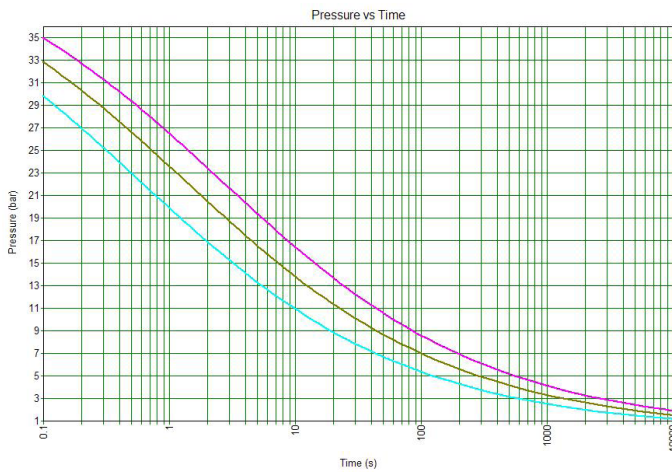


Figure 9c Pressure at 'orifice'

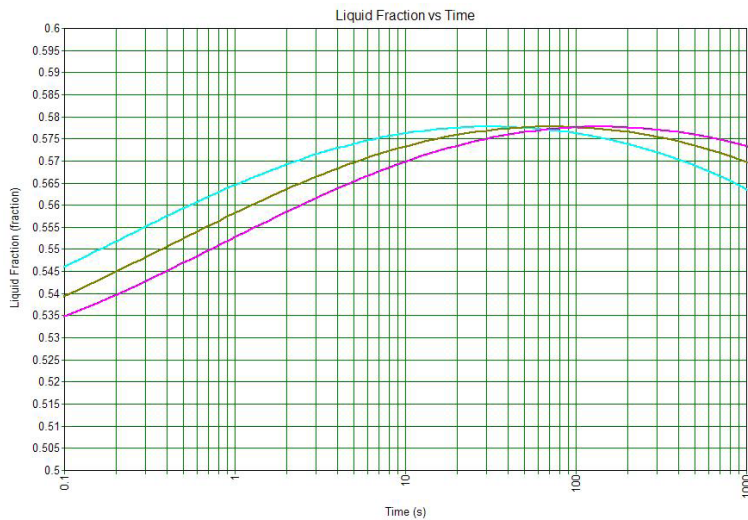


Figure 9d Post-expansion solid mass fraction

From Figure 9a, typically on rupture there will be an instantaneous high energy release at a flow rate that cannot be sustained because of the physical constraints to the fluid upstream within the pipeline. The initial dispersing cloud (including the effect of sublimation of any solid carbon dioxide separated out from the bulk of the jet release) is constantly changing mass, and has characteristics closer to the release of a 'puff' of gas rather than a fully developed cloud resulting from a long term steady jet flow release.

To ascertain the maximum distance the initial release may travel before sufficient dilution, an average flow rate value needs to be selected for the first few seconds of release in order to carry out the computation as a semi-continuous cloud. This analysis method is typical for hazard effects that result within this short duration high flow condition (usually blast, jet impact, debris or fragmentation, plus flammable effects if appropriate). For a gas such as carbon dioxide with a time-dependent dose-response relationship, computation of consequences may require a series of time-averaged flows of reducing magnitude to determine the level of harm at any given location resulting from a release over an extended period. Where available, more accurate results would be achieved using a time-varying along-wind-diffusion model to represent rapidly changing release rates. However, this type of model is not widely available.

In the current version of PHAST, time-varying discharge results are first averaged into a specified number of equal-mass segments before being input into the unified dispersion model (UDM) for dispersion calculations. For time-varying long pipeline releases, division into multiple segments is not always appropriate given the possibly very long durations of release.

The method used in this document is one where a single release rate has been used. The mass release rate chosen being equal to the averaged release rate over the first twenty seconds and with the release duration such that the expelled mass corresponds with the total expelled mass. We recommend that those undertaking this type of modelling assess the mass emission segmentation carefully and choose the appropriate mass release rate to use for dispersion modelling on a case-by-case basis under the guidance of expert modellers and/or their software providers.

3.4.3 Dispersion results for 8" horizontal full bore release

These results are for above-ground, unimpaired release of carbon dioxide (other cases are discussed in section 4). Using the recommended default PHAST method (averaged mass release rate over the first twenty seconds), the source term calculation for 'long pipeline' gives the following results:

Release rate through orifice	kg/s	321,6
Final velocity after expansion	m/s	203,7
Post expansion temperature	°C	-87,5
Post expansion 'liquid fraction'	%	58
Equivalent release duration	s	4 414

Figure 10 shows the fully developed semi-continuous isopleths resulting from this initial stage of the 8 inch pipeline release (modelling is for weather stability D with a uniform wind speed of 5m/s at all elevations). Figure 11 shows the side elevation of the cloud.

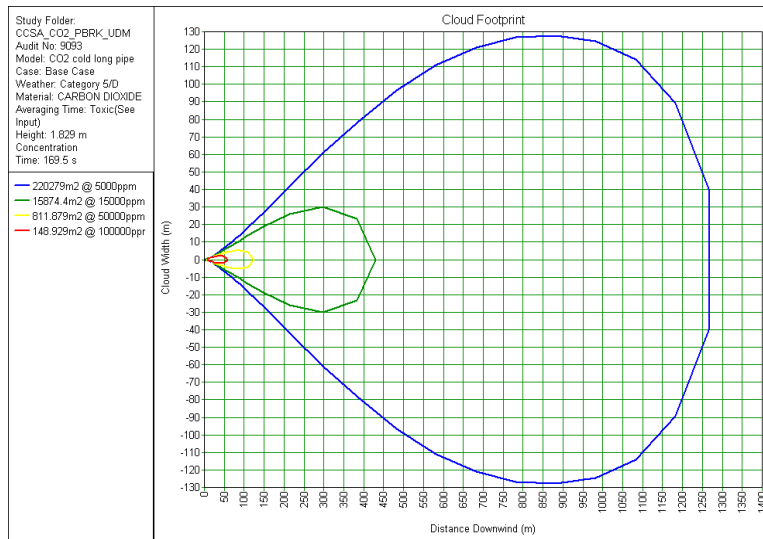


Figure 10 Isopleth of release of CO₂ from 8" line rupture

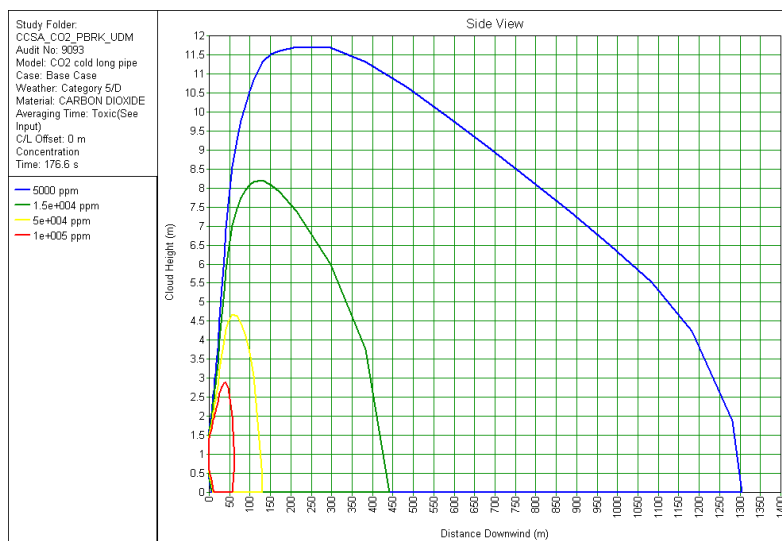


Figure 11 Side view of release of CO₂ from 8" pipe rupture

3.4.4 Dispersion results for 16" full bore horizontal release

Using the recommended default PHAST method (averaged mass release rate over the first twenty seconds), the source term calculation for 'long pipeline' gives the following results:

Release rate through orifice	kg/s	1602,3
Final velocity after expansion	m/s	196,8
Post expansion temperature	°C	-87,5
Post expansion 'liquid fraction'	%	57
Equivalent release duration	s	3 544

Figure 12 shows the fully developed semi-continuous isopleths resulting from this initial stage of the 16" pipeline release (modelling is for weather stability D with a uniform wind speed of 5m/s at all elevations). Figure 13 shows the side elevation of the cloud.

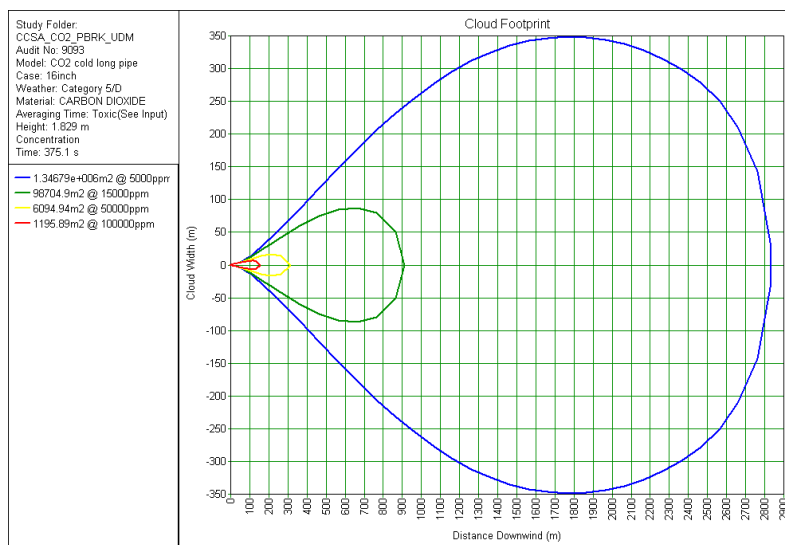


Figure 12 Isopleth of release of CO₂ from 16" line rupture

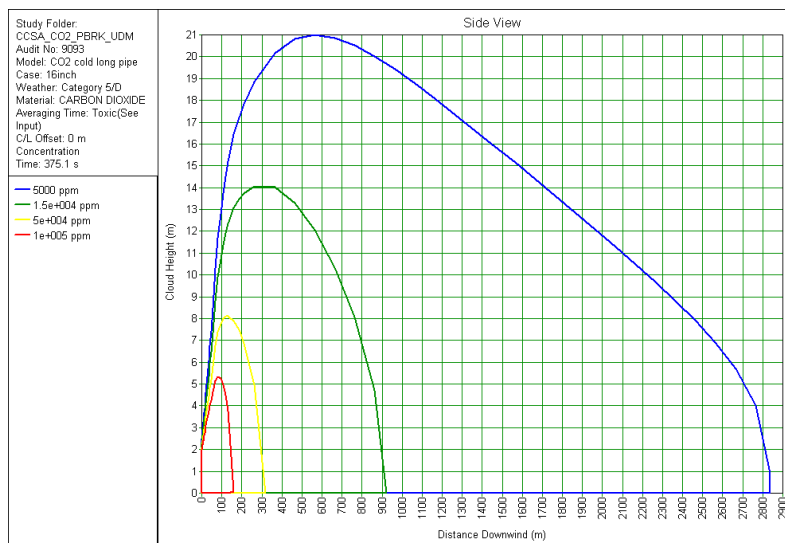


Figure 13 Side view of release of CO₂ from 16" pipe rupture

3.4.5 Dispersion results for 28" full bore horizontal release

Using the recommended default PHAST method (averaged mass release rate over the first twenty seconds), the source term calculation for 'long pipeline' gives the following results:

Release rate through orifice	kg/s	5768,3
Final velocity after expansion	m/s	190,7
Post expansion temperature	oC	-87,5
Post expansion 'liquid fraction'	%	57
Equivalent release duration	s	3 015

Figure 14 shows the fully developed semi-continuous isopleths resulting from this initial stage of the 28" pipeline release (modelling is for weather stability D with a uniform wind speed of 5m/s at all elevations). Figure 15 shows the side elevation of the cloud.

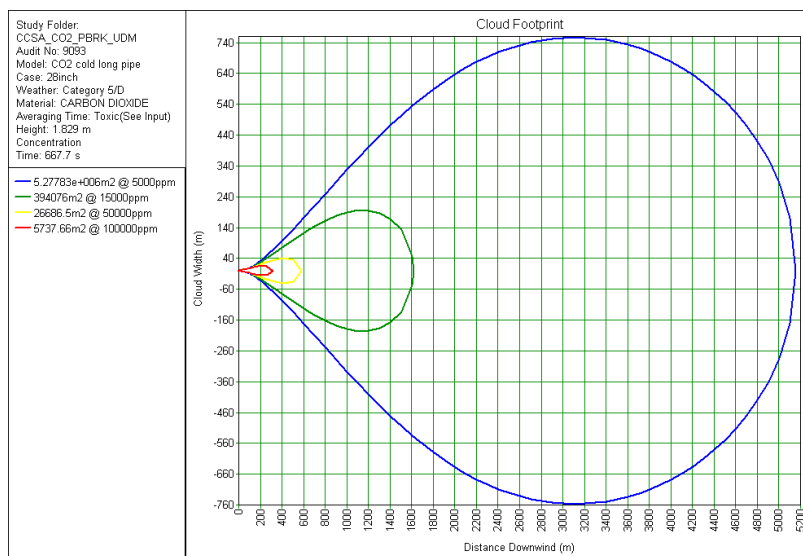


Figure 14 Isopleth of release of CO₂ from 28" line rupture

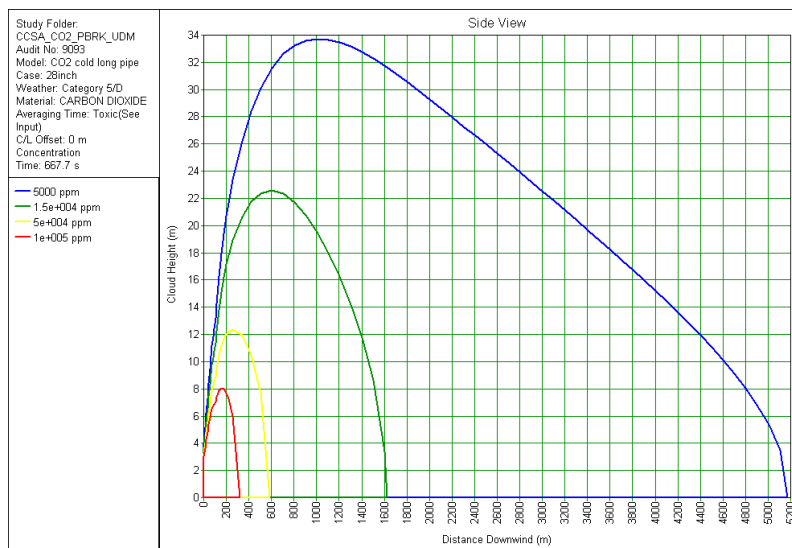


Figure 15 Side view of release of CO₂ from 28" pipe rupture

3.4.6 Limits of lethality from the gas cloud

Using the Probit developed in section 2 from the dispersion calculations in the previous section, with constant flow rates for uninterrupted releases lasting either until the pipeline is totally depressurised or one hour if depressurisation is longer²⁸, Figure 16 shows the 1 % probability of fatality limit of the outdoor toxic lethality footprint for the three release cases considered. Figure 16 includes the results for the case considered so far (full-bore rupture at end of 54 km long pipe), while Figure 17 includes results for the case of a full-bore rupture at the end of a 16 km long pipe.

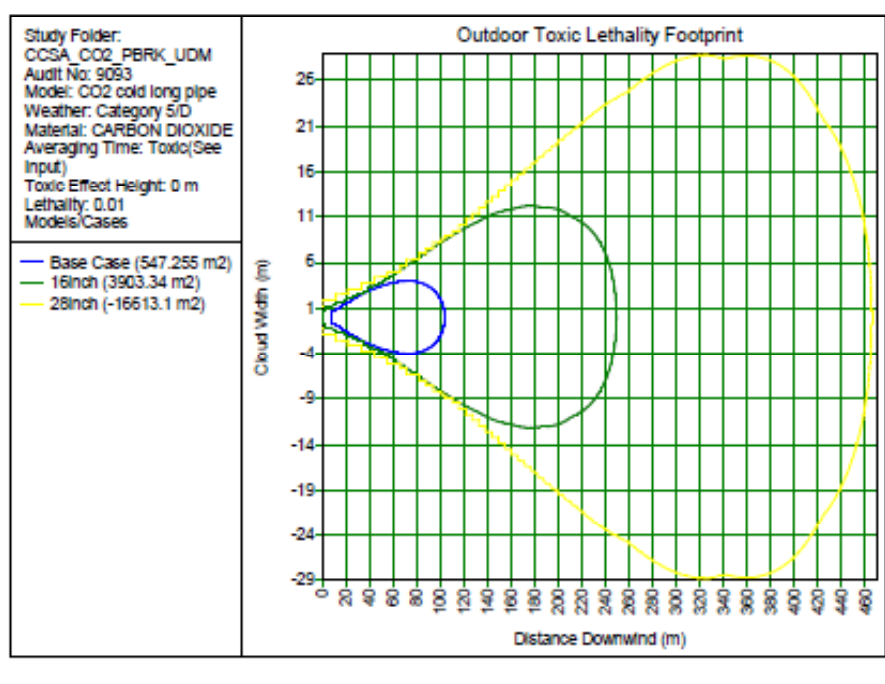


Figure 16 Outdoor lethality footprints to 1 % probability of fatality for 8", 16" and 28" pipeline ruptures with a 54 km valve scenario

²⁸ The assumption is that, in the event of an incident involving a release, emergency measures can be put into operation within one hour to mitigate the effects of a release lasting longer than that duration despite the pipeline continuing to depressurise.

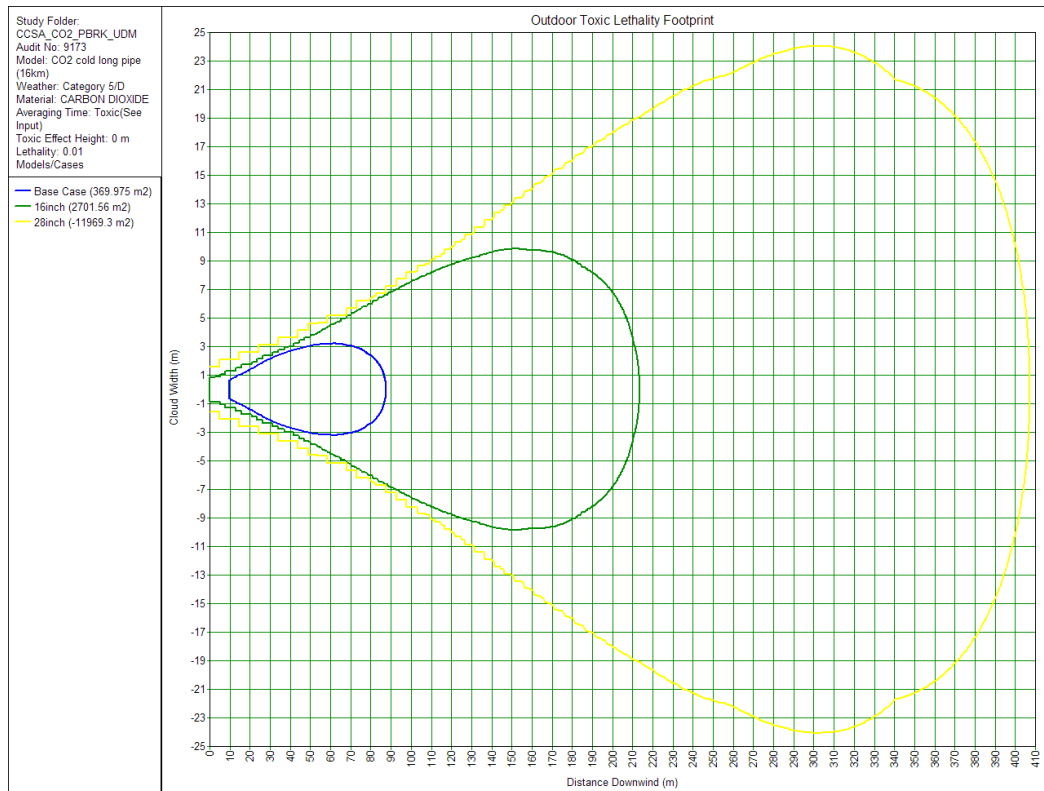


Figure 17 Outdoor lethality footprints to 1 % probability of fatality for 8", 16" and 28" pipeline ruptures; 16km valve scenario

Thus for a 54 km long pipe the limits of toxic risk of fatality are not expected to exceed approximately 100 metres, 250 metres and 470 metres in the direct line from the above ground rupture for failure of 8", 16" and 28" pipelines respectively. Note that because of the jet release conditions, the released cloud effects are highly directional down to the concentration levels at which fatality is possible (the fatal cloud width for an above ground unimpinged release is not expected to exceed 60 metres).

For a 16 km long pipe, the limits of 1 % probability of death are approximately 90, 210 and 410 metres from the rupture for failure of 8", 16" and 28" pipelines respectively.

3.4.7 Risk calculation

In order to calculate individual fatal accident rates for any of these release cases, an estimation of the frequency of such pipeline failures is required (as in section 2.3). Table 1 gave a summary of data from the various sources. Taking the UKOPA pipeline incident database for 1962-2006 as representative for the potential failures for a carbon dioxide pipeline, an upper limit estimation of the frequency of major pipeline ruptures of 0,25 per 1 000 km/year can be made²⁹.

²⁹ UKOPA pipeline data are not specific to carbon dioxide but provide analogous results. The failure data from a smaller sample of carbon dioxide pipelines in the US provide broadly similar failure frequencies (see 4.33). Practitioners will have to decide what data to apply to their project.

Detailed data within UKOPA show that pipeline rupture incidents are only a small proportion of the incidents reported³⁰, and examination of the data³¹ suggests that the reported ruptures are primarily for thin-walled pipes of less than 10" diameter. However from previous discussion on current accuracy of the dispersion modelling, a deliberate selection of a conservative value for frequency is justified for this example.

The illustrated rupture cases, being specifically above ground and directed horizontally, would only be likely within a valve cage or pipeline booster station. For illustrative purposes if it is assumed that the overall length of exposed vulnerable pipe is 40 metres, then the estimated release frequency for a rupture at the pipeline station will become 1×10^{-5} per year.

The individual fatal risk at point of release is then the same value if all or most causes of rupture are human errors (i.e. resulting from external interference).

Thus, from the results in Figure 16, for the 8" case the individual fatality rate for a person exposed range from 1×10^{-5} /yr at the release point to 1×10^{-7} /yr at 100 metres downstream for the 8" case, with the same frequency range to the corresponding distances of 250 and 470 metres for the larger pipe diameters. The intermediate fatality rate-distance relationships can be computed from the data.

For the 28" rupture case, Figure 18 shows the 100 %, 10 % and 1 % predicted fatality limits for an outdoor population.

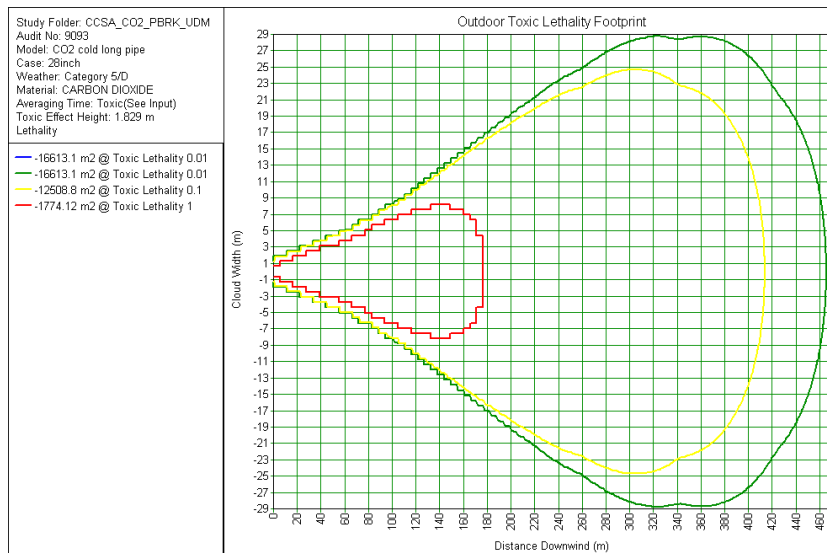


Figure 18 28" pipeline release outdoor fatality footprint

The corresponding individual fatality rate therefore remains 1×10^{-5} /yr to 180 metres from the release point and reduces to 1×10^{-6} /yr at 415 metres. The probit indicates that there is practically no risk of fatality for such a release beyond 500 metres from the release point.

³⁰ UKOPA document 07/0050 (ibid.) Figure 6.

³¹ UKOPA document 07/0050 (ibid.) Figure 7.

3.4.8 Physical blast effects

In addition to dose-related gas release effects, any rupture failure of the 117 barg carbon dioxide pipeline will create a blast effect due to the release of energy from the initial rupture. This blast effect would not be directional in relation to the point of release.

There can be multiple effects to humans from blast including direct overpressure effects (primary effects on organs such as ears and lungs), impact from fragments and debris, or collapse of other structures including buildings (secondary effects through damage to tissue and body parts), and explosion velocity effect (cloud wind carrying people away and impacting them on obstacles). The degree of injury and survivability also depends on the initial orientation of the human body in relation to the direction of blast and presence of obstacles.

Literature might indicate complex relationships for all or any of these items. But for this illustrative analysis, an empirically derived upper boundary fatality against overpressure is used for illustration purposes.

For illustration purposes in Table 6, a linear relationship between vulnerability and overpressure has been assumed to be between 1,0 and 10,0 psi (68,9 and 689 mbar) overpressure for outdoor populations.

Table 6 Assumed effect criteria for outdoor populations

mbar	psi	Assumed effect criteria
68,9	1,0	0 % fatality assumed
689	10,0	100 % fatality assumed

Table 7 shows the relationship for indoor populations between vulnerability and overpressure, accounting for hazards such as collapsing structures and fragments (such as from windows). As an illustration, this has been assumed to be between 0,5 and 2,0 psi (34,5 and 138 mbar) overpressure.

Table 7 Assumed effect criteria for indoor populations

mbar	psi	Assumed effect criteria
34,5	0,5	0 % fatality assumed
138	2,0	100 % fatality assumed

Blast comes from the shockwave produced by the energy from the expansion of the initial release of gas from the pipe. Since this shockwave travels faster than sonic velocity (that is faster than the potential release rate of the gas) the initial impulse has only a limited duration, and only a very small proportion of the volume of gas inside the pipeline will be involved in the initial energy release.

Basic derivation of volumes involved in this phenomenon can be expressed in lengths of pipe (L) of given diameter (D) upstream of the rupture point. Since the rupture will generally initially release gas from both sides of a pipe break, the L/D value calculated from fluid flow will usually be doubled.

To illustrate possible blast effects of a pipeline rupture, a separate set of calculations has been used for the physical blast effect from pipe rupture (with $2 \times L/D = 10$ taken for the volume involved in the initial pressure release).

The physical blast effect calculation results using PHAST for the three release cases are as follows.

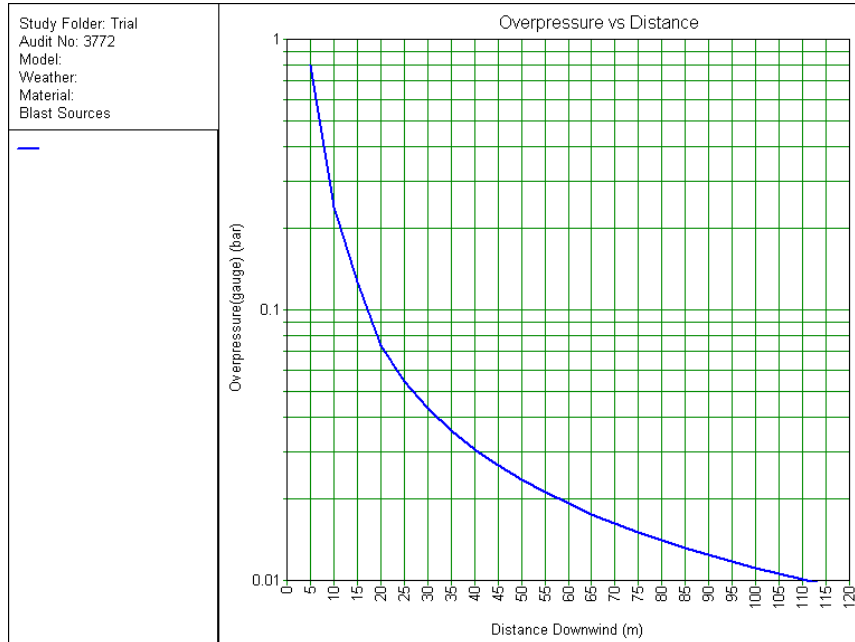


Figure 19 Blast-distance relationship for 8 inch pipe rupture

For an 8" pipeline, it should be noted that the limit of any probability of fatality outdoors (equivalent to a side-on overpressure of 0,035 bar) being calculated at 35 m for an 8" line rupture is less than the maximum lethal range from the toxic effects. The blast is calculated to be 100 % lethal (0,7 bars) for anyone within 5 m of the rupture in any direction from the release point. This is therefore a more severe outcome local to the release than the directional toxic cloud.

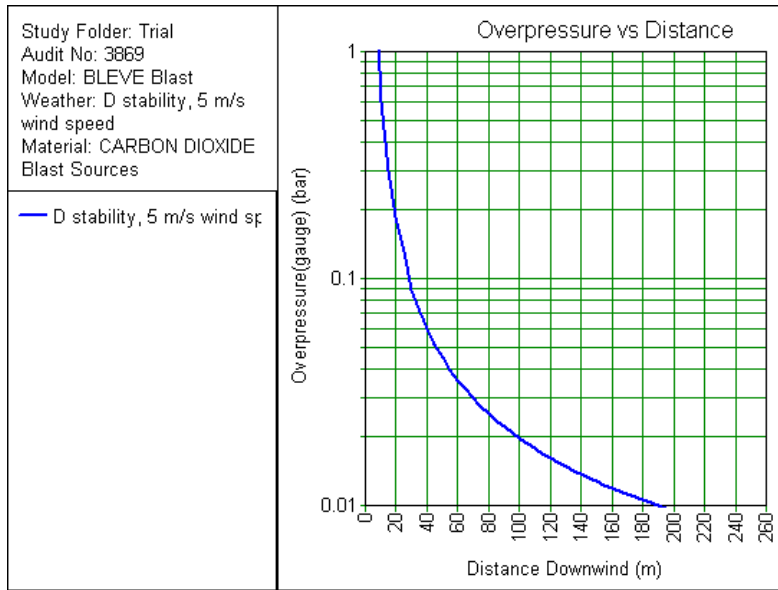


Figure 20 Blast-distance relationship for 16" line rupture

For a 16" line rupture, both the 100 % fatal range and the limit of fatal risk from blast being calculated as 10m and 60m respectively are less than the corresponding toxic effects.

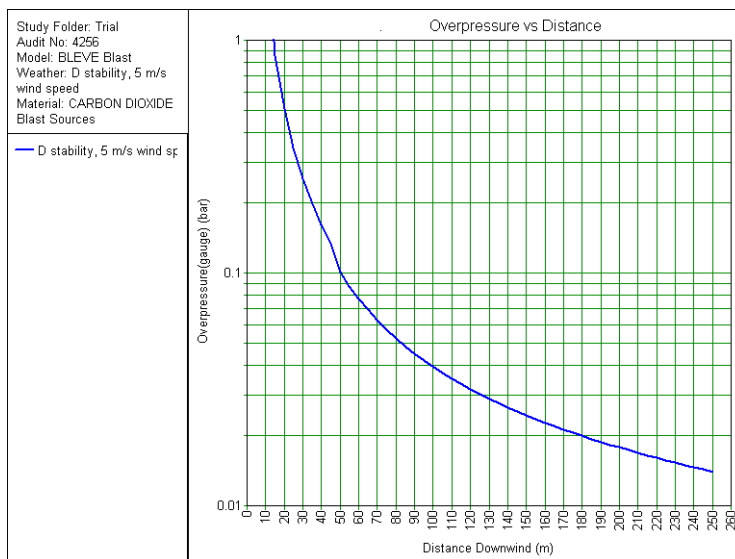


Figure 21 Blast-distance relationship for 28" line rupture

For the blast effects from a 28" line rupture, both the 100 % fatal range and the limit of fatal risk being calculated as 17 m and 105 m respectively are less than the corresponding toxic effects.

4 DISCUSSION OF RESULTS

4.1 TIME AVERAGED FLOW RATES IN COMPUTING LIMITS OF LETHALITY FROM THE DISPERSION CALCULATIONS

The current recommended default method is to approximate (in a suitable modelling software package) the time-varying flow rate from the long pipeline by a single release segment with the average release rate over 20 seconds. This gives what is believed to be a conservative set of results. Where more accurate and less conservative results are required, and there is a rapid variation in the release rate of carbon dioxide, then the more rigorous time varying along-wind-diffusion (AWD) modelling method should be used. Where the technology to conduct (or employ) AWD modelling is unavailable, other 'single segment' time averaging methods may be applied on a case-by-case basis, but with care and expert guidance.

The default method is considered to give more accurate results than averaged release rates over longer periods and/or the use of multiple release segments. This is particularly the case for carbon dioxide where larger concentrations will contribute significantly more to the toxic load than lower concentrations.

The relevant time period to evaluate the 'maximum concentration' is the cloud travel time from the release point to the concentration of interest (say 5 000 ppm), which is around three minutes for the 8" case and 54 km pipe. Thus for this case only the flow rate before three minutes will affect the maximum concentration results.

Particularly for releases from long pipelines, the release rate reduces significantly with time and the current method (adopting an average over the first 20 seconds) is rather crude. DNV has developed an improved version of the UDM that much more rigorously and accurately accounts for time-varying effects (e.g. along-wind diffusion) and also would allow calculations of dangerous toxic loads for carbon dioxide (and this can also be easily extended to probability of death). However, at the time of drafting, this model needs further testing and verification, and has not yet been implemented in PHAST. This new model will eliminate the need for averaging of flow rates altogether. For now, users are strongly advised to use the current default method.

4.2 TYPE AND DIRECTION OF RELEASE

The full bore pipeline rupture cases analysed have considered only above-ground horizontal releases that result in dispersion from a true jet. However such cases are only a small proportion of the possible release scenarios; often the length of any distribution pipeline will be below-ground, or the leak size/direction of release is different.

Leaks either from holes or developing cracks may initially be orientated in any direction in relation to the pipe location. For above-ground events the initial direction of the jet may be vertical or angled upwards resulting in at least part of the dispersing cloud being above a height at risk to people nearby. Leaks or pipe ruptures below-ground may be caused by deliberate excavation or natural events such as landslips or corrosion. A spontaneous rupture of a well-designed and inspected and maintained pipeline is likely to be a rare occurrence. If such a rupture occurs, a crater is likely to be created as a result of the blast and velocity. In either case the resultant release to atmosphere at grade or above-ground may again be initially vertical or angled. In the case of a release from an excavation or crater, the initial jet is likely to have been modified either by impingement against objects underground or by the new crater acting as a nozzle reducing the effective velocity of release from the source. The

crater may in itself cause the release to be direction specific³².

Some of these effects are illustrated in the following figures. Figure 22 shows the directional effects of high flow releases from an angled 28" pipeline rupture.

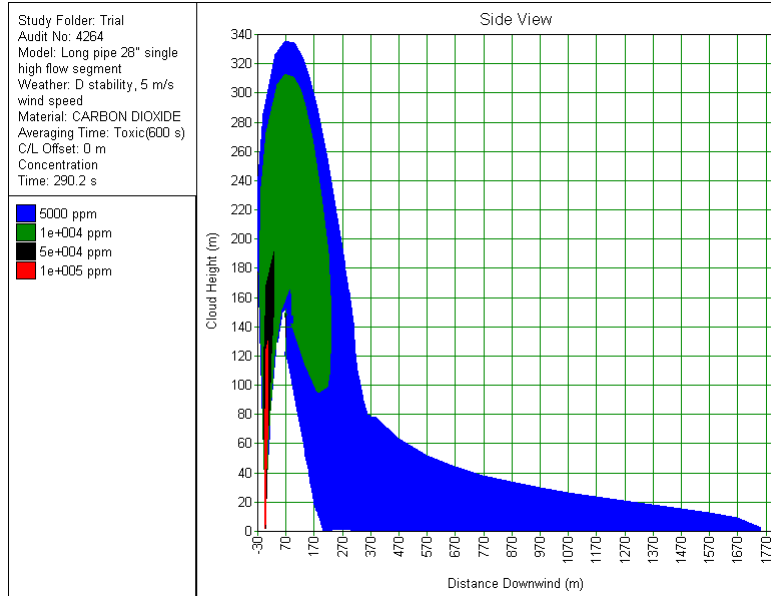


Figure 22a Dispersion from a vertical release viewed from the side

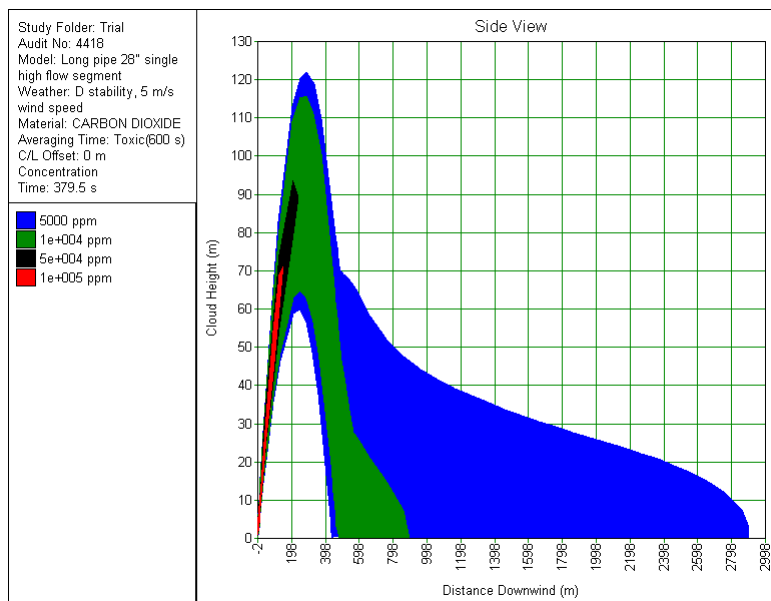


Figure 22b View from dispersion from a release angled 30° from the horizontal

³² Where there is significant impingement at a release site, so as to cause a low momentum dispersion event, this guidance does not apply.

Comparison of Figure 22 with Figure 15 indicates that even a full bore pipeline rupture will disperse harmlessly if the release conditions result in the jet being angled upwards from the point of release.

Cases discussed so far have only been full bore pipe ruptures. More frequent events for a pipeline (from the data) would be leaks from holes or cracks caused by corrosion, external damage or construction defects. Such leaks can represent a serious additional risk even for a large diameter pipeline, as the large pipe inventory allows the initial release flow to be sustained for longer until emergency procedures to mitigate the consequences can be put in place.

Calculations for a leak of 100 mm (4") equivalent diameter hole size have been carried out under various release conditions.

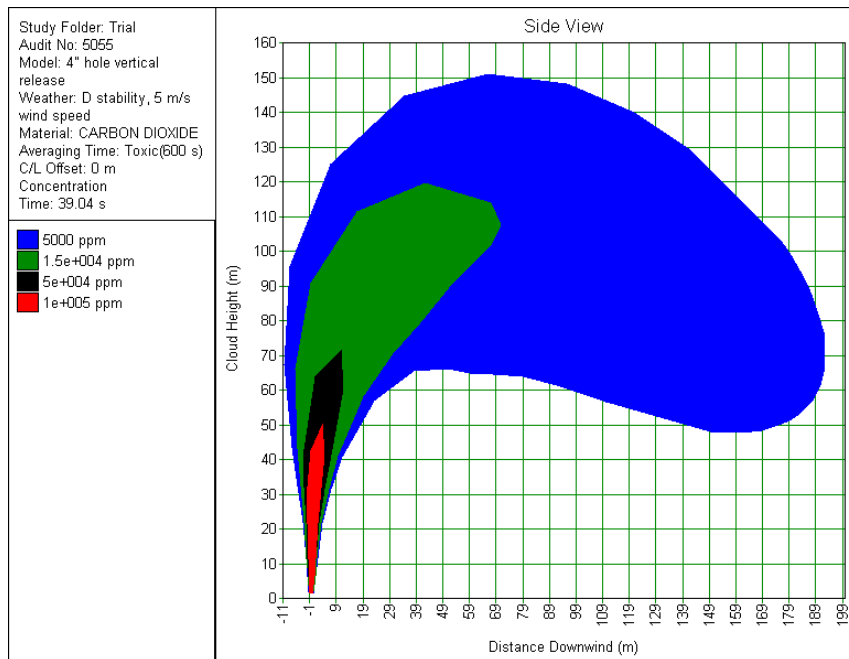


Figure 23 Dispersion from a 4" jet released vertically viewed from the side

Figure 23 shows that an unimpeded leak released vertically (as from a cut or hole punched in a buried line) has no anticipated risk except at the point of release.

However if the same leak occurred horizontally in an above ground section of line, the impact could be significant.

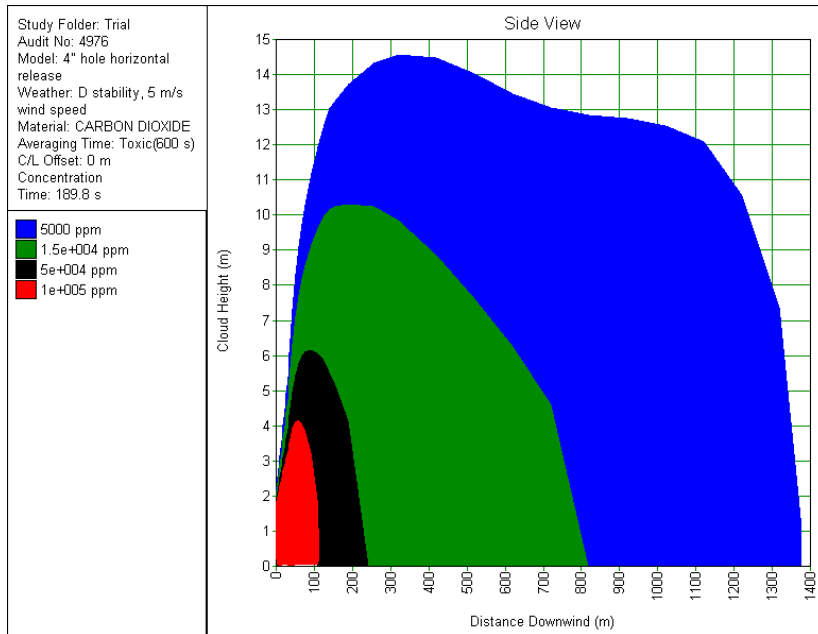


Figure 24 Side view of dispersion from a 4" jet released horizontally

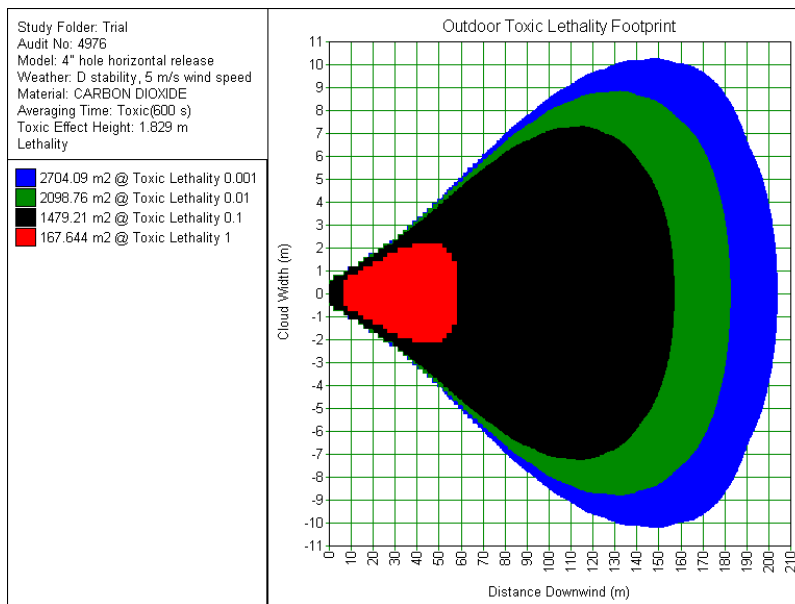


Figure 25 Horizontal 4" jet release outdoor fatality footprint for one hour exposure viewed from above

Comparison of Figures 24 and 25 with Figures 16 and 17 respectively indicates that even a relatively small failure in a large line can have a significant impact downstream of the release if the release conditions are appropriate³³.

³³ All other parameters are generated by PHAST for the 4" release case.

It should also be noted that the calculated frequency of such a leak event is likely to be an order of magnitude higher than for a rupture.

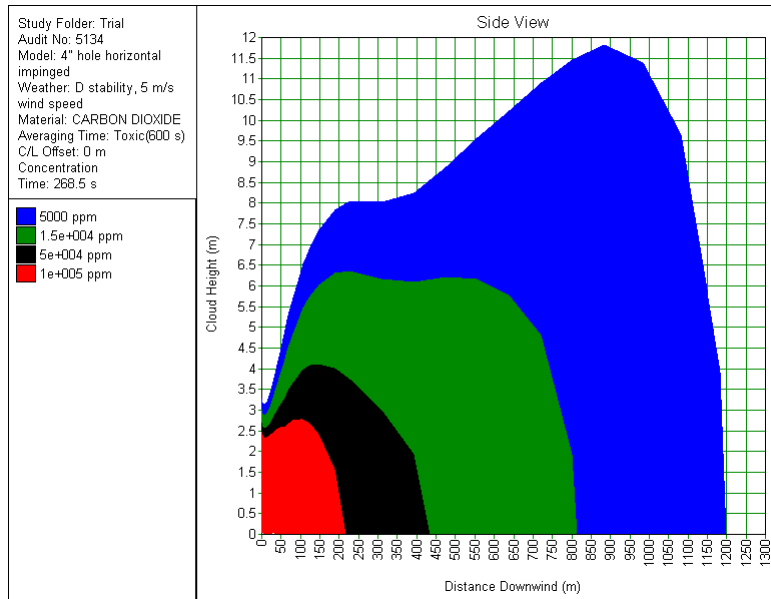


Figure 26 Horizontal dispersion from a 4" release with jet impinged viewed from the side

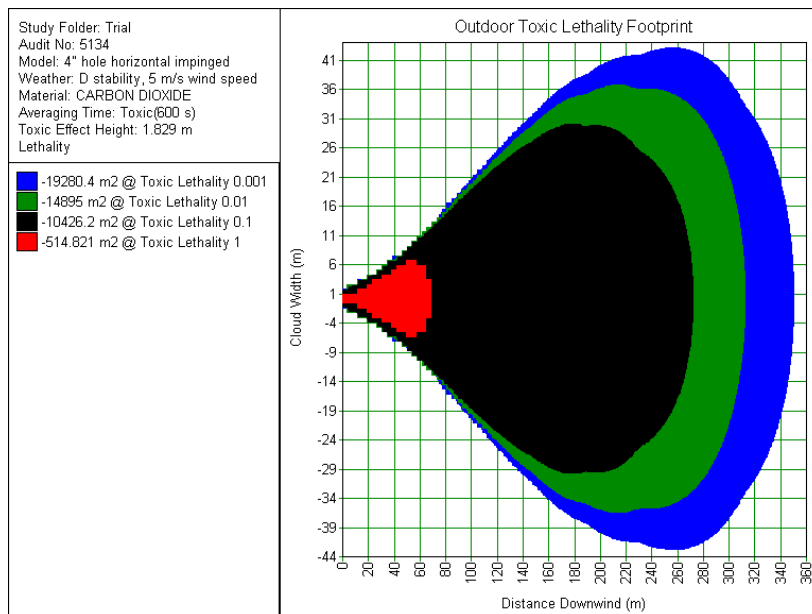


Figure 27 Horizontal impinged 4" jet release outdoor fatality footprint for one hour exposure viewed from above

Figures 26 and 27 consider the situation where the initial jet release loses a large proportion of its momentum by impact with very hard ground or large solid objects before dispersing horizontally. This case would have a significantly larger impact than an unimpinged release because of the reduced entrainment of air into the jet cloud (see Figure 16).

Observations of releases from buried pipelines indicate the following issues need to be considered carefully in order not to over- or underestimate the consequences of a release:

- Large jets released from high pressure below-ground pipelines will not always be obstructed by soil. Surprisingly large amounts of soil and even concrete can be blown away from areas above and below high pressure pipelines and result in little or no reduction in velocity and momentum.
- Smaller leaks in deeply buried pipelines will have little or no momentum when they migrate to open air. This lack of momentum means that the concentration of carbon dioxide will be high at the source of release and potentially more dangerous.

4.3 VISIBILITY OF PLUME

In the calculated cases, carbon dioxide jet release on expansion to atmospheric pressure will initially cool to approximately -87 °C. Mixing this jet with ambient air for the dilution process will result in a mist, produced by water vapour condensing from the air in the cold air-carbon dioxide mixture, in addition to precipitation of solid carbon dioxide particles within the initial cloud on expansion. Thus the jet plume will remain visible until the diluted cloud has warmed sufficiently to sublime all the solid particles within it, and for the cloud temperature to be above the 100 % humidity level for the air-carbon dioxide mixture. This temperature will vary according to the initial atmospheric ambient conditions, and in some cases (e.g. in winter where the ambient air has been cold enough for little or no water to remain as vapour) the plume will be practically invisible except for the solid carbon dioxide particles initially contained within it. Similarly a release into weather conditions where atmospheric fog already exists may be hard to detect visually except for the solid carbon dioxide.

Indicative values for carbon dioxide concentration at the limit of the visible cloud under the weather conditions used for the dispersion calculations (ambient air at 10 °C, 70 % relative humidity) are 1 % to 1,5 % depending on the release case. Thus, for these particular conditions, the anticipated visible plume will always be far larger than the hazardous concentration limit of the dispersing gas cloud.

4.4 EFFECT OF DIFFERENT WEATHER AND WIND CONDITIONS

The calculations reported in this section have been carried out for releases at a sample set of weather and wind conditions namely Pasquill stability class D (neutral or cloudy weather) and a uniform wind speed of 5 m/s. Often for QRA it is necessary to evaluate the releases through a range of weather and wind conditions of known but varying likelihood in order to obtain either the worst case scenario or to give a specific overall risk (individual or societal) accounting for all conditions pertinent to that location.

The following range of weather stability and wind speeds are often used as best practice for capturing the worst case results from atmospheric dispersion. Other weather conditions of A through G may be recorded in weather data but detailed evaluations usually show that the tabled values below are sufficiently representative to cover most conditions.

Table 8 Stability and wind speed

Stability*	Wind speed
D	5 m/s
D	9 m/s
F	1,5 m/s

*The stability is represented according to the Pasquill Stability Class (D: neutral conditions; F: moderately stable conditions).

Depending on the physical properties and operating conditions of the gas being released extremes might be reached either under high wind (D, 9) or stable weather (F, 1,5) rather than being represented by the more average conditions (D, 5). However sensitivity checks - as in the following figures - for variations in weather conditions show relatively little calculated difference in dispersion, and hence the risks from the evaluations using D stability and 5 m/s wind speed.

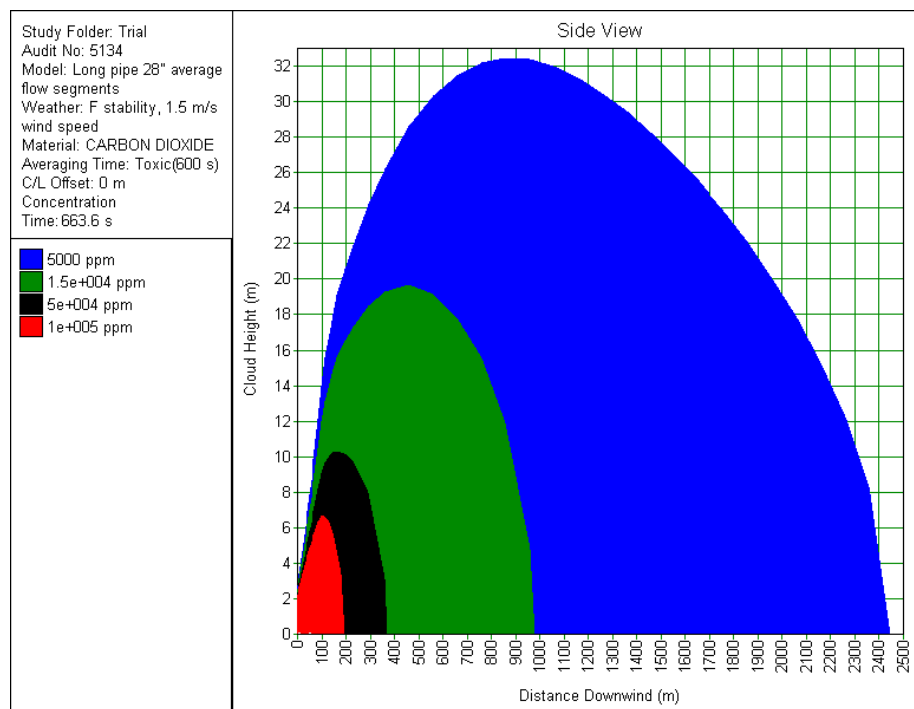


Fig 28 Time averaged fully developed initial dispersion horizontally from 28" pipeline rupture (F stability, 1,5 m/s wind) half-section, viewed from the side

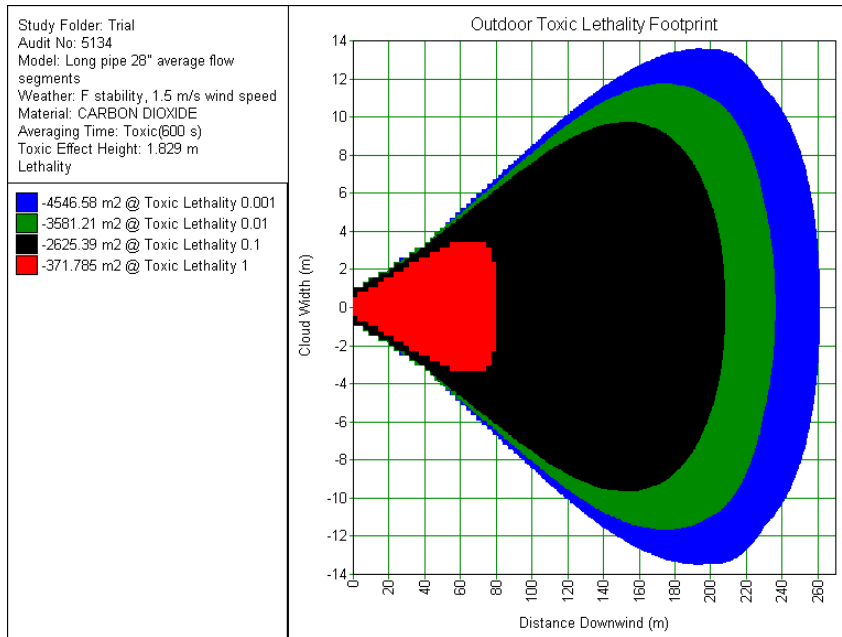


Figure 29 One hour time-averaged calculation of horizontal 28" pipeline release outdoor fatality footprint (F stability, 1,5 m/s wind) viewed from above

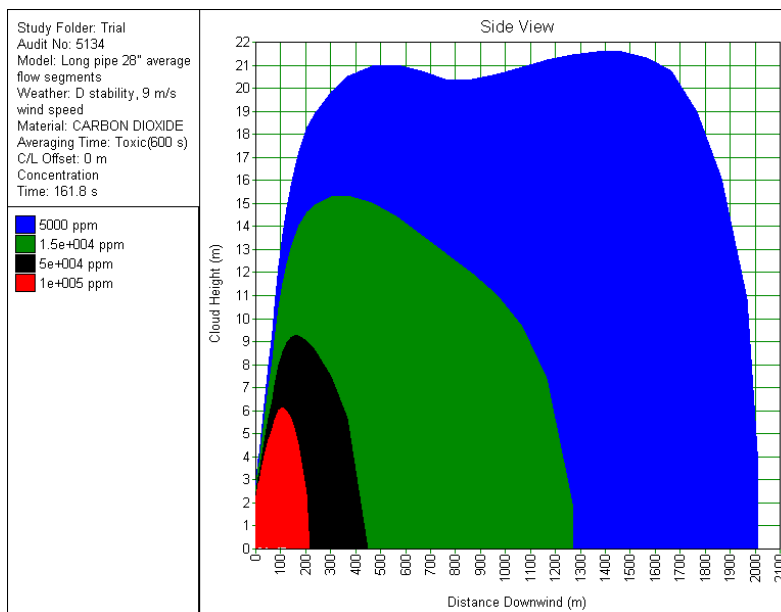


Figure 30 Time averaged fully developed initial dispersion horizontally from 28" pipeline rupture (D stability, 9 m/s wind) half-section, viewed from the side

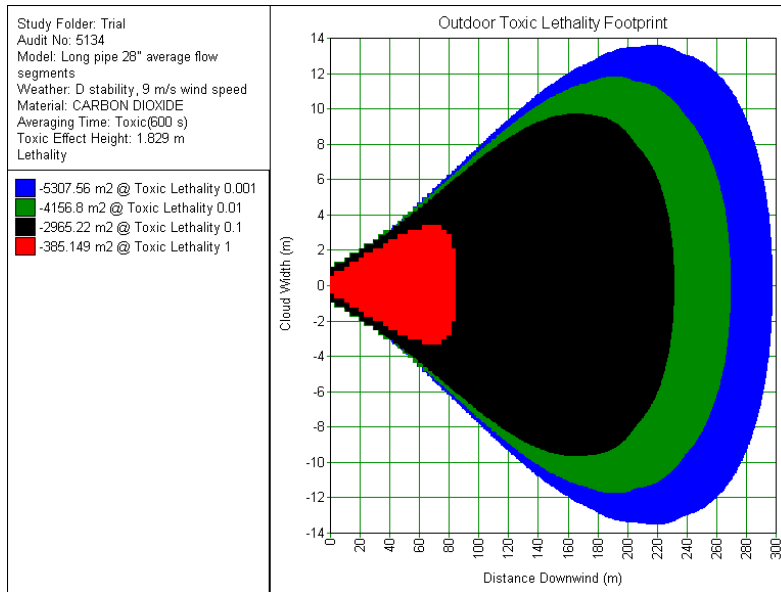


Figure 31 One hour time-averaged calculation of horizontal 28" pipeline release outdoor fatality footprint (D stability, 9 m/s wind) viewed from above

Figures 28/29 and 30/31 are comparable with Figures 14/15 for the limited effect of weather variations on the dispersion of large volumes of carbon dioxide.

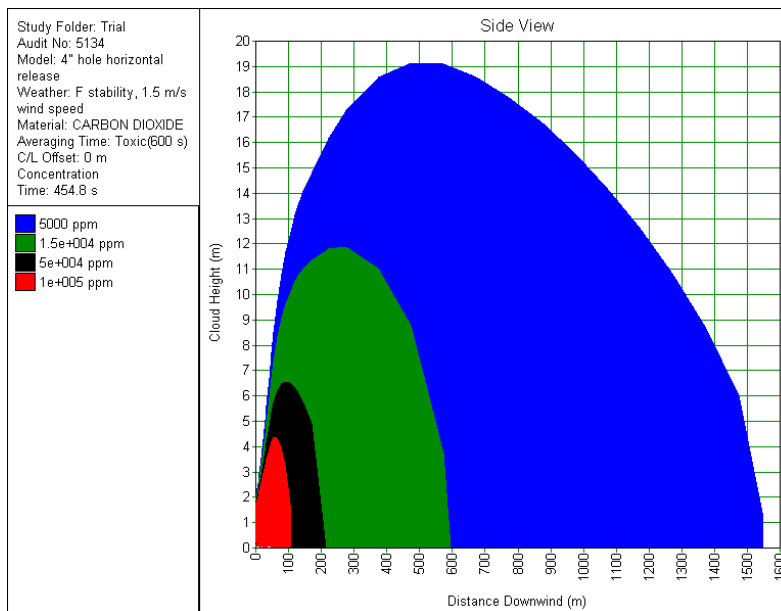


Figure 32 Dispersion from a 4" jet released horizontally (F stability, 1.5 m/s wind) half-section, viewed from the side

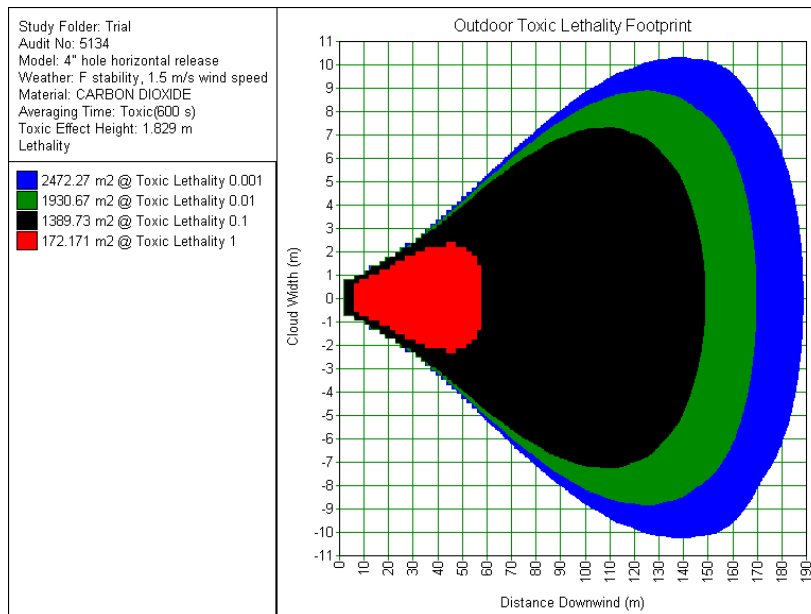


Figure 33 Horizontal 4" jet release outdoor fatality footprint for one hour exposure (F stability, 1,5 m/s wind) viewed from above

Figures 32 and 33 should be compared with Figures 14 and 15.

4.5 OTHER FACTORS THAT MIGHT BE PROJECT SPECIFIC

4.5.1 Simplifications within dispersion modelling

Dispersion modelling using computer programmes represents a simplified solution for the possible calculations. Variables are either generalised (e.g. ambient conditions, surface roughness, uniformity of release condition over its entire duration) or the modelling takes no account of site-specific conditions such as terrain or the effect of buildings or structures. This is in addition to any limitations inherent in the models (e.g. inability to handle crosswind effects on dispersion).

4.5.2 Topography and impingement

Topography will always be site- or project-specific. As carbon dioxide is heavier than air, on release, unless flowing at high velocity, it will always tend to follow land contours, and collect in hollows or low points where there is no wind to create turbulence and aid dispersion. In addition, even if weather statistics have been collected site-specifically, it is likely that the wind conditions will not be fully representative (e.g. data collected at a local airport will be for an open flat space with little constriction on wind direction by contours or presence of sheltering trees, etc.).

The project site or sites for an extended pipeline distribution system may have different conditions over its length that could in practice give different dispersion results for identical release cases (source terms).

Changes in conditions over the extent of a release can in part be due to surface roughness or nature of the ground. It is also important to note the effects of large buildings and other obstructions on wind directions and velocity.

If completing societal risk calculations on a project specific basis, the results are absolutely dependent on locating the real population potentially at risk in the vicinity of the plant or distribution system. Generic studies can only be indicative or used to provide data on recommendations for exclusion zones and other mitigation factors to be applied to any carbon dioxide distribution system. It is important that complementary modelling to assess the issues of topography and impingement are carried out using models that are capable of modelling these scenarios accurately.

4.5.3 Low momentum releases

The guidance within this report does not apply to low momentum releases onshore or offshore. Underground releases on land are briefly discussed in 4.2.

4.5.4 Solid formation

A release of dense phase carbon dioxide can result in a mixture of gas and solid carbon dioxide. Some solid carbon dioxide will become entrained in the gaseous release where it will sublime into the cloud. Under certain conditions, particularly as the velocity of the release and the pressure of the inventory reduce, some solid may 'rain out' onto the ground.

Solid that rains out onto the ground, will in general fall in the form of carbon dioxide 'snow', and will sublime very slowly. Solid carbon dioxide will generally form a limited hazard at the release site. The main hazard will be that a higher concentration of carbon dioxide gas will form within centimetres of the solid and that under some meteorological conditions the gas may collect in low-lying areas or areas where there is insufficient wind to disperse it. In addition there will also be a risk to personnel of cryogenic burns. Staff awareness of these hazards should be included within any emergency procedures and the appropriate equipment e.g. gas detectors and protective clothing should be provided.

5 CONCLUSIONS AND RECOMMENDATIONS

5.1 CONCLUSIONS

Appropriate hazard analysis is fundamental to assessing the risks of carrying carbon dioxide in onshore pipelines and installations. Using conventional tools, it is possible to carry out hazard analysis for projects involving carbon dioxide.

As with all hazard analysis, selecting appropriate data is key. Throughout this document, we have set out an approach to produce what will be a conservative set of analyses. Although there are comparatively few carbon dioxide pipelines in operation, the construction of these pipelines is not vastly dissimilar to many other conventional pipelines. Consequently there is a large dataset for estimating incident rates that can be applied to pipelines carrying carbon dioxide.

Current dispersion models are not exclusively designed for carbon dioxide, but we have set out methods to allow carbon dioxide to be modelled. This has been the accepted approach in the industrial gases sector for many years in relation to carbon dioxide and other cryogenic liquid installations. This approach has also been acceptable when modelling carbon dioxide releases to assess their environmental impact³⁴.

5.2 RECOMMENDATIONS

The methods that we have recommended are generally conservative, which may result in overestimating the hazard and thereby increasing mitigation unnecessarily. We recommend that these conservative assumptions are used to screen CCS projects until there is a wider body of work to reduce the uncertainties. In particular, we recommend the following future work to reduce uncertainties.

5.2.1 Control of moisture

A key cause for failure within carbon dioxide pipelines can be corrosion. It is recommended that operators of carbon dioxide pipelines define moisture contents for product entry into their pipeline systems, and rigorously monitor moisture content, specifying what corrective action needs to be taken if exceeded. In this way there will more confidence that pipeline failure data obtained from non-carbon dioxide carrying pipelines realistically represent carbon dioxide carrying pipelines.

5.2.2 Reducing the uncertainties around the modelling

We have suggested conservative source term data be used for dispersion modelling of carbon dioxide, but this may result in overestimation of the consequences of a release. We recommend a programme of work to reduce these uncertainties and particularly the development of dispersion models that can manage the solid/vapour transition more effectively.

³⁴ *Air dispersion modeling of well blowout and pipeline rupture scenarios, Salt Creek Field* prepared for Howell Petroleum Corp by Cameron-Cole 22 Sep 2005. This report is appended to the Salt Creek Phase III/IV Environmental Assessment (dated 27 Jan 2006), US Dept of the Interior; Bureau of Land Management (Casperfield Office) and compares results of approximately 96 % CO₂ physically released from wellheads to the results from US EPA dispersion models suits DEGADIS and SLAB.

5.2.3 Database of incidents

At present, there is no database of carbon dioxide incidents. We recommend setting up an industry group to monitor incidents and to compile a database for industry to learn from.

5.2.4 Sharing of pipeline maintenance data

We recommend that in the early years of CCS industry, operators should maintain high levels of integrity checking on all installations. We also recommend that data on pipeline conditions should be shared collectively so that the industry can come to agreement on what maintenance and inspection requirements and schedules constitute good practice. This should allow both the general public and regulatory authorities to have confidence that carbon dioxide pipeline failures are being managed to an acceptably low level.

5.2.5 Refining of risk assessment methods

The work carried out in this document has by necessity been limited in scope, and it is recommended that as further studies are commissioned, the CCS industry should agree a consistent approach to risk assessment. Scenarios should be modelled for typical installations and more guidance on data selection and input provided.

ANNEX A

MODELLING CARBON DIOXIDE

A.1 INTRODUCTION

This chapter provides guidance from a health and safety perspective on the approaches required for modelling of carbon dioxide in carbon capture and storage (CCS) projects. The principal concerns are how to model the release and subsequent dispersion of carbon dioxide as an aid to understanding the hazards which may be presented by operational, emergency and accidental releases. The consequence of such releases are generally presented in the form of contours or isosurfaces of carbon dioxide concentration at values which relate to differing levels of harm to exposed persons. Harm criteria range from occupational short and long-term exposure limits, through to fatality thresholds. In addition it is typical to produce isopleths that show the probability of fatality limits based on probit i.e. dose models which account for the concentration and the duration of exposure (see section 2). In general it is desirable for predictive models to be conservative, but not overly so, since highly conservative models can unduly impose constraints on a facility design. Equally, predictive models should not lead to key aspects of a potential hazard being overlooked. Ultimately, as with all hazard modelling, the competent selection and use of the appropriate tools and techniques is critical.

Modelling for carbon dioxide consequence analysis typically takes place in two stages. In the first stage the release rate from a given inventory or scenario is calculated. In the second, the dispersion of the released carbon dioxide is calculated. It can be noted that some hazard modelling packages may carry out both stages without the need for the user to transfer data, or even being aware that this procedure takes place.

The level of complexity or difficulty associated with each of these tasks depends on the particular scenario. For release rate calculation, the thermodynamic state of the inventory is a key parameter. This is also true for dispersion, where additional parameters need to be considered such as the impact of surrounding buildings or landscape.

For example, if the requirement is to calculate low concentration level contours from a warm, vertical, low speed gaseous release into a moderate wind with no influence from surrounding buildings, then a simple Gaussian plume model may suffice. In practice it has been found that this type of scenario is very rare in CCS projects where the effect of the high density or high momentum of the gas cannot usually be neglected.

On the other hand, for the release of a very cold gas and its interaction with the topsides of an offshore platform in a low wind, such a model would be entirely inappropriate and a CFD model would be needed. Cases intermediate between these two extremes should be treated individually, and it may be most appropriate to use a more sophisticated integral modelling tool. In some cases, such as the release of carbon dioxide from a liquid inventory, a high proportion of solids can be produced and off the shelf models may not be able to handle the physics. In either case special procedures must be carried out (examples are given later) or a particular model version obtained.

There are numerous scenarios where modelling needs to be carried out. Two possibilities include:

- Due to a shutdown or problem at one end of a pipeline, blowdown of the pipeline and/or plant through a stack. It is then important to understand the following: can a carbon dioxide plume touch down inside or outside of the site boundary; at what concentration level; in what wind conditions. It may necessary to modify the vent

- stack, or its location. This information may also influence the rate at which the carbon dioxide is released dependent on weather and wind conditions.
- If a gas plume could spread offsite by an accidental release from pressurised vessels and pipes. At what concentrations; how far and for how long will a gas plume persist.

Several scenarios will be described in the next section.

It should be noted here that the observations and suggestions made in this document are based largely on the experience of the EI and its contributors. Other parties may be able to add other insights to subsequent updates to the current document.

A.2 TYPICAL SCENARIOS IN A CCS PROJECT

A.2.1 Planned/emergency releases

During planned venting, carbon dioxide will often be released in the gaseous phase, perhaps upstream of export compression. This is not always the case - blowdown of some inventories directly from the liquid state may be required in some circumstances, and is the preferred method in many cases. For example, in the industrial gases industry it is common practice to blow down from the liquid side of a vessel, whilst maintaining a pressure that will keep the material in the vessel in the liquid state, without reaching too low a temperature. The reason for this practice is that blowing liquid carbon dioxide is faster than blowing down gaseous carbon dioxide, and blowing down from the liquid side of a vessel rather than gas side reduces the likelihood of solid formation within the vessel as the pressure starts to decrease. However, transferring this practice may be difficult where it is a buried pipeline that is being blown down.

Planned releases can occur at a variety of temperatures from close to the sublimation temperature to over 100 °C. Offshore, where the carbon dioxide may be used for enhanced oil recovery (EOR) the gas may not be pure carbon dioxide, but may contain hydrocarbon components. The gas exported for CCS purposes is unlikely to be pure either and the impact of these impurities needs to be considered.

Venting can be designed to give either a sub-sonic release or a release which is sonic at the exit - sonic releases tends to give better dispersion and reduce the likelihood of solid rain out.

In some cases the venting can occur over a long period of time and a steady-state calculation can be carried out. In other cases, though the flow rate may fall over the period during which the venting takes place, the rate at which it falls may be sufficiently small to allow a pseudo-transient calculation to be used. A pseudo-transient calculation is a number of separate steady-state calculations, each corresponding to flow rates at fixed points during the transient. For some calculation methods, such as CFD, this technique can substantially reduce the required computing time and should be used when practical.

A.2.2 Accidental releases

Accidental releases can occur from a huge variety of process conditions, including both gaseous and liquid inventories, together with the supercritical fluid state. In general, these releases will be above water, either onshore, or on offshore platforms. Offshore or sub-sea releases are not considered within this publication.

Gaseous releases from a hole in a vessel or broken pipework have a similar effect to planned releases, though there are notable differences:

- In general they will be sonic releases from pressurised vessels.
- They will generally be close to ground level (onshore cases), or associated with one of the modules (offshore cases), rather than from a high stack.
- They may be of short duration and inherently transient if the vessel inventory is small.

Releases from vessels with liquid and some supercritical inventories are significantly more complex. In these cases, as the carbon dioxide enters the atmosphere it makes a transition from the liquid state to a two-phase gas/solid mixture where the solid fraction depends on the upstream conditions. During this transition the fluid expands in a characteristic 'tulip' shape. The solid particles which are formed then sublime back to gas.

A second distinct class of accidental release is that from a pipeline rupture. Normally, for risk assessment purposes, a full-bore rupture is considered, as this is the worst case scenario in terms of peak flow rate. Again, while the case of a gaseous pipeline is relatively straightforward with analytical expressions in common use, the case of a liquid or supercritical pipeline is significantly more complex to calculate.

A.3 DEFINING AND SPECIFYING SOURCE TERMS

Releases of carbon dioxide must be considered under a range of circumstances as described in A.2. In each case a source term is required for the numerical model to calculate the dispersion. There are essentially two aspects to this process. Firstly, the mass flow rate must be calculated. However, in general, additional information, such as the temperature of release, is required in order to fully specify the source term in the software used to calculate the dispersion. How this additional information is found and used depends on the upstream conditions of the particular case under consideration.

A.4 FLOW RATE CALCULATION

A.4.1 Planned venting

In the case of venting, the flow rate is generally known as part of the process design and will be provided by the process engineering contractor and may be related to the production flow at the facility. Correct implementation of the source term into the dispersion model is still required, as described in A.7.1.

A.4.2 Accidental release from vessels with gaseous inventory

Under most circumstances there is no reason to assume that the flow rate from a gaseous carbon dioxide inventory should be calculated in a different manner from other gases. The mass flow rate from a gaseous inventory can often be found by assuming ideal gas behaviour and using standard expressions which are given in a number of text-books such as Lees³⁵. Generally, for accidental releases the flow will be choked and will be sonic at the exit plane.

³⁵ *Loss Prevention in the Process Industries* F.P. Lees, 2nd Edition, Butterworth-Heinemann, ISBN 0-7506-1547-8, 1996.

Choking occurs if the ratio of the inventory pressure, p_v to the atmospheric pressure p_a is greater than a critical value which depends on the ratio of specific heats, γ , for the gas. For carbon dioxide the release will be choked if $p_v/p_a > 1,89$.

A discharge coefficient should be applied for a sharp-edged orifice, but this is typically given as around 0,85³⁶ so that neglecting the discharge coefficient is pessimistic, but not overly so.

In some cases, ideal gas behaviour may not be appropriate and there are two possible causes for this. The first is simply that the ideal gas law is inappropriate due to high pressure or proximity to the critical point. The second is that the isentropic path taken by the gas between stagnation and exit plane conditions enters a two-phase region before choking occurs, so that there is a two-phase mixture at the exit plane.

The first problem can be overcome by using a better assumption for the gas properties than the ideal gas equation, e.g. a cubic equation of state such as the Peng-Robinson equation. As an example, Figure A.1 shows the mass flow rate per unit area calculated for a number of upstream temperatures and pressures, using both the ideal gas and Peng-Robinson equations of state. It can be observed that using the ideal gas law represents a reasonable approximation at lower pressures, but starts to become less reliable as the pressure increases, where it begins to under-predict.

The second problem, where the thermodynamic path enters a two phase region, is more difficult to overcome in a rigorous manner. However, the solid fraction is generally relatively small in gaseous releases, and is expected to sublime rather quickly (due to small particle size and high velocity) and so in many cases it is likely that it can be neglected. For cases where the two-phase region is the gas/liquid region, the more general homogenous equilibrium method (HEM) for release rate calculations described in A.4.3 can be used.

In general, for accidental releases, no information is available regarding connecting pipework through which the release may occur. Therefore, it is normal to assume a round hole directly in a vessel with the given inventory conditions. If, however, a specific case needs to be investigated including a length of pipe-work, then methods exist to account for this. A graphical presentation of the ratio of the mass flow rate through a length of pipe-work to the case of a simple hole with the same vessel conditions is available in Lees' or Perry's³⁷. Alternatively, a numerical approach which requires the construction of a small computer program is given in the TNO *Yellow book*³⁸.

³⁶ *Critical flowmetering: The characteristics of cylindrical nozzles with sharp upstream edges* A.J. Ward-Smith, Int. J. Heat and Fluid Flow, Vol. 1, Num. 3, pp. 123-132, 1979.

³⁷ *Perry's Chemical Engineers' Handbook* R.H. Perry and D.W. Greed (Eds.), 7th Edition, McGraw-Hill, ISBN 0-07-049841-5, 1997.

³⁸ *Methods for the calculation of physical effects due to releases of hazardous materials (liquids and gasses)* C.J.H. van den Bosch and R.A.P.M. Weterings (Eds.), Third Edition, Committee for the Prevention of Disasters, The Hague, 1997.

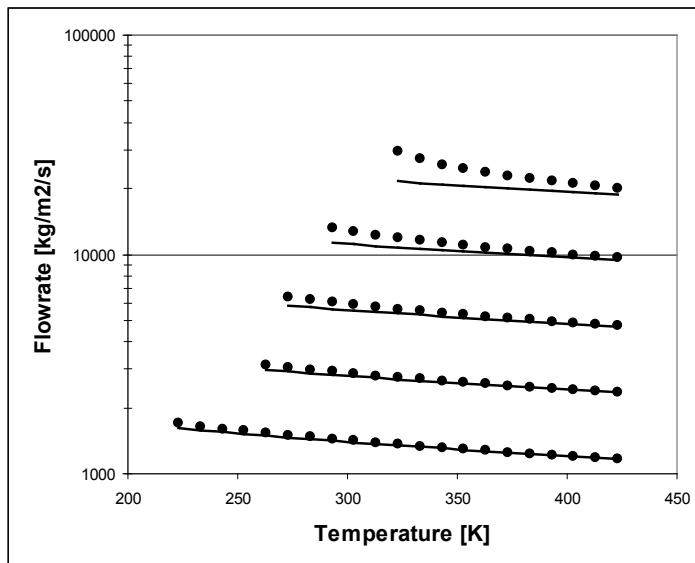


Figure A.1 Mass flow rate per unit area as a function of temperature at pressures of 5, 10, 20, 40 and 80 bar. The lines show the flow rate calculated using an isentropic assumption together with the ideal gas law, while the points use a Peng-Robinson equation of state.

A.4.3 Vessels with liquid Inventory

In many circumstances there is no reason to assume that the flow rate from a liquid inventory should be calculated in a different manner to other compressed volatile liquids.

For releases of non-flashing liquid, the normal method for calculating release rate is to use the Bernoulli equation which is given by:

$$G = \sqrt{2\rho_v\Delta p}$$

The value of Δp in this equation must be specified - for a non-flashing liquid it would normally be the difference between the stagnation pressure and atmospheric pressure. In the case of a flashing liquid this is not necessarily the most appropriate approach - as the pressure at the exit plane will not be equal to atmospheric pressure. If the state of the liquid in the vessel is below the critical pressure, or far to the left of the critical point, then the lines of constant temperature and of constant entropy are approximately parallel (this can be observed on a pressure-enthalpy diagram where both sets of lines are approximately vertical). Hence, assuming that the liquid is substantially sub-cooled and is flashing off at the exit plane, in expanding to the saturation line the liquid temperature will be *approximately* constant. The pressure at the exit plane will then equal the saturation pressure at the temperature of the liquid inside the vessel. This will give a less pessimistic estimate of the flow rate and will be referred to as a 'modified' Bernoulli equation.

A more rigorous general method can be used to find the choked flow rate. In this method an isentropic assumption is still made together with the assumptions that thermodynamic equilibrium exists and that vapour and liquid have a common velocity. The static pressure at the exit plane is then varied and the resulting mass flow rate found.

This produces a graph of flow rate versus exit plane pressure. Choked flow occurs at the maximum of this graph. This is known as the homogenous equilibrium method (HEM) and in the examples shown here fluid properties are calculated using the Peng-Robinson equation of state.

The flow rate per unit area is found from the isentropic assumption in which there is no heat transfer so that:

$$h_{vessel} = h_{exit} + \frac{1}{2}v_{exit}^2$$

which leads to:

$$G = \rho_{exit}v_{exit} = \sqrt{2\rho_{exit}^2(h_{vessel} - h_{exit})}$$

This method works equally well for any upstream state and can therefore be used for the gaseous releases also. However for a straightforward gas case, choking is generally considered in terms of the gas reaching a sonic condition at the exit plane. It can be noted that this is consistent with the approach described here.

For a vessel containing either a sub-cooled liquid or a supercritical fluid with a thermodynamic state to the left side of the saturation dome on a p-h diagram, a typical thermodynamic path from the vessel conditions to the exit plane is shown by case A in Figure A.2. In this case the corresponding curve of flow rate against exit pressure has a sharp maximum in the curve which corresponds to the point where the isentrop crosses the saturation curve. The reason for the maximum being in this position is that a further drop in pressure along the isentrop results in a liquid/vapour two-phase state at the exit plane where the density rapidly falls due to the vapour portion.

As an aside, it can be noted that in some cases, a gaseous vessel condition may be close enough to the saturation line that the isentropic path leads into the two phase gas/liquid region. Such a thermodynamic path is shown by case B in Figure A.2. In this case, the reason for the path terminating on the saturation dome is more subtle and due to a discontinuity in the gradient of the isentrops across the saturation line on the p-h plane. It can be noted that this discontinuity is difficult to see in typical p-h diagrams due to the logarithmic scale used for pressure.

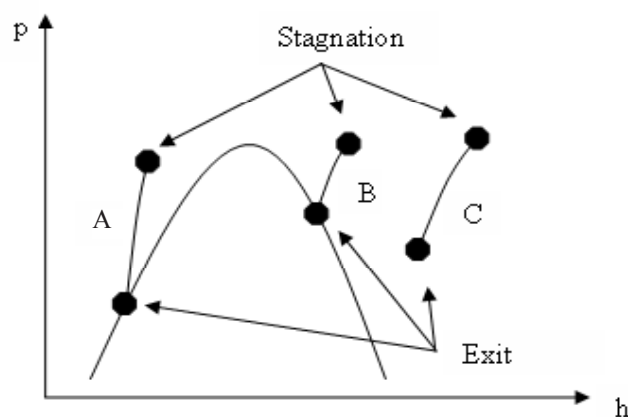


Figure A.2 Typical thermodynamic paths from vessel (stagnation) to exit plane conditions for three vessel thermodynamic states

It can be noted that for a saturated liquid where the thermodynamic state lies on the saturation dome (for example the bottom point of line A in Figure A.2), the 'modified' Bernoulli equation is not valid, and indeed at this point it begins to break down. The normal form of the Bernoulli equation can still be used, but as shown in the example in Figure A.3 it is very pessimistic.

The middle ground between the simple approach of using the Bernoulli equation (with the exit pressure equal to the saturation pressure) and the approach of maximising the flow rate with respect to the exit pressure, is the Omega method³⁹. In this method a correlating factor (ω) for compressibility is used with an assumed equation of state. The advantages of the ω -method are that only upstream conditions are required and the process of varying the exit pressure required in the full method is not needed. Because the thermodynamic data required by the method are less than in the full method, tabulated data can be used. In addition, the method has been extended to allow it to deal with a release which takes place through a length of pipework. The main disadvantage of the method is that it is generally only valid for pressures below the critical pressure; above the critical pressure ω must be derived differently.

The various methods described for sub-cooled and supercritical liquids are compared in Figure A.3 and Figure A.4. In Figure A.3 the upstream temperature is 0°C while in Figure A.4 it is -20°C. These graphs show mass flow rate per unit area as a function of pressure, without any discharge coefficient applied. It can be seen that the straightforward application of the Bernoulli equation gives a significantly higher flow rate than the other methods. On the other hand, all three other methods are in agreement. This is because they are essentially following the same practices in the particular region of thermodynamic states under consideration, well above the saturation dome.

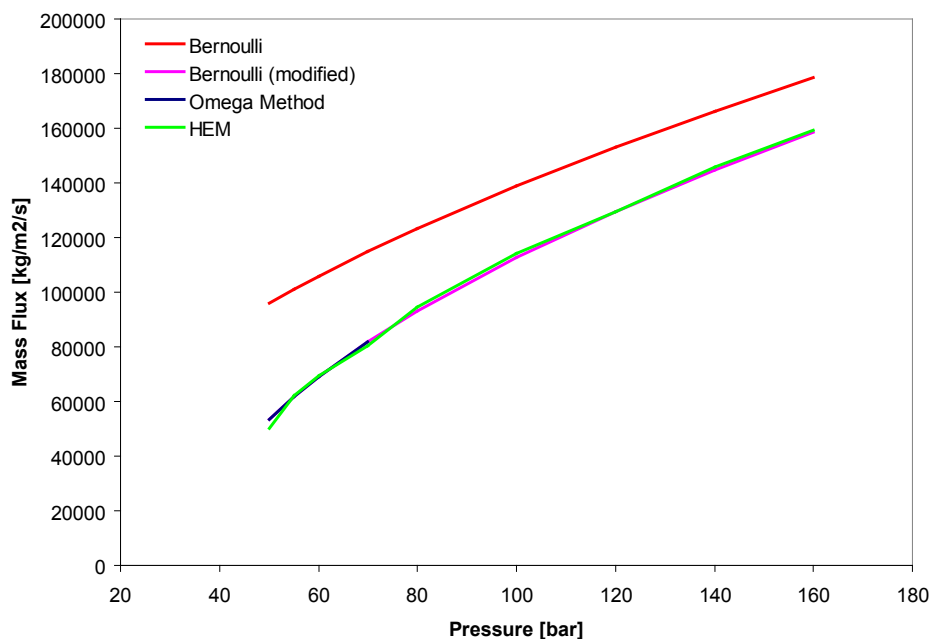


Figure A.3 Mass flow rate per unit area as a function of pressure for sub-cooled liquid and supercritical inventories. In each case the temperature is 0°C. Flow rates are calculated using the Bernoulli equation, the Bernoulli equation assuming the saturated vapour pressure at the exit, the ω -method and HEM.

³⁹ *The Omega method for discharge rate evaluation* J.C. Leung, Paper 46e, AIChE Meeting "Update on Relief System Design", Denver, August 1994. Available from <http://www.fauske.com>.

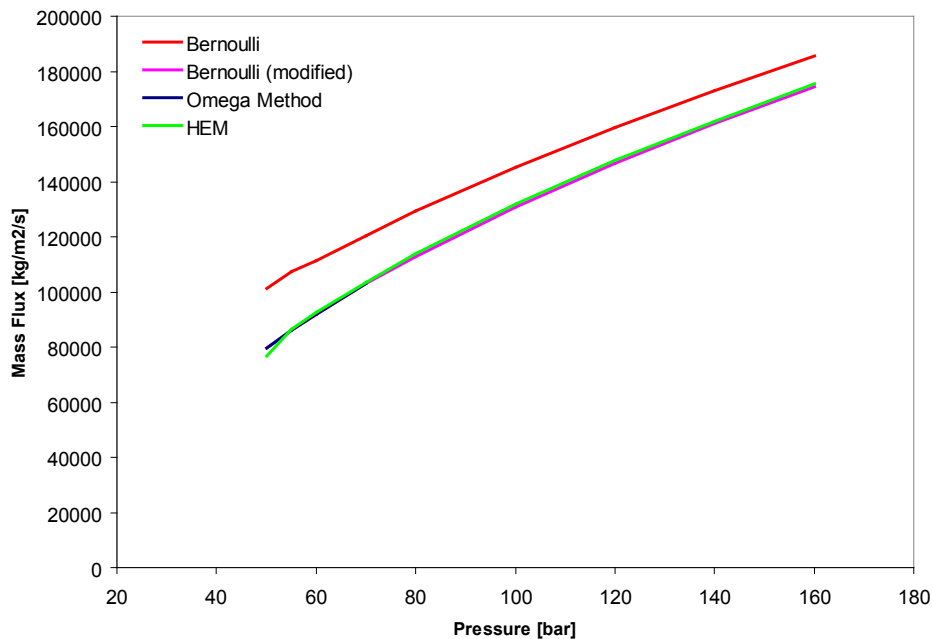


Figure A.4 Mass flow rate per unit area as a function of pressure for sub-cooled liquid and supercritical inventories. In each case the temperature is -20°C. Flow rates are calculated using the Bernoulli equation, the Bernoulli equation assuming the saturated vapour pressure at the exit, the ω -method and HEM.

Figure A.5 shows a graph for the case of a saturated liquid inventory. In this case it is not possible to use a modified form of the Bernoulli equation as this would give a flow rate of zero. The remaining three methods are compared, and again the ω -method and the general method are found to be in good agreement, but the Bernoulli equation is higher by up to a factor of four. Hence it is clear that the Bernoulli equation should not be used in this case.

It can be noted that in all of the cases used to populate these graphs, the pressure at the exit plane was calculated to be above the sublimation pressure of 5,2 bar. While this is the case the fluid is either liquid, vapour or a two-phase liquid/vapour mixture for which the various models (HEM and ω -method) are valid. If the pressure falls below this then the models become invalid and it is unclear of the effect.

In summary, for liquid and liquid-like supercritical cases the Bernoulli equation will always over-predict flow rate, sometimes grossly. The ω -method, on the other hand, works well when valid and is simpler than the more general HEM method.

As in the gaseous case, the above methods neglect losses and these can be accounted for using a discharge coefficient. There is some uncertainty to the discharge coefficient for the liquid case. For liquid discharge, a value of 0,62 is commonly used, while for gaseous releases, Lees recommends a value found from:

$$C_D = \pi / [\pi + 2(\rho_{out} / \rho_{in})]$$

which typically produces values only slightly above 0,62.

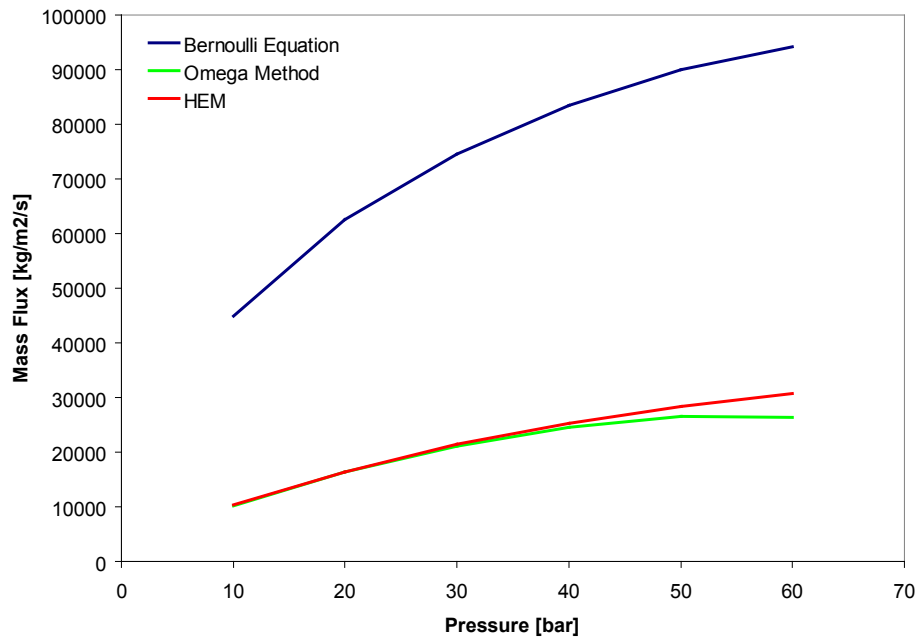


Figure A.5 Mass flow rate per unit area as a function of pressure for saturated liquid inventories. Flow rates are calculated using the Bernoulli equation, the general method, and the Omega method.

In this example flashing occurs at the exit and it is not clear that these are the best values. Cumber⁴⁰ suggests a value of 0,8 for both gaseous and two-phase releases. For the releases considered in this section, the flow will generally be a saturated two-phase mixture at, or close to, the outlet. Hence, if the thermodynamic state of the fluid within the vessel is a sub-cooled liquid, a two-phase liquid/vapour mixture or a supercritical fluid with entropy below the critical entropy, it is suggested that the discharge coefficient is chosen to be 0,8. If the fluid within the vessel is a gas or a supercritical fluid with entropy above the critical entropy a value of 0,85 is suggested.

A.4.4 Pipelines with gaseous inventory

For blowdown of gaseous pipelines a number of simplified models, which assume the gas is ideal, are currently available. Of these Wilson's 'double exponential'⁴¹ model is commonly used, being described in the TNO *Yellow book*⁴² and also the method used in the *Shell FRED* code⁴³. In this method, the mass release rate is approximated by a function containing a pair

⁴⁰ *Modelling top venting vessels undergoing level swell* P. Cumber, J. Hazardous Materials, Vol. A89, pp. 109-125, 2002.

⁴¹ EUBH2S *A model for calculating emergency response and planning zones for sour gas facilities. Volume 1: technical reference document* Alberta Energy and Utilities Board, 2006.

⁴² *Methods for the calculation of physical effects due to releases of hazardous materials (liquids and gasses)* C.J.H. van den Bosch and R.A.P.M. Weterings (Eds.), Third Edition, Committee for the Prevention of Disasters, The Hague, 1997.

⁴³ *Shell FRED fire, release, explosion, dispersion hazard consequence modelling package: technical guide*, Shell Research Ltd, 2004.

of exponentials given by:

$$\dot{m} = \left(\frac{1}{1 + \alpha} \right) \left[\dot{m}_0 \exp\left(-\frac{t}{\alpha^2 \beta} \right) + \frac{M_0}{\beta} \exp\left(-\frac{t}{\beta} \right) \right]$$

Where \dot{m}_0 is the initial mass flow rate, M_0 is the initial mass in the pipeline, β is a time constant and α is given by $M_0 / \beta \dot{m}_0$. Wilson gives the time constant β as:

$$\beta = \left(\frac{2d}{3\gamma c} \right) \left[\left(\frac{\gamma + 1}{2} + \frac{fL}{d} \right)^{\frac{3}{2}} - \left(\frac{\gamma + 1}{2} \right) \right]^{\frac{3}{2}}$$

where d is the pipe diameter, L is the pipe length, c is the sound speed in the gas and f is the friction factor. In the TNO *Yellow book* and the FRED *Technical guide* this is simplified to:

$$\beta = \left(\frac{2L}{3c} \right) \left[\frac{fL}{d} \right]^{\frac{1}{2}}$$

The criteria for this to be valid is that

$$\frac{fL}{d} \gg \frac{\gamma + 1}{2\gamma}$$

which is usually the case for pipelines so that the simplified expression can normally be used. The initial mass flow rate is given by Wilson as:

$$\dot{m}_0 = K_{inertia} \dot{m}_{0,isentropic}$$

Where $\dot{m}_{0,isentropic}$ is the initial mass flow rate assuming an isentropic expansion, and $K_{inertia}$ is a constant to account for the effect of inertia on the initial mass flow rate. This factor is neglected in both the TNO *Yellow book*, and the FRED *Technical guide*. The initial isentropic mass flow rate is given by:

$$\dot{m}_{0,isentropic} = A \left(\frac{2}{\gamma + 1} \right)^{\frac{\lambda + 1}{2(\gamma + 1)}} \sqrt{\gamma P_0 P_0}$$

Omitting the factor $K_{inertia}$ will result in a higher initial mass flow rate and in that sense is pessimistic. Extensions exist to account for flow during ESDV closure⁴⁴. If the rupture is in the middle of a pipeline, then the release from each end must be accounted for.

If more detail is required, further fundamental methods can be used which solve the underlying fluid dynamic equations (mass, energy and momentum conservation). For example a technique called the 'method of characteristics' has, in some cases, been used. The general theory is described in detail in 'Gas dynamics'⁴⁵. Applications to natural gas pipelines are described in *Unsteady compressible flow in long pipelines following a rupture; A study of the dynamic response of emergency shutdown valves following full bore rupture*

⁴⁴ EUBH2S *A model for calculating emergency response and planning zones for sour gas facilities. Volume 1: technical reference document* Alberta Energy and Utilities Board, 2006.

⁴⁵ *Gas Dynamics* vols. I and II, M.J. Zucrow and J.D. Hoffman, Wiley 1976.

of gas pipelines and Numerical simulation of full bore ruptures of pipelines containing perfect gases⁴⁶. A few notes on this model are:

1. The method of characteristics solves the fundamental conservation equations for mass, momentum and energy and in this sense is not an 'approximate' method like the Wilson model.
2. Real gas behaviour can be captured using the Peng-Robinson equation of state.
3. The model solves the equations on a number of nodes along the pipeline length.
4. It is numerically intensive (due to 2 and 3).

It can be noted that other methods can be used, such as spectral methods⁴⁷, but these have received less attention in the literature.

An obvious possibility for assessing the hazard associated with a pipeline rupture is to carry out a dispersion calculation based on the initial, peak, mass flow rate from the pipeline. However, care must be taken in using this approach as, in addition to being very conservative, it is possible for the steady-state assumption to give a non-physical mass of gas in the domain, greater than the total pipeline inventory.

A.4.5 Pipelines with liquid inventory

As for pipelines with a vapour inventory, for liquefied gases there are a number of methods available with varying levels of complexity. In the case of liquefied gases, the approximate methods have to make substantial assumptions.

A representative example of an approximate model is the Cumber model, discussed in two papers⁴⁸. The first describes a model for a volatile liquid pipeline (typically used for propane, but also applicable to carbon dioxide so long as the pressure remains above the triple point pressure, 5,2 bar. Below this pressure, solids can be produced in carbon dioxide). The second extends this model to the case of a supercritical fluid.

The overall basis of the Cumber method is to take the equation for pressure gradient in the two-phase region and approximate a number of factors as functions of pressure (only) so that it can be integrated. To allow the integration to be carried out, several significant assumptions are necessary including:

1. The pipeline is assumed to be infinitely long.
2. Flow is assumed to be isenthalpic.
3. Mass flow rate is assumed to increase linearly from the liquid/two-phase interface to the location of the rupture.
4. Several assumptions relating to the method by which some integrals are estimated, which can be found in the published papers.⁴⁸

⁴⁶ *Unsteady compressible flow in long pipelines following a rupture* R. Flatt, Int. J. for Numerical methods in fluids, vol. 6, pp. 83–100, 1986; *A study of the dynamic response of emergency shutdown valves following full bore rupture of gas pipelines* H. Mahgerefteh, P. Saha and I.G. Economou, Trans. IChemE, vol. 75, part B, pp 201–209, 1997; and *Numerical simulation of full bore ruptures of pipelines containing perfect gases* J.R. Chen, S.M. Richardson and G. Saville, Trans. IChemE Part B, vol. 70, pp. 59–69, 1992.

⁴⁷ *Gas flow in pipelines following a rupture computed by a spectral method* E. Lang, J. Appl. Math. and Physics, vol. 42, pp. 183–197, 1991.

⁴⁸ *Modelling outflow from a ruptured pipeline transporting compressed volatile liquids* R.P. Cleaver, P.S. Cumber and A. Halford, J. Loss Prev. in the Process Ind., vol. 16, pp. 533–543, 2003 and *Outflow from fractured pipelines transporting supercritical ethylene* P.S. Cumber, J. Loss Prev. in the Process Ind., vol. 20, pp. 26–37, 2007.

The model was originally applied to volatile liquid pipelines. The extension to supercritical fluids is described in *Outflow from fractured pipelines transporting supercritical ethylene*. In this paper the fluid considered is ethylene, but the physics is the same with carbon dioxide.

The model for supercritical fluids is the same as for a liquid pipeline on a practical level. This is because three pressure waves are assumed to travel up the pipeline from the ruptured end. The first wave, travelling at the local speed of sound initiates motion in the fluid, the second causes a transition from a supercritical fluid to a liquid and the final one causes a transition to a two-phase gas-liquid state.

It is assumed that the amount of fluid which is released at the exit, prior to a two-phase condition being reached, is small. Hence the liquid model is used and it only remains to describe how the liquid thermodynamic state used for this calculation is obtained from the initial, supercritical state. Some outcomes are:

- If the intent is to compare two cases with thermodynamic states about the critical pressure the comparison may be inaccurate or, in some cases, impossible.
- The method is really only intended for a relatively small sub-set of the thermodynamic space.
- It is not suited for short lengths of pipe with initially high pressure.

Other simplified models exist, and these will need to make similar assumptions to that of Cumber.

Since approximate methods are unsuitable for calculating the flow rates from, for example, short lengths of pipeline, the 'method of characteristics' can be used as for the vapour case. The theory is essentially the same as in the vapour case, but a real gas equation is needed to describe the two-phase thermodynamics. A cubic equation of state such as the Peng-Robinson equation is typically used. Applications to liquefied gases and supercritical conditions are described, in reference 21. Finite difference models can also be used in place of the method of characteristics, as in references 22 and 23.

A.5 SOURCE TERM IMPLEMENTATION

The precise mechanism for implementing the carbon dioxide source term into a code for calculating dispersion may depend on the details of the code. The purpose of this section is to show that some thought should be given to finding an appropriate method. Here the example of inserting the source into a CFD code is used, but similar methods will apply for integral models.

In some cases it is possible to calculate the release of carbon dioxide and its subsequent atmospheric dispersion in the same model; in other cases it may be necessary to calculate the release separately from the dispersion and use the results of the release calculation to provide the initial/boundary conditions of the dispersion calculation.

A.5.1 Gaseous releases

Once again, in many cases there is no reason to expect carbon dioxide to differ from other gases. When the carbon dioxide is released from an inventory where the ratio of inventory pressure to atmospheric pressure $p_i/p_a > 1.89$ the release will be a choked flow at the sonic velocity and an under-expanded jet results. For accidental releases, this is the most common case. In the flow region immediately beyond the release, the flow structure is rather complex with shocks and expansion waves. It is inconvenient to attempt to calculate these detailed features within the numerical domain required for a dispersion calculation because of the separation of scales between the shock structure and the dispersion domain.

Therefore, some form of a pseudo-source approach is required. In this approach, instead of modelling the actual release source, the release is modelled from a point or plane downstream of the actual release position. This pseudo-source is defined such that the flow behaviour further downstream closely resembles that resulting from the actual leak source.

There are several possible approaches which can be taken, one being CFD. In this method the source is resolved explicitly by the CFD grid, i.e. it takes the form of a number of faces at a boundary in the mesh at the 'sonic point' (the point where the jet equilibrates into a sonic stream). Some simple assumptions are needed that allow the jet to be represented by a sonic jet at atmospheric pressure with the same mass flow rate as the original high pressure jet. Research carried out by the Health and Safety Laboratory⁴⁹ suggests that this sonic approach appears to give the best results.

In order to calculate the parameters at the effective inlet, it is assumed that between the actual release point and the sonic point there is very little entrainment of the surrounding air into the jet due to high pressure. Hence, at the sonic point the mass fractions of the component gases will remain the same as at the release. Also, assuming an isenthalpic expansion and ideal gas behaviour, the temperature at the sonic point will be the same as at the exit plane of the release. The sonic point is typically 10-15 diameters downstream from the release point. Often this dimension is small in comparison to the overall model dimensions so that for the purposes of the CFD model it is considered to be collocated at the release. This is also typically done in integral models.

A.5.2 Liquid and supercritical releases

For a release where the vessel inventory is a liquid the fluid state at the exit plane is expected to be a saturated liquid or a liquid/vapour mixture. Beyond the exit the liquid will flash to a vapour and rapidly expand in a 'tulip' shape whilst simultaneously cooling such that particles of solid carbon dioxide are formed. These particles will then sublime externally to the vessel.

This process is expected to be rather complex with three phases present, gas/liquid, liquid/solid and solid/gas phase changes occurring and very steep gradients. In addition, the length and timescales are separated from those of the far-field dispersion, so that including the detail of the region immediately adjacent to the nozzle in a CFD model for the far field dispersion is not considered viable.

A simplified method for dealing with the region immediately adjacent to the release needs to be employed giving a pseudo-source in a similar manner to that employed in the case of an under-expanded sonic jet. One method to fix the parameters of the pseudo-source is based on the work of Fauske and Epstein⁵⁰. The first stage is to find the flow rate and the exit plane conditions. These conditions are calculated using the method described in A.4.3.

Beyond the exit plane, the fluid expands and the resulting jet structure is shown schematically in Figure A.6, where the jet is divided into two regions: a depressurisation zone and a two-phase entrainment zone. The inlet to the CFD model is taken to be at the end of the depressurisation zone where the pressure in the jet has reduced to atmospheric pressure. The following assumptions are made:

- There is no entrainment of air into the jet in the depressurisation zone, due to the pressure being above ambient in this region.
- Friction and heat transfer are neglected in the depressurisation zone.

⁴⁹ *Outstanding safety questions concerning the use of gas turbines for power generation: Final report on the CFD modelling programme of work* M. Ivings, HSE report CM/03/08, 2004.

⁵⁰ *Source term considerations in connection with chemical accidents and vapour cloud modelling* H.K. Fauske and M. Epstein, *J. Loss Prev. Process Ind.*, vol. 1, pp. 75-83, 1988.

Conservation principles are then used to find the jet properties at the end of the depressurisation zone, specifically conservation of momentum flux, conservation of energy and conservation of mass.

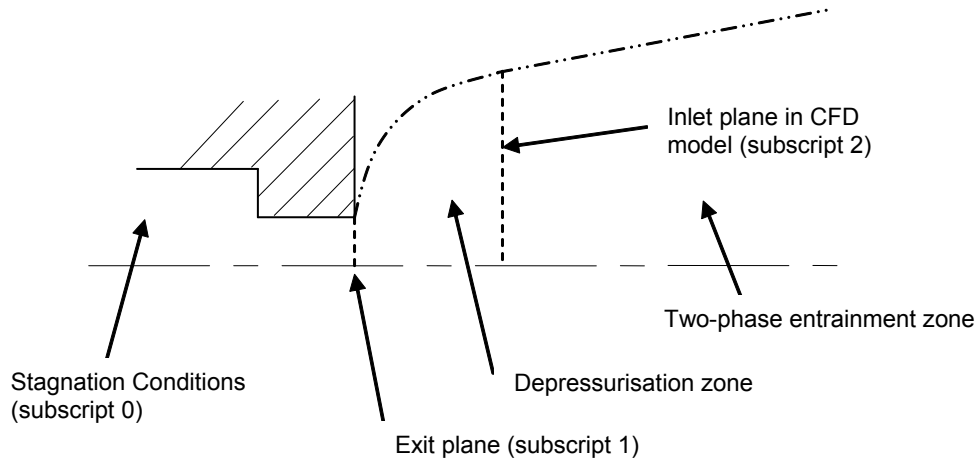


Figure A.6 Schematic diagram of the jet structure for a flashing liquid

In order to solve the resulting equations some additional assumptions are required, and these can be found in Fauske and Epstein. Firstly, the assumption is made that the velocity terms can be neglected in the energy equation so that:

$$h_2 = h_1$$

With $p_2 = p_{atm}$, this places the thermodynamic state at the end of the depressurisation zone in the two phase solid/gas region of the phase diagram. In order to find the mass fraction split between gas and solid, the enthalpy is written as:

$$h_2 = h_s + Y_{2g} h_{sg}$$

where Y_{2g} is the vapour mass fraction at the end of the depressurisation zone, h_s is the solid enthalpy and h_{sg} is the enthalpy difference between solid and vapour at atmospheric pressure. This equation gives the gas mass fraction.

From these considerations, the temperature, velocity and mass fraction can be found at the end of the depressurisation zone together with the jet area. The inlet to a CFD model can then be placed here with known characteristics. There will still be solid carbon dioxide within the jet in very small particles and these must be tracked as they sublime, either explicitly, or by employing a scalar variable to track the concentration.

It is also possible to move the inlet into the CFD domain further downstream, to a point where the solid carbon dioxide particles have all sublimed. This removes the need to track carbon dioxide particle concentration, but adds the requirement for explicitly calculating the entrainment of air into the jet over the first part of its development. This can be done with empirical relations.

A.6 DISPERSION

The main features of carbon dioxide dispersion are:

- It is denser than air so that it will tend to slump, particularly in low wind speeds.
- It is often cold at its release point (accentuating its dense nature).
- In releases from the liquid state it expands rapidly in a characteristic 'tulip' shape and carries solid particles.

Some of these aspects are shared with other gases. The only truly unique aspect is the solid particles carried by the plume. It must be noted that releases from CCS plants, particularly pipelines, will be at high pressure. The high momentum of these releases will result in rapid entrainment of air and a subsequent reduction in density and increase in temperature due to mixing with air.

There are several general methodologies which can be employed for dispersion calculations for carbon dioxide and other gases. Parameters which need to be considered in choosing a methodology include whether or not surrounding plant and/or terrain needs to be accounted for, wind speed and direction relative to the release, and length scales of interest. The two broad methodologies which can be employed are integral models and CFD. These two general classes of technique are described in A.7.

A.7 INTEGRAL MODELS

Many atmospheric dispersion models for environmental analysis are conducted with Gaussian plume models. The Atmospheric Dispersion Modelling Liaison Committee (an independent organisation which advises on matters of atmospheric dispersion modelling) has developed a simple Gaussian plume model which has been widely used and is often referred to as the R91 model⁵¹. The R91 model has been extended to include a variety of effects (deposition, coasts, plume rise, buildings) which led to the development of more complex Gaussian models⁵². This provides the basis for commercial codes/models.

Gaussian plume models have a number of limitations, some of which are: the minimum wind speed for applicability is generally taken as 1 m/s; zero wind speed cannot be calculated; any vertical component of the wind, which might be generated by upwash or downwash over buildings, structures and terrain, cannot be included; they are only applicable when the release source is sufficiently distant from surrounding buildings for airflow at release height to be undisturbed; any momentum in the released plume is accounted for by specifying an 'equivalent height' of release; and no transient calculations.

Gaussian plume models are not expected to be appropriate for the majority of atmospheric dispersion calculations in CCS projects since they will only be applicable at concentrations of carbon dioxide at which the hazard is negligible. A possible exception may be if the carbon dioxide contains significant quantities of a more toxic material such as hydrogen sulphide.

There are more advanced integral models available than the simple Gaussian plume models, which can deal with heavy gases. These include HGSYSTEM⁵³ and PHAST⁵⁴. Under

⁵¹ *A Model for short and medium range dispersion of radionuclides released to the atmosphere* R.H. Clarke, NRPB-R91, 1979.

⁵² *Models to allow for the effects of coastal sites, plume rise and buildings on dispersion of radionuclides and guidance on the value of deposition velocity and washout coefficients* J.A. Jones, NRPB-R157, 1983.

⁵³ HG System website www.hgsystem.com/summary.html.

⁵⁴ PHAST website www.dnv.com/services/software/products/safeti/SafetiHazardAnalysis/phast.asp.

some circumstances these models can deal with the negative buoyancy of carbon dioxide and the tendency of a plume to slump on the ground. In some cases they can also deal with the transition from a momentum dominated jet, through a slumping gas to a passively dispersing cloud. At least one model (PHAST) can also deal with the formation and subsequent sublimation of carbon dioxide particles, though *advice* must be sought from the code vendor to ensure that an appropriate code version is being used.

These more advanced integral models still have some disadvantages with regard to carbon dioxide dispersion:

- Some cannot be used with very low wind speeds.
- They cannot deal with cases where the plume interacts with itself, for example where a jet is directed into the wind so that the gas blows back around the jet. However it is worth noting that most cases assume the wind is in the same direction as the release which gives conservative cloud sizes.
- The effect of interaction with buildings and/or plant cannot be accounted for except in a very general way which accounts for the cloud travelling over certain types of terrain, eg. woodland, farmland or urban low-rise housing.

Another limitation of many integral models is that they do not include carbon dioxide as a material that can be modelled automatically, so scenarios cannot be attempted without manual intervention which requires some additional knowledge on the behaviour of carbon dioxide when released.

The primary advantages of integral models are that they are quick to set up and run, work well in appropriate scenarios and the main codes are well validated and accepted by regulators.

A.7.1 CFD models

CFD overcomes many of the limitations of integral models but it is not suitable for carrying out wide ranging and rapid project screening analysis. CFD codes are based on the solution of mass, momentum and energy conservation equations (Navier-Stokes equations) to provide full 3D flow maps in an identified volume. Additional transport equations can be included to calculate the effects of turbulence and model the transport of different gas species (CO₂, CH₄ etc.), pollutants or particulates. Calculated flows may be steady or transient, there are no limiting wind speeds, and momentum of releases and buoyancy are included explicitly. Physical obstructions such as buildings, structures and terrain which modify the flow and subsequent dispersion can be included in the models. General purpose CFD codes are available commercially and lend themselves to modification to include particle transport etc.

There are several disadvantages still to overcome with CFD:

- In comparison with integral models the cases are slow to set up and slow to run.
- They typically require specialist staff and significant computer power to run.
- The codes are general purpose and are not specialised to dispersion so that there is more work required by the analyst, setting up source terms and atmospheric profiles, etc.
- CFD solvers are not designed to deal with the atmospheric boundary layer so that the profiles typically change slowly though an empty terrain. Also, only wind and turbulence profiles for stability class D have received significant attention in the CFD literature.

There are several commercially available CFD solvers, the primary ones being FLACS, FLUENT⁵⁵ and ANSYS-CFX⁵⁶, the latter two are owned by ANSYS Inc and which will shortly be integrated to form a new code with the best features of each. Alternatively there is an open source code called Open-FOAM⁵⁷ which is receiving increasing attention.

A.8 VALIDATION

In this section notes are made regarding the validation data which demonstrate the applicability and robustness of the models described in A.7. In general there is no evidence to suggest that carbon dioxide behaves in a way which is different to other materials when dispersing after a release. Hence model validation for other materials will in many cases be applicable to carbon dioxide.

The main difference is that carbon dioxide does not exist as a liquid at pressures below 5,2 bar. Hence, for release rate experiments, so long as the pressure in any pipeline or vessel remains above this all the way to the exit plane, methods developed for other gases and liquids should function correctly. Similarly, so long as the initial expansion from the liquid inventory and the subsequent formation of solids can be handled reasonably, dispersion should then be similar to that for other heavy gases.

A.8.1 Experiments specific to carbon dioxide

A set of experiments specifically designed to investigate both the release and subsequent dispersion of carbon dioxide were carried out by BP and Scottish & Southern Energy⁵⁸ at Spadeadam towards the end of 2007. Four contractors modelled the release and dispersion of carbon dioxide for several of these experiments as part of a carefully controlled modelling exercise. Full data are not yet available from these experiments but some comparisons between experiment and calculations have been published⁵⁹.

Release rates for carbon dioxide from a supercritical/liquid inventory have also been experimentally investigated by Gebbeken and Eggers⁶⁰ and this has been used to demonstrate that calculating vessel blowdown with the Peng-Robinson equation of state is satisfactory⁶¹.

A.8.2 Experiments relating to blowdown of process vessels

In operation, wherever possible vessels and pipelines should always be blown down from the liquid side. When this is not possible, vessel blowdown models should be used to guide

⁵⁵ FLUENT website www.fluent.com.

⁵⁶ ANSYS-CFX website www.ansys.com/Products/cfx.asp.

⁵⁷ Open-FOAM website <http://www.opencfd.co.uk>.

⁵⁸ BP assigned the intellectual property rights to Hydrogen Energy.

⁵⁹ *Calculating the release and dispersion of gaseous, liquid and supercritical CO₂*, C Dixon and M Hasson, I.Mech.E. Seminar on Pressure Release, Fires and Explosions, London, October 2007.

⁶⁰ *Blowdown of carbon dioxide from initially supercritical conditions* B. Gebbeken and R. Eggers, J. Loss Prev. Process Ind., vol. 9, num. 4, pp. 285–293, 1996.

⁶¹ *Calculating the release and dispersion of gaseous, liquid and supercritical CO₂*, C Dixon and M Hasson, I.Mech.E. Seminar on Pressure Release, Fires and Explosions, London, October 2007.

the operations. Several have been validated using other gases⁶². The only obvious issue for carbon dioxide is that of solids formation if/when the pressure anywhere in the vessel drops below 5,2 bar.

The experiments most often quoted are reported by Haque et al⁶³. They carried out a number of experiments on the blowdown of vessels. Vessels were used together with materials including pure nitrogen, several hydrocarbon mixtures and nitrogen/carbon dioxide mixtures. In the latter case the highest proportion of carbon dioxide was 55 % by mole fraction. However, detailed results for these cases were not reported.

Other experiments have been carried out for materials such as water, methanol and Freon. Several are listed in the references section.

A.8.3 Experiments relating to blowdown of pipelines

Validation of pipeline blowdown is largely based on a set of experiments carried out at the Isle of Grain on 100 m long LPG pipelines with a diameter of 2" or 6"⁶⁴. There are additional lab-scale experiments⁶⁵ carried out on various hydrocarbon mixtures, but these are not generally quoted in the numerical papers.

A.9 GAPS AND UNCERTAINTIES

A.9.1 Blowdown of pipelines

The validation data for pipelines are limited, partly due to the cost of carrying out such tests at full scale. The Isle of Grain test data are quoted in almost every paper on numerical modelling of pipeline blowdown. There is no particular reason to believe that carbon dioxide will behave differently from any other liquefied gas so long as the pressure throughout the pipeline remains above the triple point pressure (5,2 bar). For long pipelines this may be the case for a considerable period; however for shorter pipelines or longer durations this may not be the case and solid formation may occur at the ruptured end of the pipeline. Typically, pipeline blowdown codes use cubic equations of state to represent the thermodynamics of the fluid. This method does not have any mechanism to deal with solid formation so the two-phase region of the pipeline would be implicitly assumed to be a gas/liquid mixture down to atmospheric pressure. It is not clear what effect this will have on flow rate calculations.

A separate issue associated with pipeline blowdown relates to the specification of the source term. Generally, during a full bore rupture a crater is formed during the event and there is uncertainty around the size and shape of the crater. It can be noted that this is not an issue which is specific to carbon dioxide but is general to all pipelines. The uncertainty

⁶² *Blowdown of hydrocarbons pressure vessels with partial phase separation* A. Speranza and A. Terenzi, Series on Advances in Mathematics for Applied Sciences, vol. 69, pp. 508–521, 2005; *A numerical blowdown simulation incorporating cubic equations of state* H. Mahgerefteh and S.M.A. Wong, Computers and Chemical Engineering, vol. 23, pp. 1309–1317, 1999; *Blowdown of Pressure Vessels I. Computer Model* M.A. Haque, S.M. Richardson and G. Saville, Trans. IChemE Part B, vol. 70, pp. 3–9, 1992.

⁶³ *Blowdown of pressure vessels II. Experimental validation of computer model and case studies* M.A. Haque, S.M. Richardson, G. Saville, G. Chamberlain and L. Shirvill, Trans. IChemE Part B, vol. 70, pp. 10–17, 1992.

⁶⁴ *Isle of Grain Pipeline Depressurisation Tests* S.M. Richardson and G.Saville HSE Report OTH 94 441, 1996.

⁶⁵ *Measurements of flow parameters and decompression wave speed following rupture of rich gas pipelines and comparison with GASDECOM* K.K. Botros, J. Geerligs, J. Zhou and A. Glover, Int. J. of Pressure Vessels and Piping, vol. 84, pp. 358-367, 2007.

regarding the crater produces an uncertainty regarding the interaction of the crater with the fluid issuing from the pipeline and hence the source term definition. Under such circumstances it is possible to define a worst case, which is that the gas loses all of its momentum and emerges from the ground slowly.

A.9.2 Blowdown of vessels

Haque et al.⁶² briefly discuss particle formation in the case of blowdown of CO₂/N₂ mixtures, but no detail is given either regarding the experimental results or the numerical handling of the situation. The industrial gases sector does not deem further research necessary and takes a thoroughly practical approach; liquid carbon dioxide-containing equipment is designed to a designated temperature. During blowdown as the liquid reaches saturated conditions, the pressure is maintained at a level that ensures the corresponding saturation temperature is not lower than the equipment design temperature.

A.9.3 Thermodynamics of mixtures containing carbon dioxide

Methods for dealing with the thermodynamics of mixtures of several components are well established. In the context of cubic equations of state this is accomplished using 'mixing rules' whereby the parameters in the equations of the components are combined to give a new set of parameters for the mixture. Research⁶⁶ gives mixing rules specifically for carbon dioxide with hydrocarbons, but is not clear how well validated these rules are or if the rules which are included in commercial process simulators are adequate. This is an area where additional validation might well improve modelling accuracy. In future CCS projects in which enhanced recovery of hydrocarbons is a feature, then it may be necessary to understand in some detail the behaviour of CO₂/hydrocarbon mixtures upon release in order to further refine carbon dioxide emission rates for input into dispersion models.

A.9.4 Scale up

There are limited experimental studies of carbon dioxide dispersion. The only full-scale study of which the authors are aware is the BP experimental programme carried out at Spadeadam. The data for this programme are unavailable at present and are limited to relatively small sizes of release - there is currently no evidence that the dispersion characteristics will vary vastly with scale up.

A.9.5 Particulates

Observation of liquid releases suggests that at lower pressures the particle sizes would be larger but not significantly so.

According to Haque et al, the solubility of nitrogen in solid carbon dioxide is very low so that for a CO₂/N₂ mixture while the gas at the end of the depressurisation tulip would be a CO₂/N₂ mixture, the particles would be essentially pure carbon dioxide. It is not clear if this would be true for other components (e.g. hydrocarbons or H₂S).

⁶⁶ *Measurements of flow parameters and decompression wave speed following rupture of rich gas pipelines and comparison with GASDECOM* K.K. Botros, J. Geerligs, J. Zhou and A. Glover, *Int. J. of Pressure Vessels and Piping*, vol. 84, pp. 358-367, 2007; *Predicting the phase equilibria of CO₂ and hydrocarbons with the PPR78 model (PR EOS and k_{ij} calculated through group contribution method)*", S. Vitu, R. Privat, J.-N. Jaubert and F. Mutelet, *J. of Supercritical Fluids*, vol. 45, pp. 1-6, 2008

A.9.6 Temperature envelope

Since the temperature envelope of releases from liquid inventories is unlikely to be lower than the solid formation temperature of carbon dioxide, a lower limit for the temperature can be set. The overall size of any potential lower temperature envelope within a cloud can be calculated by some integral models, but rely on manually inputting the temperature within the source term. Onshore, it is unlikely that the size of the temperature envelope will be a concern, except immediately near the release point. This issue will need to be looked at in more detail to address possible releases on offshore installations where space is more restricted.

A.9.7 Vertical releases

For operational and emergency releases the more interesting case is often vertical releases, particularly with a low wind speed. There are some slightly different mechanisms with vertical releases, as validation for horizontal releases does not give an absolute guarantee that vertical releases will also be correctly predicted under all atmospheric and release conditions. However there is no evidence that existing models for vertical releases cannot model carbon dioxide or other dense material releases adequately.

A.9.8 Specific dispersion modelling issues

There may be modelling issues which could ideally warrant study. These would depend on the specific type of model. In the case of CFD, one issue is the way that atmospheric turbulence is handled. In essence it is generally assumed to be isotropic, which it is not, and it is normally assumed to have a profile corresponding to stability class D (as is the velocity profile)⁶⁷. For long stretches of ground it is also difficult to force the turbulence profile to remain constant⁶⁸ - it tends to revert slowly to the profile appropriate to a flat plate.

A.10 SUMMARY

A.10.1 Release rate calculation

- For gaseous inventory an ideal gas assumption is often adequate.
- In some cases a real gas assumption is needed if the pressure is high.
- Some releases from gas phase inventories may involve two-phase thermodynamics.
- For a sub-cooled liquid inventory, Bernoulli equation is overly pessimistic.
- For a highly sub-cooled liquid a 'modified' Bernoulli equation using the saturation pressure instead of atmospheric pressure can be reasonable. But it will begin to become increasingly in error as sub-cooling is reduced.
- The ω -method gives very similar results to HEM for sub-cooled liquids.
- For a saturated liquid inventory the Bernoulli equation is grossly pessimistic.

⁶⁷ *Appropriate boundary conditions for computational wind engineering models using the k- ϵ turbulence model* P.J. Richards, and R.P. Hoxey, Journal of Wind Engineering and Industrial Aerodynamics, 46 & 47: 145-153, 1993.

⁶⁸ *Practical considerations for the use of CFD in wind engineering* Y. Sinai, NAFEMS Seminar on Quality and reliability of CFD simulations III: Quantifying and reducing uncertainty 14 March 2007.

- For a saturated inventory the ω -method is in very close agreement with HEM.
- The discharge coefficient for a choked gas release can be taken as 0,85, while for a release from the liquid phase a value of 0,8 can be used.
- Gaseous pipeline release rates can, in some cases, be found from simplified methods with analytical solutions.
- There are approximate methods for liquid and supercritical pipelines, but they have limited applicability.
- More rigorous pipeline release calculations can be carried out but require more computationally expensive numerical solution.

A.10.2 Dispersion

- Some simple releases may be soluble with Gaussian plume models.
- In some cases, more complex releases, but with no influence from large structures , topology and into the wind direction can be calculated with integral models.
- Releases where the influence of buildings and topology is important or where the release direction is not the wind direction need to be calculated using CFD.
- If more complex releases with high solids fraction are to be carried out, special procedures may be required and/or particular codes may be needed. However for screening analysis, it is sufficient to neglect solid formation and assume all release inventory contributes to cloud formation; this is likely to give a conservative cloud size.
- All modelling should be carried out by suitably experienced and qualified personnel.

ANNEX B

MODELLING TECHNIQUES FOR CARBON DIOXIDE HAZARD ANALYSIS USING PHAST

This section includes recommendations for carbon dioxide modelling using DNV's software package PHAST using either the current (at the time of drafting) released version PHAST 6.54 or PHAST 6.6.

B.1 SUMMARY OF MAIN DIFFERENCES BETWEEN PHAST 6.54 AND PHAST 6.6

For carbon dioxide releases the PHAST user is advised to use PHAST 6.6 as soon as this version has been released. This is because considerably more accurate results can be obtained in PHAST 6.6 because of inclusion of effects of carbon dioxide solid formation and inclusion of non-ideal gas effects for supercritical carbon dioxide releases from long pipelines.

PHAST (6.54) does not include effects of solid formation of carbon dioxide, and does not provide warnings to the user when solid formation will occur. PHAST (version 6.6) will account for effects of solid formation downstream of the orifice. For the dispersion equations the new model always assumes equilibrium model without solid deposition (no rainout), i.e. snow-out of carbon dioxide is not modelled. This assumption is justified since for most scenarios rainout is not expected to occur (or conservative predictions are given if rainout is ignored). Furthermore PHAST 6.6 does not account for effects of solid formation upstream of the release orifice, but it does apply appropriate warnings in case this should happen. The latter assumption is justified since for most scenarios the hazardous distance will be governed by the flow rate before the onset of solid effects upstream of the orifice.

For discharge of supercritical carbon dioxide from long pipelines PHAST 6.54 assumes the gas to be 'ideal' while PHAST 6.6 includes non-ideal effects (compressibility factor, Z will not always be 1). At very large pressures non-ideal effects are important and may therefore significantly increase the expelled mass (for example, about a factor of 1,8 at an initial pressure of 200 bar).

B.2 CHANGE OF DEFAULT PARAMETERS AND CARBON DIOXIDE MATERIAL SETTINGS IN PHAST 6.54 AND PHAST 6.6

For pipeline releases (short or long pipes, line rupture or long pipeline scenarios in PHAST), the user may obtain more accurate predictions in 6.54 and 6.6 by choosing a non-default value of the atmospheric expansion method ('discharge parameters/defaults' input tab). This is achieved by changing the default 'closest to initial conditions' (applying minimum thermodynamic change between isentropic and conservation-of-momentum expansion) to 'conservation of energy' (always applying conservation-of-momentum expansion).

If the PHAST user wishes to produce toxic effects, he or should modify carbon dioxide to be a 'toxic' material and specify the appropriate probit function. Furthermore it is recommended to set the 'core' averaging time equal to the 'toxic' averaging time of 600 seconds. The latter however only affects the results following transition to passive dispersion, and for most scenarios the cloud is no longer hazardous at this distance.

B.3 VALIDITY OF CARBON DIOXIDE PREDICTIONS IN 6.53.1/6.54

Carbon dioxide modelling in versions 6.53.1/6.54 is considered by the vendor to be correct as long as no solid effects occur both upstream of the orifice and downstream of the orifice. However in the case where solid effects would occur, 6.53.1/6.54 applies incorrect liquid properties (incorrectly extrapolated from PHAST's internal data base for data below triple-point temperature) instead of the solid properties. This includes the material properties: solid saturated vapour pressure, solid enthalpy and solid density. See Figure B.1 for a carbon dioxide phase diagram and Figure B.2 for the saturated vapour pressure.

B.3.1 Detailed PHAST modelling notes

The following notes apply with regard to the validity of the 6.53.1/6.54 CO₂ predictions.

1. 6.53.1/6.54 prediction of orifice flow rate (from expansion between stagnation and orifice conditions).

- a. Liquid stagnation state and leak scenario (meta-stable liquid assumption): 6.53.1/6.54 flow rate is always considered to be 'correct', since 'liquid' is assumed to remain in the liquid phase between stagnation state and orifice (non-equilibrium with atmospheric pressure applied at the orifice).
- b. Liquid stagnation state and line-rupture/long-pipe scenarios: 6.53.1/6.54 flow rate is 'correct' only if orifice pressure $P_{\text{orifice}} > \text{triple-point pressure of } 5,1 \text{ atm}$; if $P_{\text{orifice}} < 5,1 \text{ atm}$, solid effects will occur upstream of the orifice and the flow rate will be incorrect.
- c. Vapour stagnation state: 6.53.1/6.54 flow rate is 'correct' if either the orifice pressure P_{orifice} is $> 5,1 \text{ atm}$ or [if $P_{\text{orifice}} < 5,1 \text{ atm}$ and the orifice temperature $T_{\text{orifice}} > T_{\text{sat}}(P_{\text{orifice}})$]. Otherwise solid effects will occur upstream of the orifice and the flow rate will be incorrect.

In PHAST 6.6 added warnings are applied in case solid effects should occur upstream of the orifice. The PHAST 6.6 predictions of orifice flow rate remain unchanged.

2. 6.53.1/6.54 prediction of final post-expansion conditions (from expansion between orifice and post-expansion conditions).

- a. Liquid stagnation state, then:
 - i. Misapplication of liquid (instead of solid).
 - ii. Too low final temperature 185,6 K, but should be 194,8 K.
 - iii. Case of conservation of momentum (labelled as 'conservation of energy' in PHAST):
 1. Too high final 'liquid' fraction, and therefore too low vapour fraction.
 2. Correct final velocity.
 3. Too low expanded diameter.
 - iv. Case of conservation of entropy:
 1. Too high final 'liquid' fraction, and therefore too low vapour fraction.
 2. Too low final velocity (because of ignoring the heat of sublimation in energy equation).
 3. Too low expanded diameter.

b. Vapour stagnation state; if final temperature $> 194,8 \text{ K} = T_{\text{sat}}(P_a)$ no solid effects occur and all results are correct; if final temperature $< 194,8 \text{ K} = T_{\text{sat}}(P_a)$, then same effects as above for liquid state but less pronounced:
i. Misapplication of liquid (instead of solid).
ii. Too low final temperature 185,6 K, but should be 194,8 K.
iii. Case of conservation of momentum: <ol style="list-style-type: none"> 1. Too high final 'liquid' fraction, and therefore too low vapour fraction. 2. Correct final velocity. 3. Too low expanded diameter.
iv. Case of conservation of entropy: <ol style="list-style-type: none"> 1. Too high final 'liquid' fraction, and therefore too low vapour fraction. 2. Too low final velocity (because of ignoring of heat of sublimation in energy equation). 3. Too low expanded diameter.

In PHAST 6.6 the above final post-expansion conditions are all applied 'correctly' using appropriate solid properties by an extended post-expansion model ATEX.

3. 6.53.1/6.54 dispersion predictions. The dispersion predictions will start from the above final post-expansion conditions.

- a. If the default non-equilibrium model is adopted and solid effects do occur, the program will normally result in a fatal error because of thermodynamic numerical convergence problems since liquid properties are incorrectly applied outside their valid DIPPR range (i.e. in the solid regime).
- b. If the program does not result in a fatal error (e.g. by modifying step sizes or using equilibrium model) and solid effects should occur, liquid properties instead of solid properties are incorrectly applied (e.g. for vapour pressure, density and enthalpy) resulting in incorrect unphysical results).

In PHAST 6.6 the above dispersion calculations are all applied correctly using appropriate solid properties by an extended UDM thermodynamics model THRM. This applies only to the equilibrium model without solid deposition (no rainout).

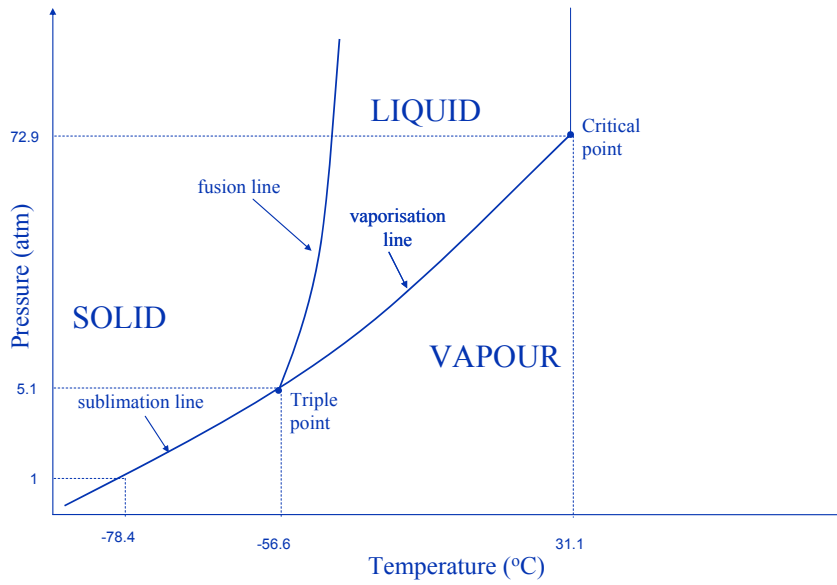


Figure B.1 Schematic phase diagram for CO₂ (not to scale)

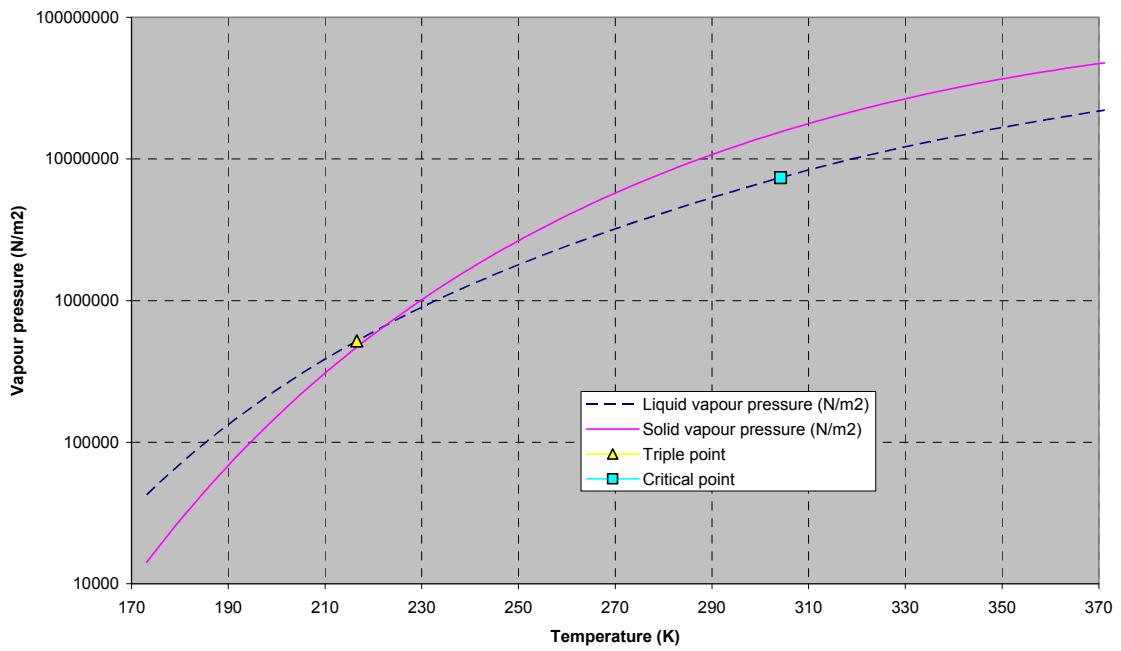


Figure B.2 Solid and liquid saturated vapour pressure for CO₂

ANNEX C

PREVIOUS INCIDENTS INVOLVING CARBON DIOXIDE

A number of incidents involving the release of CO₂ have been documented, both in the industrial context (production, handling, transport in pipeline) and in the natural context (due to geological conditions). These incidents can be examined and should help build up knowledge for the CCS industry.

It is critical that current learning and experience from industry is incorporated into this knowledge base. The incidents in this section are included here to ensure that they and other relevant incidents are considered when examining CCS schemes.

C.1 LAKE NYOS

Lake Nyos is a volcanic lake situated in North West Cameroon. Around 5 000 tonnes of carbon dioxide enters the base of the lake every year via the volcano mantle. In August 1986 over 1 700 people were killed after an estimated 1,6 million tonnes of carbon dioxide were suddenly released from the lake⁶⁹. It should be noted that this amount of carbon dioxide is an order of magnitude larger than the likely largest CCS carbon dioxide pipeline inventory.

Scientists from all over the world travelled to Cameroon to help with the investigation and several scientific papers and further study arose in the wake of this natural disaster. Lake Nyos resides in relatively unique environmental conditions. Usually the water within lakes circulates due to convection; the surface of the lake is cooled by wind or rainfall creating a more dense layer of water which sinks and displaces the warmer less dense, layers of water just below. Any carbon dioxide dissolved in the water bubbles out and escapes into the air as the water is circulated and brought to the surface. However at Lake Nyos the temperature remains relatively constant. The lake is surrounded by tall hills and is sheltered from the wind. Cameroon's tropical climate also means that there is very little temperature change from season to season⁷⁰. Small disturbances at the surface of the lake do not create sufficient mixing due to the depth of the lake, averaging at 208 m⁷¹. The strong stratification of Lake Nyos enables it to trap carbon dioxide in its lower layers. The amount of carbon dioxide dissolved in Lake Nyos remains under discussion; further detail can be found in Nojiri et al (which also aims to estimate the flux of carbon dioxide through the lake in order to predict the possibility of future disasters). Scientists are aware of just three lakes in the world where such conditions are possible and this type of hazard exists; Lakes Nyos and Monoun in Cameroon and Lake Kivu in East Africa. Kling et al. explores the depth of mixing and stratification stability of lakes in Cameroon further⁷²; this paper also has several useful references to work surrounding this phenomenon.

⁶⁹ Joint UNEP/OCHA Environment Unit *Lake Nyos dam assessment* Geneva, Joint UNEP/OCHA Environment Unit, 2005.

⁷⁰ *An estimate of CO₂ flux in Lake Nyos, Cameroon* Yukihiro Nojiri, Minoru Kusakabe, Klaus Tietze, Jun-ichi Hirabayashi, Hiroaki Sato. 4, s.l: American Society of Limnology and Oceanography, Inc., 1993, Vol. 38.

⁷¹ George Kling, William Evans, Gregory Tanyileke, Minoru Kusakabe, Yutaka Yoshida, Hiroshi Satake, Dimitri Rouwet *Technical Report on the January 2006 Field Expedition to Lakes Nyos and Monoun, Cameroon* 2006.

⁷² *Comparative transparency, depth of mixing, and stability of stratification in lakes of Cameroon, West Africa* Kling, George W. 1, s.l. : American Society of Limnology and Oceanography Inc., 1988, Vol. 33.

Several theories have been put forward as to why there was a sudden release of carbon dioxide from the lake. The most likely cause is cited as rockfall into the lake, possibly caused by seismic activity or the heavy rainfall preceding the incident⁷³. The rockfall could have caused sufficient displacement of the deep, gas-rich water closer to the surface beginning a chain reaction as described:

"As deep water rises, the weight of water above it (the hydrostatic pressure) decreases, and at some point the dissolved gas pressure will become equal to the hydrostatic pressure. At this point there is nothing to force the gas to remain in solution, and gas bubbles begin to form. This process is identical to the removal of the cap from a bottle of soda - when the cap is removed there is no more pressure to keep the gas dissolved in the soda, and bubbles are formed. Once bubbles are formed in the lake they rise rapidly and drag the deep water toward the surface, at which point additional deep water is drawn upward and depressurized. This leads to a chain reaction that eventually results in the violent release of enormous amounts of lethal CO₂ gas."⁷⁴

Currently work is being undertaken to de-gas the lake and also to assess the stability of a natural dam separating the lake from the river downstream which runs through the Nyos valley. The aim of the work is to prevent a repeat of the 1986 disaster and potentially resettle approximately 12 000 people who are displaced from the area. Further details on the degassing project and a live webcam on lake Nyos can be viewed online⁷⁵.

Although carbon sequestration to deep within the sea is possible, it should be noted that is not within the scope of this project. If the reader is interested in ocean storage technology a good introduction can be found within reference Herzog et al⁷⁶.

C.2 MAMMOTH MOUNTAIN, CALIFORNIA⁷⁷

After several reports of the early stages of asphyxiation from forest service personnel and the death of 40 hectares of coniferous forest the US Geological Survey began an investigation into the area of Mammoth Mountain, a dormant volcano in Eastern California.

Investigators found that carbon dioxide was seeping up towards the soil surface rather than venting in specific locations, gradually increasing the soil acidity. Carbon dioxide is a key ingredient in photosynthesis and elevated levels of carbon dioxide are deliberate in some plant nurseries as a method of accelerating plant growth. However, at high concentrations, around 20 %, root development is inhibited, starving the tree of the nutrients it needs to

⁷³ George Kling, William Evans, Gregory Tanyileke, Minoru Kusakabe, Yutaka Yoshida, Hiroshi Satake, Dimitri Rouwet *Technical Report on the January 2006 Field Expedition to Lakes Nyos and Monoun, Cameroon 2006* and Joint UNEP/OCHA Environment Unit *Lake Nyos Dam Assessment* Geneva:Joint UNEP/OCHA Environment Unit, 2005.

⁷⁴ George Kling, William Evans, Gregory Tanyileke, Minoru Kusakabe, Yutaka Yoshida, Hiroshi Satake, Dimitri Rouwet *Technical Report on the January 2006 Field Expedition to Lakes Nyos and Monoun, Cameroon 2006*.

⁷⁵ Halbwachs, Michel *Degassing the killer lakes, lakes Nyos and Monoun, Cameroon: mitigation of a natural hazard* 28 September 2005 <http://pagesperso-orange.fr/mhalb/nyos/index.htm>.

⁷⁶ Howard Herzog, Elisabeth Drake, Eric Adams *CO₂ Capture, Reuse, and Storage Technologies for Mitigating Global Climate Change* s.l.:White Paper sponsored by the US Department of Energy, Office of Fossil Energy, 1997. DOE Order No. DE-AF22-96PC01257.

⁷⁷ Christopher D. Farrar, John M. Neil *Magmatic Carbon Dioxide Emissions at Mammoth Mountain California* Sacramento:US Geological Survey, 1999. Water-Resources Investigations Report 98-4217.

survive.

Low points such as snow pits more than 1 m deep, below ground level water valve boxes and poorly ventilated nearby buildings around the mountain were found to have concentrations of over 10 % carbon dioxide, a concentration able to cause unconsciousness.

Researchers also found that during heavy periods of snowfall the levels of carbon dioxide within the soil increased as carbon dioxide was sealed in, unable to diffuse any further into the atmosphere. The rate of emission of carbon dioxide is also affected by other meteorological factors such as heavy rainfall. For the meantime some highly affected areas of forest around the mountain have been closed off and studies continue into the rate of carbon dioxide release for the purpose of determining the potential health hazards and possible future volcanic activity.

C.3 NAGYLENGYEL CO₂ RELEASE

Nagylengyel is a small town in the west of Hungary, where there was a significant escape of naturally-occurring carbon dioxide from an EOR project in 1998. As a consequence, about 5 000 inhabitants from three adjacent villages, Sárhida, Bak and Bocsföld were evacuated.

In 1949, following nationalisation, five national oil companies were formed, under the control of the Transdanubian Mineral Oil Centre. Exploration efforts were accelerated and the first positive result was when, in 1951, the Nagylengyel-2 well uncovered the Nagylengyel oil field in the Zala basin.

During the 1950s, Hungary was forced to implement a high-speed industrialisation programme and oil demand increased accordingly. This demand could only be met with enforced field production programmes. In 1952, these companies were merged into the Hungarian-Soviet Oil Co. (MASZOIL). MASZOIL, as a single Hungarian-Soviet joint venture (50 - 50 %) constituted the entire Hungarian oil industry until 1954.

The Nagylengyel wells, which have the largest initial reserves of any field found to date in Hungary, produced 1,2 million tons of crude oil in 1955 and peaked in 1993 at 1,3 million tonnes. The oil produced is low (13-30 API) gravity and highly viscous, with high concentrations of V, Ni, and S, isotopically light hydrocarbons, low pristane/phytane (P/Ph) ratio (<1,0), and no oleanane. As production tailed off secondary measures were applied, and oil recovery was enhanced by pumping water into the well.

Some time later, gas (a mixture of carbon dioxide and hydrogen sulphide⁷⁸) from a naturally-occurring underground source (including some crude oil) was used to restore well pressure. The installation included a carbon dioxide compressor at Gellénháza. The carbon dioxide contained a proportion of hydrogen sulphide, which, in EOR terms, would be seen as an advantage.

The incident took place on collection well NIT 10⁷⁹ on 13 November 1998. Routine work was put in hand to replace a blowout preventer with a Christmas Tree well-head completion, and during this the operators tried to disengage the quick-release packer (some 202 m below the surface) from the production pipe so that the pipe string could be lifted up. Instead of the quick-release coupler being released, it is likely that they dislodged the packer seal some 2 175 m further down the well, providing a passage for carbon dioxide gas to escape through the annulus between the 2 $\frac{7}{8}$ " (73 mm) production pipe and the 6 $\frac{5}{8}$ " (168

⁷⁸ A gas analysis of an adjacent well also contained 3 400 mg/m³ (2 400 ppm) H₂S and 10 mg/m³ (8 ppm) CO₂.

⁷⁹ *Carbon dioxide gas eruption, suppression and experiences* Bencsik & Dercsenyi, MOL, 33rd Oil and Gas (133.) Grades 5-6. No. 2000. May-June.

mm) conductor casing.

When the operators disconnected the blowout preventer, carbon dioxide gas started to leak out, so they tried to replace the blowout preventer and retighten the mounting bolts. However, they had only inserted two when the carbon dioxide blowout started with the full force of 3 000 psi (207 bar). At 11.30 pm on 13 November 1998, carbon dioxide started to escape (Figure C.1), and the immediate area was evacuated⁸⁰.



Figure C.1 Outbreak of CO₂ escape

Oil well fire-fighters were immediately sent to the scene and by 6.30 am the following morning, as a precautionary measure, three adjacent villages, Sárhida, Bak and Bocföld were evacuated, a total of about 5 000 people. An emergency plan was implemented.

The hydrogen sulphide in the carbon dioxide reacted with oxygen in the air to form sulphur dioxide within a few hours: the residence time of the sulphur dioxide in the atmosphere is about two days, allowing it to travel some distance with normal atmospheric air movements. There was more concern over the possible effects of the sulphur dioxide than there was over the carbon dioxide.

Using self-contained breathing apparatus (SCBA), which were changed every 25 minutes, access to the well base was possible using tracked vehicles (the temperature was about -30 °C). A large capacity hot air blower, which arrived on the Sunday morning, was used to disperse the ice and carbon dioxide snow from the area, which had built up to a depth of 1,5 to 2 m. However, attempts to get close enough to the well proved unsuccessful, and an alternative plan

⁸⁰ *Accidental release of H₂S in Hungary Peljto and Bencetic Kalic, Geofizica, Vol. 16-17, 199-2000, 43-51.*

was developed.



Figure C2 Melting the ice with the large capacity hot air blower

It was 12.20pm on Tuesday (16 November) by the time that temporary access had been constructed and a repair rig had been fabricated and eventually lowered into place over the well, into which 150 l/minute of warm water (at 40 °C) was pumped, allowing the blowout preventer to be defrosted and turned. Unfortunately, the rubber sealing rings had been damaged during the insertion of the repair rig, and a new one had to be installed.

There were no reports of any fatalities as a result of this incident, not even of any injuries. A significant amount of carbon dioxide had escaped over a period of 60 hours. The environmental impacts reported were:

- Local soil damage, some long-term.
- Local flora and fauna damage, some long-term.
- Evacuation and temporary disturbance of three towns.
- The nearby Lake Baki (where the gas seemed to concentrate) did not test positive for dissolved carbon dioxide or hydrogen sulphide.
- Hydrogen sulphide tended to build up during the night and early morning and fall as soon as warm air caused movement: the maximum level recorded was 28,4 mg/m³ (20 ppm).

C.4 WORMS⁸¹

On the 21 November 1988 there was a catastrophic failure of a vessel containing liquid carbon dioxide at Proctor and Gamble's citrus facility in Worms, Germany. The vessel over-pressurised leading to loss of containment. The force of the explosion propelled the majority

⁸¹ *Catastrophic Failure of a Liquid Carbon Dioxide Storage Vessel* W Edward Clayton, Michael L Griffin. 125, s.l. : IChemE Loss Prevention Bulletin, 1994.

of the vessel into the river Rhine approximately 300 m away. The incident resulted in three fatalities, eight employees hospitalised with serious injuries, three months' lost production and 20 million dollars' worth of property damage.

The vessel was TUV approved and had passed the required inspections during manufacture and installation. It had a nominal capacity of 30 tonnes carbon dioxide and was a 2,6 m diameter horizontal tank with overall length of 6,45 m.

The incident occurred shortly after two modifications had been made by the vessel supplier; the relief valve liquid fill and vapour fill lines were moved to the midpoint of the side of the tank in order to make them more easily accessible and stud pad flanges were welded to spare nozzle openings near each end of the vessel shell and blanked off.

On inspection of the failed vessel it was found that the circumference of the vessel shell had permanently increased by 2 - 4,5 % in one area and the thickness of the metal had decreased by 40 % leading investigators to conclude that a bulge had formed due to tank overpressure.

The vessel had been designed for -50 °C at 20 bar and was constructed of TT StE36 carbon steel. The vessel material was re-examined and the properties still matched that of TT StE36 material including level of toughness. However, Proctor and Gamble identified several failings in the method with which the stud pad flanges were welded to the spare nozzle openings on the vessel. After the overpressure and vessel bulge the evidence indicated that the vessel seam had then unzipped, beginning at one of the stud pad flanges.

Another additional cause of the vessel failure was that five weeks prior to the incident the vessel heater had failed and the vessel reached -60 °C. This low temperature incident could have caused the welded joint to become brittle and crack.

The vessel heater was also able to fail - allowing too much carbon dioxide to be vaporised relative to carbon dioxide take off and hence allowing too much pressure build-up. Vessels are designed with safety margins so that they can typically withstand 1,5 times the vessel design pressure; however investigators calculated the possible pressure build-up during the 17 hour general power failure which occurred before the explosion and found that the pressure could have been up to 1,75 to 2,5 times the vessel design pressure.

The vessel had a safety relief valve as a safeguard against overpressure; however, it did not release. Investigators propose that since the inlet piping to the relief valve was routed through liquid carbon dioxide the cooling of the piping was such that the relief valve outside of the tank was also cooled to a sufficiently low level that atmospheric moisture could ice up the valve seat and freeze it into position. There is also the possibility that dry ice could have formed at the relief valve outlet, blocking the relief pathway.

As a result of the incident at Worms, Proctor and Gamble identified several lessons to be learnt including: implementing better vessel inspection techniques; additional process alarms and interlocks, and care required in thawing out vessels which have experienced a low temperature excursion. Further detail on the Worms incident can be found in the article *Catastrophic failure of a liquid carbon dioxide storage vessel* by W Edward Clayton and Michael L Griffin in the IChemE's loss and prevention Bulletin 125, 1994.

C.5 FIRE FIGHTING INCIDENTS

A high pressure carbon dioxide fire suppression system was unexpectedly discharged in the

test reactor area of Idaho National Engineering and Environmental Laboratory (INEEL) on 28 July 1998. The incident resulted in one fatality and several workers sustained life threatening injuries⁸².

Workers inadvertently activated the carbon dioxide suppression system whilst they were de-energising electrical circuit breakers in preparation for maintenance activity on the building's electrical system. Usually a pre-discharge alarm would be activated in order to warn personnel to clear the area. However in this case although the system was designed to have a 25 second pre-discharge alarm it was not installed, despite being listed as a safeguard. Personnel therefore received no warning before the carbon dioxide flooded the room. Workers were ill-prepared to escape, with no emergency breathing apparatus, no exit pathway lighting, no emergency ventilation system and no emergency exit training. Rescue attempts were also impeded due to poor availability of self-contained breathing apparatus onsite. It seems that due to site budget cuts breathing apparatus and search and rescue training was limited.

This was not the first incident of its kind at the INEEL. In their report, the Accident Investigation Board cites that there were several accidents and two incidents warranting type A investigations (any incident causing fatal or likely to be fatal injury or losses in excess of \$2,5 million). INEEL is criticised for poor work process planning and controls as well as insufficient operator training. If INEEL had followed requirements and physically locked out the carbon dioxide system, the incident could have been prevented.

C.6 ASPHYXIATION INCIDENTS

A carbon dioxide delivery driver in Cincinnati lost his life due to carbon dioxide asphyxiation. The seal of the connection between his truck and the bulk system he was filling was incomplete and allowed carbon dioxide to leak into the area. In addition, the filling station was located in a relatively confined space, in a stairwell with partial overhead covering limiting the ability of carbon dioxide to disperse⁸³.

The HSE also issued a warning to the manufacturing industry after three people succumbed to carbon dioxide asphyxiation whilst working on a slurry tank on a farm near Thetford, Cambridgeshire. The workers were overcome by the carbon dioxide and drowned in less than a metre of liquid⁸⁴.

C.7 RELIANT PROCESSING VESSEL

In September 2002 a worker from the Reliant Processing Group in Muleshoe, Texas, was killed while the vessel he was insulating (which contained carbon dioxide) exploded. Reports indicate that the vessel suffered from brittle fracture having been exposed to extremely low temperatures and a build-up of pressure finally caused the tank to explode. The Occupational

⁸² *Type A Accident Investigation Board Report of the July 28, 1998 Fatality and multiple injuries resulting from the release of carbon dioxide at Building 648, Test Reactor Area Idaho National Engineering and Environmental Laboratory.* s.l.:Office of Oversight Environment, Safety and Health U.S. Department of Energy, 1998.

⁸³ Mallinger, Stephen. OSHA Hazard Information Bulletins *Hazard Information Bulletin 1: Potential Carbon Dioxide (CO₂) Asphyxiation Hazard when Filling Stationary Low pressure CO₂ Supply Systems* s.l.:OSHA, 1996.

⁸⁴ Health and Safety Executive *HSE warns - confined spaces kill.* *Health and Safety Executive: Press Releases* (Online) 29 July 2004. (Cited: 20 October 2008) <http://www.hse.gov.uk/press/2004/e04109.htm>. HSE Press Release: E109:04 - 29 July 2004.

Safety and Health Administration of the U.S. Department of Labor (OSHA) investigated the incident and found that Reliant had "failed to maintain the pressure vessels and follow safety standards to prevent hazardous conditions". The company was cited with one alleged wilful, violation of the OSHA standards and paid penalties⁸⁵.

The incident in Muleshoe prompted OSHA to investigate other Reliant plants including that in Guymon, Oklahoma. OSHA found further wilful non-conformances and several serious violations of OSHA law and regulations. These non-conformances included "failing to train employees on the purpose and function of energy control, failing to implement or maintain a written hazard communication plan, failing to provide training on hazardous chemicals in the work area and failing to provide lockout/tagout procedures for energized equipment"⁸⁶.

C.8 FUKUSHIMA CARBON DIOXIDE EXPLOSION⁸⁷

In March 1969 a storage tank (cold evaporator) containing carbon dioxide exploded at a steel mill in Fukushima, Japan, killing three people and injuring 38 others.

The tank had been isolated in preparation for some repair work, including the isolation of the main relief valve and bursting disc. The power supply to the refrigerator stopped but the power supply to the tank heater remained on. The liquid carbon dioxide present in the tank, combined with the continued heating, caused the temperature and pressure of the carbon dioxide in the tank to rise until the burst pressure of the tank was exceeded, and a crack was generated in the tank wall. The tank pressure then equalised the atmospheric pressure via the crack but this rapid drop in pressure meant that the liquefied carbon dioxide within the vessel generated a vapour explosion, causing tank rupture.

Debris from the rupture was scattered up to 60 m away and a slate-roofed factory within a 50 m radius was completely destroyed, only its pillars remained. The roofing tiles were scattered within a 100 m radius, causing further damage to doors and windows. Windows of houses located within a 500 m radius were reported to be also damaged.

⁸⁵ OSHA. Worker's Death at Muleshoe, Texas, Worksite Brings OSHA Penalties of \$70,000. s.l. : US Department of Labor Office of Public Affairs, 2003. Vol. Region 6. OSHA-03-42.

⁸⁶ Guymon, Okla., Company Cited for Exposing Workers to Safety Hazards *OSHA Regional News Release* s.l.:US Department of Labor, Office of Public Affairs, 2003. Vol. Region 6. OSHA-03-41.

⁸⁷ Koseki Hiroshi, Tamura Masamitsu. *Cryogenic tank for liquefied carbon dioxide ruptured upon closing a block valve of a safety valve. Failure knowledge database.* (Online) Japan Science and Technology Agency. <http://shippai.jst.go.jp/en/Detail?fn=0&id=CC1000038&kw=Carbon+Dioxide>.

ANNEX D

GLOSSARY

ALARP: as low as reasonably practicable.

ATEX: abbreviation used to refer to the framework for controlling explosive atmospheres as set out under the EU Directives 99/92/EC and 94/9/EC.

CCS: carbon capture and storage.

CCSA: Carbon Capture & Storage Association.

CFD: computational fluid dynamics.

CONCAWE: Conservation of Clean Air and Water In Europe.

DOT: Department of Transport.

DSEAR: Dangerous Substances & Explosive Atmospheres Regulations 2002 (which enables EU Directive 99/92/EC in UK legislation).

DTi: Department of Trade & Industry.

DTL: dangerous toxic load.

EGIG: European gas pipeline incident group.

EGR: enhanced gas recovery.

EI: Energy Institute.

EOR: enhanced oil recovery.

FAR: fatal accident rate.

F-N curve: fatality - number curve.

HAZOP: hazard and operability study.

HSE: Health & Safety Executive.

IGCC: integrated gasification combined cycle.

MAHP: major accident hazard pipelines.

PHAST: dispersion model.

QRA: quantitative risk assessment.

SLOD: significant likelihood of death.

SLOT: specified level of toxicity.

UKOPA: UK Pipeline Operators Association.

ANNEX E

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