

# Assessment of the major hazard potential of carbon dioxide (CO<sub>2</sub>)

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## Introduction

Carbon dioxide (CO<sub>2</sub>) is a substance which has many domestic and commercial uses and over the years standards and legislative controls have been built up to maintain an acceptable level of risk for those who could be harmed by it.

HSE has long established its approach for evaluating hazards from dangerous substances that involves an estimation of the consequences of exposure to a level of harmful agent and the time of exposure needed to give an accumulation to cause harm.

The advent of carbon capture and storage (CCS) will result in CO<sub>2</sub> being handled in quantities many orders of magnitude greater than it is today. For example, a coal-fired power station consuming 8000 te a day of coal (in the region of one GW power generation) will produce up to 30 000 te/day of CO<sub>2</sub> to be captured and transported to long-term storage facilities. Whereas in existing CO<sub>2</sub> handling facilities an inadvertent release of CO<sub>2</sub> may have created a small-scale hazard, potentially only affecting those in the local vicinity, a very large release of CO<sub>2</sub> from a CCS scale of operation has the potential to produce a harmful effect over a significantly greater area and as such it would be likely to affect a significant number of people. CCS scale of CO<sub>2</sub> operation, therefore, has the potential to introduce a major accident hazard (MAH) where currently one does not exist.

This paper sets out an initial assessment of the hazards resulting from loss of containment incidents from vessels containing large quantities of CO<sub>2</sub> and discusses the subsequent major hazard potential associated with such events.

## Issue

CCS is viewed globally as a key carbon abatement technology as it will enable the capture of millions of tonnes of CO<sub>2</sub> from significant CO<sub>2</sub> emitters (eg power stations) and then for the CO<sub>2</sub> to be transported in pipelines or ships before being injected deep into the earth's rock formations where it will remain trapped. Within the EU there are plans for 10-12 demonstration projects to be built by 2015 and recommendations for a further 80-120 plants to be on line by 2030.

Given the scale of CCS projects and the need to handle very large quantities of CO<sub>2</sub>, for economic and technical reasons the captured vapour phase CO<sub>2</sub> may be compressed at high pressures into its liquid (<31°C) or supercritical phase (≥31°C)

in some circumstances. The CO<sub>2</sub> may also be temporarily stored at lower pressures in refrigerated or semi-refrigerated vessels for intermediate storage prior to transfer to ships.

Combining the known impact from receiving a harmful dose of CO<sub>2</sub> with what could be very large hazard zones due to the release of very large inventories of CO<sub>2</sub> (particularly if it exists in the liquid or supercritical phase), creates the potential for CO<sub>2</sub> to be a major accident hazard (MAH). The likelihood of a CO<sub>2</sub> MAH occurrence should be very low due to the risk management measures, however, to ensure this in this case, appropriate risk management standards and regulation need to be put in place.

## Background

### Dangers of CO<sub>2</sub>

CO<sub>2</sub> has been recognised as a significant workplace hazard for over 100 years. Noteworthy properties of CO<sub>2</sub> are:

- at standard temperature and pressure it has a low viscosity and a density of around 1.5 times that of air (1.98 kg/m<sup>3</sup>);
- at atmospheric pressure and a temperature of -78.51°C it changes directly from a solid phase to a gaseous phase through sublimation, or from gaseous to solid through deposition;
- a supercritical fluid exists above a substance's critical temperature and pressure (31.04°C and 73.82 bar for CO<sub>2</sub>), above which supercritical CO<sub>2</sub> exhibits the density of a liquid and viscosity of a gas;
- a dense phase fluid is a collective term generally used to describe both a liquid and supercritical fluid; and
- CO<sub>2</sub> has been shown to exhibit a level of toxicity related to the concentration and time of exposure.<sup>1,2</sup>

CO<sub>2</sub> is commonly thought of as posing a threat to life through asphyxiation when it displaces the oxygen in air down to dangerously low levels. For CO<sub>2</sub> to reduce the oxygen concentration in air down to a level that is immediately dangerous to life, the CO<sub>2</sub> concentration would need to be in the order of 50% v/v. Evidence shows, however, that CO<sub>2</sub> does create an immediate threat to life at a concentration of only 15% in air due to the toxicological impact it has on the body when inhaled at this concentration.

In humans, CO<sub>2</sub> is a normal component of blood gases at low concentrations, however, at high exposure inhalation levels it is lethal. In humans one of the most powerful stimuli known to affect the respiration is CO<sub>2</sub> and this results in humans being very sensitive to changes in CO<sub>2</sub> concentrations. The inhalation of elevated concentrations of CO<sub>2</sub> can increase the acidity of the blood triggering adverse effects on the respiratory, cardiovascular and central nervous systems. Depending on the CO<sub>2</sub> concentration inhaled and exposure duration, toxicological symptoms in humans range from headaches (in the order of 3% for 1 hour), increased respiratory and heart rate, dizziness, muscle twitching, confusion, unconsciousness, coma and death (in the order of >15% for 1 minute).

At CO<sub>2</sub> concentrations in excess of 50% in air whether a person dies due to the toxicological effect of CO<sub>2</sub> inhalation or due to oxygen depletion is not clear and arguably immaterial. In both cases death would be the outcome.

To assess the toxicity of substances HSE has developed what is known as an assessment of Dangerous Toxic Load (DTL) to calculate the exposure conditions in terms of concentration and duration of exposure. In this assessment the specified level of toxicity (SLOT) and the significant likelihood of death (SLOD) are defined. For land use planning the HSE has defined the SLOT as causing:

- severe distress to almost everyone in the area;
- substantial fraction of exposed population requiring medical attention;
- some people seriously injured, requiring prolonged treatment;
- highly susceptible people possibly being killed, likely to cause 1-5% lethality rate from a single exposure to a certain concentration over a known amount of time.

SLOD is defined as causing 50% lethality from a single exposure over a known amount of time. Data for this calculation is collected from routine toxicity testing on animals, using cautious results. More detailed background information on the SLOT and SLOD calculations can be found on the HSE website ([www.hse.gov.uk/hid/haztox.htm](http://www.hse.gov.uk/hid/haztox.htm)).

Table 1 presents the output of the HSE's Dangerous Toxic Load assessment for CO<sub>2</sub>. The table illustrates a significant danger to humans if they inhale CO<sub>2</sub> at concentrations above around 7% in air (ie > 70 000 ppm). It also highlights, the effect of that toxicity increasing rapidly for only small changes in concentration above a certain level (ie there is not a large difference between the SLOD and SLOT values).<sup>2</sup> Differences in CO<sub>2</sub> concentration between different lethality levels and exposure times are relatively small; concentrations for lethality levels 1-5% and 50% for a given exposure time differ by only 33%. Although CO<sub>2</sub> is only mildly toxic to humans when compared with hydrogen sulphide, for example, above concentrations of about 7% in air, humans are particularly sensitive to further increases.

**Table 1:** Concentration vs time consequences for CO<sub>2</sub> inhalation

Inhalation exposure time	SLOT: 1-5% Fatalities		SLOD: 50% Fatalities	
	CO <sub>2</sub> Concentration in air*		CO <sub>2</sub> Concentration in air*	
	%	ppm	%	ppm
60 min	6.3%	63 000 ppm	8.4%	84 000 ppm
30 min	6.9%	69 000 ppm	9.2%	92 000 ppm
20 min	7.2%	72 000 ppm	9.6%	96 000 ppm
10 min	7.9%	79 000 ppm	10.5%	105 000 ppm
5 min	8.6%	86 000 ppm	11.5%	115 000 ppm
1 min	10.5%	105 000 ppm	14%	140 000 ppm

**Note:** \* Concentration by volume

In addition to the hazard posed by CO<sub>2</sub> if inhaled, there are additional hazards associated with dense phase CO<sub>2</sub> that are likely to occur when CO<sub>2</sub> is handled in large quantities and at high pressure. These can arise when a release occurs and the pressure suddenly falls or is lost completely. These hazards include cryogenic burns, embrittlement of pipe work, toxic contamination and possibly 'grit blasting' of neighbouring plant (although information suggests that CO<sub>2</sub> snow also needs to be compressed in order to give a grit blasting effect).

# CO<sub>2</sub> inhalation incidents

There are a number of natural and industrial releases of CO<sub>2</sub> that have recorded injuries and death due to CO<sub>2</sub> inhalation. Here are details of some CO<sub>2</sub> incidents that highlight the potential dangers when a significant quantity of CO<sub>2</sub> is released and inhaled by people.

## Fire suppression systems

CO<sub>2</sub> (followed by nitrogen) is the most commonly used 'inert' gas extinguishing agent. A comprehensive review of CO<sub>2</sub> incidents related to use in fire protection was undertaken by the US Environmental Protection Agency (EPA),<sup>3</sup> which reviewed governmental, military, public, and private document archives. From 1975 to 2000, a total of 51 incident records were located that reported a total of 72 deaths and 145 injuries resulting from accidents involving the discharge of CO<sub>2</sub> from fire extinguishing systems. The review indicates that the majority of reported incidents occurred during maintenance on or around the CO<sub>2</sub> fire protection system itself.

## Mönchengladbach

Approximately 15 tonnes of CO<sub>2</sub> was accidentally released from a fire extinguishing installation in Mönchengladbach, Germany (2008).<sup>4</sup> Due to coincidental failure of door seals, the released CO<sub>2</sub> was not contained by the building and it spread outside where there were very still air conditions. There were no fatalities from the incident but 107 people were intoxicated, 19 of whom were hospitalised.

## Lake Nyos

Lake Nyos, in the Cameroon, is one of only three lakes in the world known to be naturally saturated with CO<sub>2</sub>, due to the existence of a magma chamber underneath which is continually leaking CO<sub>2</sub>. In 1986<sup>5</sup> an estimated 1.6 million tonnes of CO<sub>2</sub> was unexpectedly released, around 1700 people and 3500 livestock were killed and thousands more were injured. The CO<sub>2</sub> destroyed trees and other vegetation near the lake.

When considering MAH potential, it is necessary to put these previous incidents in perspective with the proposed scale of CO<sub>2</sub> handling likely to occur in the near future through implementation of CCS operations. In a CO<sub>2</sub> capture facility the amount of CO<sub>2</sub> on the site at any one time is likely to be less than 50 tonnes, a point to point CO<sub>2</sub> pipeline from capture plant to injection facility could hold as much as 10 000 tonnes of CO<sub>2</sub> and a large pipeline cluster perhaps 100 000 tonnes. It should also be noted that these CCS CO<sub>2</sub> inventories are likely to be sectionalised into smaller inventories upon detection of a leak through the use of isolation or block valves.

With respect to the Lake Nyos incident, inventories in CCS operations will be orders of magnitude smaller and will therefore pose a much smaller risk. The Mönchengladbach incident is more similar to the scale of incident should there be a large CO<sub>2</sub> release at a capture plant. The fire suppression incidents will have been from CO<sub>2</sub> inventories that were much smaller than those in CCS operations but these CO<sub>2</sub> releases were within confined spaces.

The above incidents show the potential consequences when CO<sub>2</sub> forms a cloud at hazardous concentration and is inhaled. It is important to bear in mind that the risk posed by any release is very dependant on the source of the release, the mass released, any containment such as buildings, the ground topography of the surroundings and the weather conditions.

## Carbon capture and storage processes

CCS can be broken down into five stages:

### Capture

Early discussions with industry suggest there may be less than 50 tonnes of CO<sub>2</sub> at the capture site. However, the nature of power generation and the potential need for stability in capture and transportation does not preclude the possibility of larger intermediate storage at a capture plant.

Operational CCS is likely to bring on to combustion plant sites other potentially dangerous substances depending on the capture technology applied. Different capture technology can require large inventories of amines, ammonia or oxygen. Depending on the hazard classification and quantities, the presence of these substances could bring capture sites into Seveso.

### Compression

It is not yet clear how much CO<sub>2</sub> will be held at compression sites. In the UK and elsewhere there are concepts being developed that include single compression hubs servicing a number of capture sites: these hubs could potentially have large inventories, although, as described above, isolation or block valves could be used to minimise the overall inventory loss in the event of a loss of containment. Other process related hazards such as over-pressurisation or fatigue of pressure equipment (as may be used in pressure swing absorption) may provide other hazards or escalation paths for loss of containment events.

### Transport

Transport by pipeline from capture plant to injection point is the most likely means of CO<sub>2</sub> transport for CCS. There are suggestions that ship transport may also be used for some projects and this would require intermediate storage.

### Injection

The CCS Directive enables onshore and offshore injection and storage of CO<sub>2</sub>. (The UK is currently planning to only license offshore storage sites.)

## Permanent storage

At present the likelihood and consequences of failure of a geological structure used for sequestration is outside the scope of this paper. There is no clear indication of whether intermediate storage facilities (onshore, above ground) will be required along the process chain to mitigate the impact of any interruptions to the process upsets.

## Other industries using CO<sub>2</sub>

The compressed gas industry generally stores and transports CO<sub>2</sub> at 20 barg and -30°C in insulated tanks. Sites may store around 1000 tonnes of liquid CO<sub>2</sub> in 350-tonne tanks. In the soft drinks industry typical CO<sub>2</sub> pressures and temperatures are around 20 barg and -17°C.

Overall, non-CCS CO<sub>2</sub>:

- is typically present under refrigerated or semi-refrigerated conditions;
- is typically kept at pressures of 20 barg and temperatures as low as -30°C for bulk storage purposes;
- could have an internal pressure as high as 850 psi (58.6 bar) at 21°C in high-pressure cylinders;
- is held at 300 psig (20.7 barg) in low-pressure, mini-bulk tanks by maintaining the internal temperature at approximately -18°C; and
- may be used to replace CFCs for refrigeration purposes. Pressures may be in excess of 100 barg.

There is nothing to suggest that CO<sub>2</sub> in CCS would not be stored under the conditions given above.

## Ongoing research

There are a significant number of uncertainties in the modelling of CO<sub>2</sub> releases. A summary of the issues is given in *Hazards from High Pressure CO<sub>2</sub> Releases during CO<sub>2</sub> Sequestration Processes*. Connolly, S and Cusco, L. IChemE, Symposium Series No 153. Consideration of the engineering aspects of handling high-pressure CO<sub>2</sub> in large quantities in a loss of containment (LOC) incident has highlighted several issues with major accident implications:

- scale of thermal cooling envelope from a supercritical CO<sub>2</sub> release;
- supercritical CO<sub>2</sub> containment issues;
- fire and explosion hazard profile changes resulting from flammable substances burning in an air/CO<sub>2</sub> mixture rather than air alone;
- toxic contamination effects on supercritical CO<sub>2</sub> release (toxic components dissolved in the CO<sub>2</sub>);
- dry ice 'grit blasting effects';
- CO<sub>2</sub> detection;
- emergency response and temporary refuge integrity issues;
- structural Integrity issues, which include:
  - rapid cooling of structural members;
  - prolonged exposure to subliming dry ice;
  - induced stresses;
  - brittle to ductile transition;
  - structural failure.

There are a large number of research projects (either current or proposed) into the various aspects of CO<sub>2</sub> hazards and risks. Some of the more relevant projects are given below:

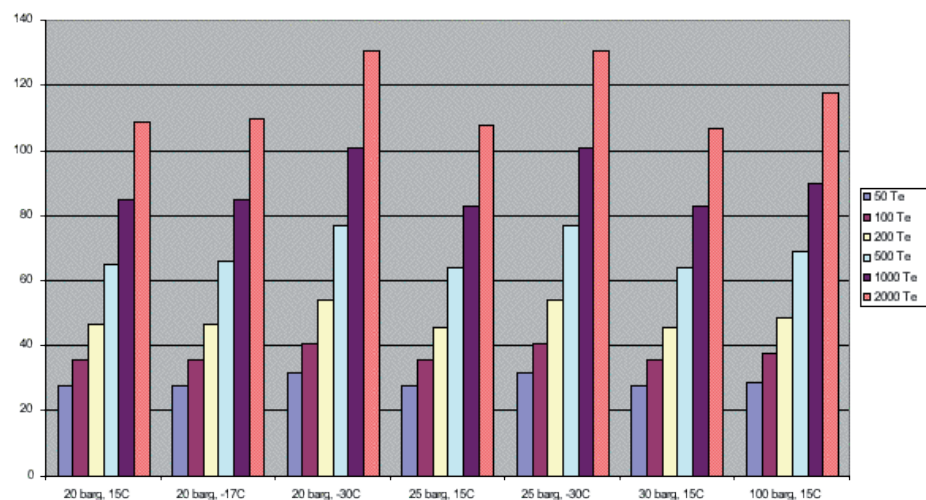
- CO<sub>2</sub>PIPETRANS – DNV led JIP covering several aspects of CCS
- MATTRAN – Newcastle University project on ‘Materials for Next Generation CO<sub>2</sub> Transport Systems’ (co-funded by E-on and the EPSRC)
- CO<sub>2</sub>PipeHaz – European (FP7) collaborative project led by UCL on ‘Quantitative Failure Consequence and Hazard Assessment for Next Generation CO<sub>2</sub> Pipelines’.
- CoolTrans – National Grid funded JIP.

## Representative hazardous distances

To establish an understanding of hazardous distances from various CO<sub>2</sub> release scenarios, HSE has undertaken various modelling exercises which are described in Annex 1.

Five separate modelling exercises for CO<sub>2</sub> releases were carried out (plus two external exercises relating to pipeline releases). Modelling software packages; IRATE, DRIFT, and PHAST were used in various combinations to estimate the hazardous distances from various large instantaneous CO<sub>2</sub> releases scenarios.

Figure 1 presents the results from PHAST 6.6.0 based on releases occurring when there is a 5m/s wind and neutral stability conditions (ie D5 conditions in modeller terminology).



**Figure 1:** Hazardous distances vs release scenarios (5 m/s wind)

The hazardous distance is taken as the distance from the release point to the CO<sub>2</sub> SLOT (based on the relevant instantaneous release cloud passage time).

Figure 1 shows that in all cases the hazardous distances are significant and could therefore impact a significant number of people in the vicinity of the incident. The total mass of CO<sub>2</sub> released has, not surprisingly, a significant influence on hazardous distance. The temperature of the CO<sub>2</sub> can also be seen to influence the hazardous distance with colder releases creating greater hazardous distances.

Figure 2 presents the same release scenarios as calculated by PHAST 6.6.0 but this time into low windspeed, stable condition (ie F2 conditions).



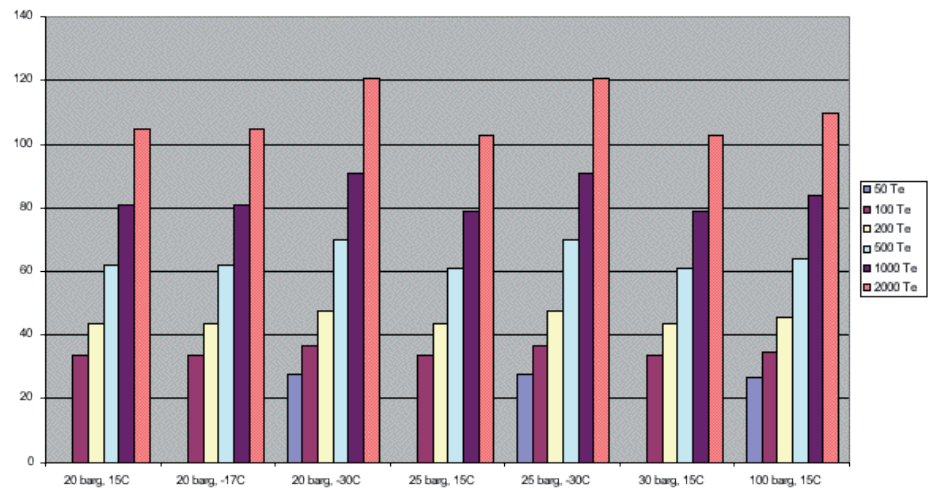


Figure 2: Hazardous distances vs release scenarios (2 m/s wind)

By comparing Figure 1 and Figure 2 it can be seen that the calculated hazardous distances are slightly smaller in calm conditions.

The results are presented as scatter charts (with results for smaller release inventories) at Annex 10 and Annex 11.

As detailed in Annex 1 there is considerable uncertainty with regard to the accuracy of the modelling. The main reason for this is that few models are available that have been developed for modelling releases of dense phase CO<sub>2</sub> and none are believed to have been validated for the purpose.

PHAST 6.6.0 has been upgraded from a previous version to enable modelling of dense phase CO<sub>2</sub> based on access to confidential experimental data. However, without access to this experimental data it is not possible to assess the accuracy of PHAST.

To indicate the range of uncertainty between models, Figure 3 presents the hazardous distance estimates for a 1000 tonne instantaneous release using the PHAST 6.6.0 model (as presented in Figure 1) and using a combination of PHAST and HSE's preferred dispersion model DRIFT. In the PHAST/DRIFT modelling the source terms calculated by PHAST 6.6.0 were used as input to the DRIFT model which then performed its own dispersion calculations.

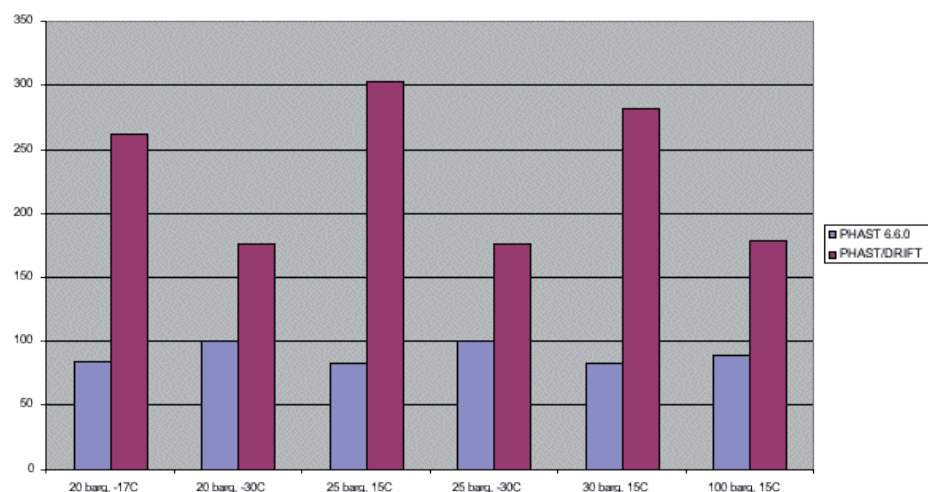


Figure 3: Hazardous distances for 1000 tonne release scenarios (5 m/s wind)



Figure 3 shows that PHAST/DRIFT results are consistently higher than PHAST 6.6.0 results by a factor of between 1.3 and 3.9. It should be noted that work ongoing within the CO<sub>2</sub>PIPETRANS JIP should soon provide data by which model developers can test and validate their models, thereby reducing the level of uncertainty associated with modelling.

In addition to the catastrophic release scenarios presented above, HSE also undertook some modelling of a 50 mm diameter release from a storage vessel. The release conditions were the same as for the instantaneous releases with CO<sub>2</sub> being released from the liquid space. This modelling concluded that hazardous ranges from this type of release could be in the order of 100 m from the release point which is comparable to the hazard ranges presented previously.

HSE believes that the modelling work undertaken and reported in Annex 1 provides the most robust indication presently available of the magnitude of hazardous distances should there be a catastrophic release of CO<sub>2</sub> from a large inventory of CO<sub>2</sub>. In all cases, the hazardous distances are significant, leading to the conclusion that (depending on situation and circumstance) it is credible for operations with a significant inventory of CO<sub>2</sub> to pose a MAH and therefore there is a need adequately to regulate its risk management.

It should be noted that the hazardous assessment presented above is based on pure CO<sub>2</sub>. It is possible that, with certain carbon capture processes, the captured CO<sub>2</sub> stream will contain impurities such as SO<sub>2</sub> and H<sub>2</sub>S. Where such impurities are toxic in their own right they may add to the overall toxicity of the CO<sub>2</sub> stream. However, the impurities are expected to constitute a small proportion of the overall flow and it is assumed that the increase in toxicity will not be significant. This assumption would require to be tested during specific assessments.

In addition, the presence of the impurities (eg hydrogen) is also known to change the phase diagram and hence behaviour of the mixture compared to pure CO<sub>2</sub>. These changes are the subject of separate research work.<sup>6</sup>

Despite these unknowns regarding impurities and modelling uncertainties, the use of pure CO<sub>2</sub> in the preceding discussion is considered a reasonable approximation for determining an estimate of the hazards of CO<sub>2</sub> releases.

## Conclusions

Based on the preceding discussion the following general conclusions can be drawn:

1. The hazard range for an instantaneous release from storage may be in the range of 50 to 400 m with large, cold, liquid phase storage producing the larger distances.
2. The hazard range for a continuous release through a 50 mm hole may be up to 100 m.
3. Releases from pressurised storage (both refrigerated and ambient temperature) have the potential to create hazard ranges that could create a MAH.
4. As such, the technical evidence suggests that CO<sub>2</sub> has a major accident potential in line with other hazardous substances currently regulated through permissioning regimes.

With regard to CO<sub>2</sub> MAH analysis modelling the following conclusions can be drawn:

5. There is significant uncertainty in the modelling of instantaneous and continuous releases of CO<sub>2</sub> from storage. A significant amount of research needs to be completed before a suitable model can be developed.
6. The current HSE instantaneous source term model will need to be updated for CO<sub>2</sub>.
7. The DNV PHAST 6.6.0 model has been updated to include some improvements to the source term calculations for CO<sub>2</sub>.
8. The use of the PHAST/DRIFT model combination suggests that the hazard ranges predicted by PHAST 6.6.0 may not be conservative. This would strengthen the conclusions given in conclusions 3 and 4 above.

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# Annex 1: Assessment modelling

A number of computer simulation software packages are available to 'model' the behaviour of gases and how they disperse, when accidentally released into the atmosphere. Different software packages are best suited to model different aspects of the release. The use of several simulation software packages gives a range of potential outcomes and indicates the uncertainty in the software predictions. The software simulations or models are used to determine the distance from the CO<sub>2</sub> source at which a SLOT equivalent dose of CO<sub>2</sub> would be received. This distance is known as the hazard range. The hazard range is dependant on a number of factors including:

- the amount of CO<sub>2</sub> released;
- the pressure of the CO<sub>2</sub> released;
- the temperature at the time of the release;
- the weather (wind, humidity etc) conditions at the time of the release.

It is possible that the captured CO<sub>2</sub> stream from power plants will contain impurities such as SO<sub>2</sub> and H<sub>2</sub>S. These impurities are toxic in their own right and may add to the overall toxicity of the CO<sub>2</sub> stream. However, the impurities are expected to constitute a small proportion of the overall flow and it is assumed that the increase in toxicity will not be significant.

The presence of the impurities is also known to change the phase diagram and hence behaviour of the mixture compared to pure CO<sub>2</sub>. These changes are the subject of separate research work.<sup>6</sup> Despite these unknowns, the use of pure CO<sub>2</sub> in the following simulations is considered a reasonable approximation for determining an estimate of the hazards of CO<sub>2</sub> releases.

Five separate modelling exercises for CO<sub>2</sub> releases were carried out (plus two external exercises relating to pipeline releases). Modelling software packages; IRATE, DRIFT, and PHAST were used in various combinations to estimate the hazards in this study.

## 'IRATE/DRIFT' assessment

The instantaneous release of 60 tonnes of CO<sub>2</sub> at 10 barg and varying temperatures was modelled using the 'standard' CI5 models IRATE<sup>7</sup> and DRIFT<sup>8</sup>. The DRIFT Dose Calculator (DDC)<sup>9</sup> was used in an attempt to determine the distance from the source at which a SLOT equivalent dose of CO<sub>2</sub> would be received. This distance is known as the hazard range. However, the DDC failed to generate any meaningful results.

The releases were remodelled assuming that the 60 te contents of the vessel were solid (ie dry ice) and that the catastrophic event causes the solid to instantaneously sublime to gas. DRIFT simulations assumed<sup>10</sup> that 1 kg of dry ice will produce 0.45 m<sup>3</sup> of gas and that a hemisphere cloud of pure CO<sub>2</sub> is produced at 253 K. The DDC calculated outdoor dose contours with downwind range of 160 m (D5) and 125 m (F2) but was unable to generate any indoor dose contour again because the concentration was too low.

The assessment was repeated with a reduced mass of 40 te. The DDC calculated outdoor dose contours with downwind range of 140 m (D5) and 107 m (F2) but no indoor dose contours.

It is not immediately obvious if IRATE can accurately simulate the transition from CO<sub>2</sub> gas to solid and the physical chemistry involved correctly (this concern has subsequently been supported by HSL). A sensitivity study has been carried out on the method with variations in the assumed contaminant mass fraction, see Annex 2. By forcing the mass fraction of the 60 te, 253 K case to unity and maintaining all other parameters, an upper limit on hazard range appears to have been found.

A continuous release was modelled using information from work by Mazzoldi et al<sup>11</sup> that a 30 te release with the solid at a constant temperature of -78.8°C produces a sublimation rate of 8 g/s.m<sup>2</sup> (reducing to 4 g/s.m<sup>2</sup> after 12 hours).

Assuming a third of the 60 te release (ie 20 te) comprises a subliming solid (with bulk density 1500kg/m<sup>3</sup>) gives a dry ice volume of 13.3 m<sup>3</sup>. Assuming a layer thickness of between 0.15 to 0.3 metres gives a surface area of between 35 to 80 m<sup>2</sup> providing a release source term of 0.1-0.6 kg/s.

DRIFT was run using a 0.6 kg/s continuous release of pure CO<sub>2</sub>, ie no air entrainment at -78.8°C (194 K). Plume half width taken as 5 m and plume velocity 5m/s (D5) and 2m/s (F2). The specific heat capacity (Cp) at 194K was set at 728 J/kg K. It was necessary to reduce the roughness length to 0.001 in order to get results from DRIFT. This level of roughness length suggests that the results are conservative.

The DDC produced results for both indoor and outdoor hazard contours.

**Table 2** DDC results for continuous release

Weather scenario	Contour	Downwind range (m)	Max half width (m)
D5	Outdoor	5	7
	Indoor	2	7
F2	Outdoor	28	10
	Indoor	10	6

### **‘PHAST 6.54’ assessment**

HID CI5 carried out modelling of releases of pure CO<sub>2</sub> from vessels with varying inventories and pressures. All the calculations were based on the inventory being in a single tank with catastrophic failure of that tank (unless otherwise indicated).

The CO<sub>2</sub> dispersion calculations were carried out using DNV’s PHAST<sup>12</sup> software (Version 6.54). The results (given at Annex 3) show that:

- hazard ranges are relatively short as would be expected for a substance with low toxicity;
- there is little difference between typical daytime weather (D5) and typical night-time (F2) whereas many toxics should exhibit greater hazard ranges for F2 weather;
- there is limited change to the hazard range with increased pressure in the gas phase. This would tend to weaken the case for choosing 25 barg (rather than 20 barg) as a limiting pressure from a hazard point of view and a ‘policy’ decision would need to be made;
- semi-refrigerated releases have greater hazard ranges than gas releases but the increase is probably not sufficient to change the conclusions; and
- the single 50 mm hole assessment gave a zero hazard range (even with a roughness length of 0.04).



## ‘HSL peer review’ assessment

HSL were asked to independently assess a random selection of the cases modelled by HID as a peer review of the CI5 work. The same version of PHAST was used and the results are given at Annex 4. It can be seen that the two sets of results are in close agreement.

## ‘PHAST 6.6.0’ modelling

PHAST 6.54 is limited in its ability to model releases of CO<sub>2</sub>, more specifically the fall out of solids during such releases. DNV are aware of these limitations which are being addressed in more recent versions. DNV also have access to experimental CO<sub>2</sub> release data generated at Spadeadam in support of the BP Miller project. This experimental data relates to releases through short lengths of pipework attached to CO<sub>2</sub> vessels. While this is not a direct representation of a catastrophic failure of the vessel, it does allow some validation of the thermodynamics in the PHAST model.

DNV have used the experimental data to validate a new version of PHAST which includes improvements to the CO<sub>2</sub> modelling capability and the inclusion of the physical properties of solid (as well as liquid) CO<sub>2</sub>. Unfortunately, the experimental data remains confidential making the validation process/results non-transparent. HSE are attempting to obtain permission from the owners of the data to be allowed to audit the validation work carried out. The intention is that this will provide a greater degree of certainty in the PHAST 6.6.0 results reported here.

The changes to the model are described in a 2009 paper published by Witlox et al.<sup>13</sup>

DNV made a pre-release version of the code (PHAST 6.6.0 Build 406) available to HSE. This has been used to repeat the earlier PHAST simulations plus a number of additional cases. The results are given at Annex 5 and it can be seen that the new code predicts hazard ranges which are lower by up to 20%, when compared with the previous version. However, the conclusions that can be drawn are similar.

It is acknowledged that the modelling in PHAST 6.6.0 ignores the possibility that a proportion of the release may be deposited on the ground rather than being carried by the dispersing jet. This may be seen as a conservatism. However, the deposited solid could sublime and a proportion of the CO<sub>2</sub> re-enter the jet and contribute to the hazard range.

Releases through 50 mm holes were further investigated. It was found that when PHAST reported ‘No Hazard’ it actually meant that the hazard range was less than 10 m. It can be seen that for 100 barg conditions, the hazard ranges for 50 mm holes are comparable to the catastrophic failure hazard ranges.

Further calculations were carried out to investigate the hazard ranges for releases between 20 and 100 tonnes. These results are given in Annex 9 and graphically (with the data from Annex 5) in Annexes 10 to 12.

## ‘PHAST/DRIFT’ modelling

As stated earlier, there is some doubt about the validity of the IRATE code being used to model instantaneous releases of CO<sub>2</sub>. The question has also been raised as to the level of conservatism in the PHAST results and whether the use of an alternative dispersion model would produce shorter hazard ranges. This might undermine the conclusions drawn in the earlier section.

However, the PHAST model is known to be non-conservative when compared to HSE's preferred dispersion model – DRIFT.

To investigate the sensitivity of the choice of dispersion model, the source term outputs (from the table termed 'Detailed Dispersion') from the PHAST 6.6.0 runs were used as the input to the DRIFT model. The data was taken from the point at which all the liquid (actually solid in this case) fraction of the release had vaporised. This was then used as the starting point for the 'contaminant gas only' model in DRIFT. The inputs included:

- total CO<sub>2</sub> released;
- contaminant mass fraction (based on CO<sub>2</sub> concentration in air);
- cloud temperature;
- cloud initial velocity; and
- initial displacement.

Discussions with the developers of the DRIFT model have confirmed that this is an appropriate method to determine the inputs to DRIFT.

Typical PHAST outputs are given at Annex 6 with the relevant data highlighted. The results for a selection of the scenarios are given in Annex 7 together with the relevant PHAST 6.6.0 results for comparison. It can be seen that the PHAST/DRIFT results are consistently higher than the PHAST 6.6.0 results by a factor of between 1.8 and 5.

The results in Annex 7 are based on mass fractions calculated using the concentration outputs from the PHAST 'Detailed Dispersion'. These are maximum centreline concentrations and, as such, are likely to be an overestimate of the actual average concentrations unless the cloud profile is truly 'top hat'. The graphical output from PHAST (concentration vs. distance) was used to estimate the average concentration and these values were used to as inputs to the DRIFT model. The results are given at Annex 8 and it can be seen that (as expected) the hazard ranges are now 1.3 to 3.9 times those given by PHAST 6.6.0.

Both sets of results suggest that the PHAST 6.6.0 results are not overly conservative and that it is appropriate to use it to make estimates of CO<sub>2</sub> hazard ranges for the purposes of determining if a release of CO<sub>2</sub> from a storage vessel has the potential to generate a major hazard. That is not to say that HSE endorses PHAST 6.6.0 as 'the model to use' since it does not yet account for all the areas of concern described earlier. It is merely the one which currently has the 'greatest potential' to accurately model the release.

## Other modelling

Work was carried out by HSL on the hazards of releases from CO<sub>2</sub> pipelines. The work is described in an HSL report.<sup>14</sup> Hazard ranges for ruptures of a gaseous CO<sub>2</sub> pipeline were of the order of 100 to 200 m. This is similar to the hazard ranges described above.

HSE is aware of modelling carried out by external organisations who have also considered releases from a CO<sub>2</sub> pipeline. While these are not directly related to large-scale releases from vessels, the hazard ranges predicted for similarly sized overall release inventories are comparable in magnitude to the PHAST and PHAST/DRIFT results described earlier.

# Annex 2: Sensitivity study of IRATE/DRIFT/DDC

## Results for instantaneous release of CO<sub>2</sub>

Filename	Mass (te)	Release temperature (K)	Mass fraction	Downwind distance to DTL				
				D5 Weather		F2 Weather		
				Outdoors	Indoors	Outdoors	Indoors	
CO2D5R & CO2F2R	40	273	0.0975	-	-	-	-	
CO2D5B & CO2F2B		253	0.1396	-	-	-	-	
CO2D5C & CO2F2C		232*	0.2442	37	-	36	-	
		253	1**	140	-	107	-	
CO2MXD5 & CO2MXF2	60	253	0.157	-	-	-	-	
CO2D5A & CO2F2A			0.5+	165	-	120	-	
CO2D5F & CO2F2F			1+	280	-	268	-	
CO2D5E & CO2F2E			1**	160	-	125	-	
CO2MAXD5 & CO2MAXF2			232*	0.2699	48	-	42	-
CO2D5D & CO2F2D				1++	240	-	220	-
CO2D5G & CO2F2G								

\* This is the lowest temperature IRATE will run without giving the liquid rainout message. At 217 K <temp<231 K 'liquid' rain out is predicted and no cloud details are calculated. At temp<217 K, IRATE says CO<sub>2</sub> less than 'boiling point'.

+ These cases are a repeat of the similar 60 te release at 253 K using IRATE but the contaminant mass fraction has been set to 0.5 or 1 in DRIFT, all other parameters have been kept the same.

++ These cases are a repeat of the similar 60 te release at 232 K using IRATE but the contaminant mass fraction has been set to 1 in DRIFT, all other parameters have been kept the same.

\*\* These results are produced using Imperial College GN028 expansion rate and not IRATE.

# Annex 3: Scoping calculations to determine the hazard ranges from releases of CO<sub>2</sub>

**Catastrophic, single vessel failure (except 1x50 mm hole)**

Storage Pressure	Weather	50 te	100 te	200 te	500 te	1000 te
		Distance to SLOT (m)	Distance to SLOT (m)	Distance to SLOT (m)	Distance to SLOT (m)	Distance to SLOT (m)
20 barg, 15°C	D5	29	37	47	68	86
	F2	27	34	45	64	83
20 barg, -17°C	D5	29	37	48	66	88
	F2	28	36	45	64	84
20 barg, -30°C	D5	36	47	63	91	122
	F2	30	40	52	77	104
25 barg, 15°C	D5	27	36	45 (0)	66	85
	F2	26	35	45 (0)	63	82
25 barg, -30°C	D5	36	47	63	91	122
	F2	30	40	52	77	104
30 barg, 15°C	D5		36			85
	F2		34			81
100 barg, 15°C	D5					96
	F2					86

Dispersion calculations carried out using PHAST V6.54

# Annex 4: HSL review of CI5 PHA5T 6.54 assessment

Black values = generated by HID CI5G

Blue values = generated by HSL as a check.

Storage conditions	Weather	50 te	100 te	200 te	500 te	1000 te
		Distance to SLOT (m)	Distance to SLOT (m)	Distance to SLOT (m)	Distance to SLOT (m)	Distance to SLOT (m)
20 barg, 15°C	D5	29	37	47	68	86 (87)
	F2	27 (27)	34	45	64	83 (84)
20 barg, -17°C	D5	29	37	48	66	88
	F2	28	36	45	64	84
20 barg, -30°C	D5	36	47	63 (62)	91	122 (117)
	F2	30	40	52	77	104 (103)
25 barg, 15°C	D5	27	36	45 (46)	66	85 (83)
	F2	26	35	45 (44)	63 (62)	82 (81)
25 barg, -30°C	D5	36	47 (47)	63 (65)	91	122 (117)
	F2	30	40	52	77	104
30 barg, 15°C	D5		36			85
	F2		34			81
100 barg, 15°C	D5					96
	F2					86

# Annex 5: Updated calculations to determine the hazard ranges from releases of CO<sub>2</sub>

## Catastrophic, single vessel failure (50 mm holes)

Storage Pressure	Weather	50 te	100 te	200 te	500 te	1000 te	2000 te
		Distance to SLOT (m)	Distance to SLOT (m)	Distance to SLOT (m)	Distance to SLOT (m)	Distance to SLOT (m)	Distance to SLOT (m)
20 barg, 15°C	D5	28+	36	47	65	85+	109
	F2	-	34	44	62	81+	105
20 barg, -17°C	D5	28+	36+	47	66	85	110
	F2	-	34	44	62	81	105
20 barg, -30°C	D5	32	41	54	77	101	131
	F2	28	37	48	70	91	121
25 barg, 15°C	D5	28	36	46 (<10)	64	83+	108 (-)
	F2	-	34+	44 (<10)	61	79	103 (-)
25 barg, -30°C	D5	32	41	54	77	101	131
	F2	28	37	48	70	91	121
30 barg, 15°C	D5	28	36	46 (<10)	64+	83	107
	F2	-	34	44 (<10)	61	79	103
100 barg, 15°C	D5	29 (58)	38 (65)	49 (72)	69 (75)	90 (76)	118
	F2	27 (60)	35 (67)	46 (74)	64 (-)	84 (-)	110

Dispersion calculations carried out using PHAST V6.6.0 Build 406

- + Indicates result obtained using larger dispersion calculation tolerance
- Indicates release temperature could not be reduced to obtain result



# Annex 6: Typical PHAST outputs for use in creating DRIFT inputs

## DETAILED DISPERSION REPORT

Unique Audit Number: 82,541



Study Folder: CO2\_20barg\_1000te\_-17C

Phast 6, 6, 0, 406



Downwind Distance m	C/Line Height m	C/Line Conc ppm	Plume Half-width m	Plume Total Depth m	Vapor Temperature deg C	Liquid Fraction fraction	Time s	Liquid Temperature deg C	Centroid Velocity m/s	Cloud Density kg/m <sup>3</sup>
0.30	1.00	924,415.61	52.56	81.45	-79.50	0.14	0.10	-79.50	3.08	3.15
0.33	1.00	917,425.18	52.76	81.60	-79.60	0.14	0.11	-79.60	3.10	3.13
0.36	1.00	910,530.11	52.95	81.76	-79.70	0.14	0.12	-79.70	3.12	3.12
0.39	1.00	903,728.56	53.15	81.90	-79.81	0.13	0.13	-79.81	3.14	3.10
0.42	1.00	897,018.75	53.35	82.05	-79.91	0.13	0.14	-79.91	3.15	3.09
0.45	1.00	890,398.95	53.54	82.20	-80.01	0.13	0.15	-80.01	3.17	3.08
0.49	1.00	883,867.45	53.74	82.34	-80.11	0.13	0.16	-80.11	3.19	3.07
0.52	1.00	877,422.59	53.93	82.49	-80.21	0.13	0.17	-80.21	3.21	3.05
0.55	1.00	871,062.77	54.13	82.63	-80.31	0.13	0.18	-80.31	3.23	3.04
0.58	1.00	864,786.39	54.32	82.77	-80.40	0.13	0.19	-80.40	3.25	3.03
0.62	1.00	858,591.91	54.51	82.91	-80.50	0.13	0.20	-80.50	3.27	3.02
0.65	1.00	851,264.52	54.74	83.07	-80.61	0.12	0.21	-80.61	3.29	3.00
0.70	1.00	842,620.90	55.01	83.27	-80.75	0.12	0.23	-80.75	3.31	2.99
0.76	1.00	832,457.80	55.34	83.50	-80.90	0.12	0.24	-80.90	3.34	2.97
0.83	1.00	820,553.97	55.73	83.77	-81.09	0.12	0.26	-81.09	3.38	2.95
0.91	1.00	806,674.10	56.19	84.09	-81.31	0.12	0.29	-81.31	3.42	2.92
1.02	1.00	790,575.54	56.74	84.47	-81.56	0.11	0.32	-81.56	3.47	2.89
1.14	1.00	772,018.29	57.39	84.90	-81.86	0.11	0.35	-81.86	3.53	2.86
1.29	1.00	750,778.95	58.15	85.40	-82.20	0.10	0.40	-82.20	3.59	2.82
1.48	1.00	726,668.70	59.06	85.98	-82.60	0.10	0.45	-82.60	3.67	2.78
1.71	1.00	699,555.08	60.11	86.63	-83.05	0.09	0.51	-83.05	3.76	2.73
2.00	1.00	669,386.24	61.35	87.37	-83.56	0.08	0.59	-83.56	3.86	2.68
2.35	1.00	636,215.50	62.78	88.19	-84.13	0.07	0.67	-84.13	3.98	2.63
2.78	1.00	600,222.89	64.43	89.09	-84.77	0.05	0.78	-84.77	4.11	2.57
3.31	1.00	561,729.43	66.31	90.05	-85.47	0.04	0.91	-85.47	4.25	2.51
3.98	1.00	521,199.90	68.44	91.06	-86.22	0.02	1.06	-86.22	4.40	2.45
4.81	1.00	479,230.64	71.49	92.62	-83.60	0.00	1.25		4.58	2.35
5.85	1.00	436,521.20	76.35	95.23	-73.77	0.00	1.47		4.78	2.19
7.15	1.00	393,831.51	81.54	97.63	-63.92	0.00	1.74		4.99	2.05

Date: 16/02/2010

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Time: 09:31:04

## DETAILED DISPERSION REPORT

Unique Audit Number: 33,747



Study Folder: CO2\_100barg\_1000te

Phast 6, 6, 0, 406



Downwind Distance m	C/Line Height m	C/Line Conc ppm	Plume Half-width m	Plume Total Depth m	Vapor Temperature deg C	Liquid Fraction fraction	Time s	Liquid Temperature deg C	Centroid Velocity m/s	Cloud Density kg/m <sup>3</sup>
8.31	1.00	382,956.63	71.47	89.80	-91.16	0.20	2.06	-91.16	4.93	2.54
10.24	1.00	340,590.17	75.01	91.03	-92.07	0.15	2.44	-92.07	5.14	2.44
12.66	1.00	300,060.53	78.69	91.96	-92.96	0.10	2.90	-92.96	5.35	2.35
15.67	1.00	261,971.47	82.38	92.44	-93.81	0.02	3.45	-93.81	5.56	2.27
19.44	1.00	226,776.69	88.21	94.23	-81.87	0.00	4.11		5.79	2.08
24.14	1.00	194,767.10	93.26	95.21	-66.17	0.00	4.91		6.02	1.89
29.98	1.00	166,075.78	95.36	94.13	-52.09	0.00	5.86		6.24	1.74
37.24	1.00	140,696.71	93.80	90.69	-39.71	0.00	7.01		6.43	1.63
46.21	1.00	118,511.83	88.16	84.40	-29.15	0.00	8.38		6.62	1.54
57.26	1.00	99,321.29	77.63	74.06	-20.48	0.00	10.03		6.79	1.47
70.86	1.00	82,872.54	59.37	56.48	-13.65	0.00	12.01		6.95	1.42
87.56	1.00	68,885.59	6.65	6.58	-8.41	0.00	14.38		7.11	1.38
87.73	1.00	68,770.00	0.00	0.00	-8.37	0.00	14.41		7.11	1.38

Weather: Global Weathers\F2

Speed: 2.00 m/s

Stability: F

\CO2\_100barg\_1000te\Study\Vessel\Pipe Source  
Material: CARBON DIOXIDE

Note: C/Line Concentration is calculated at an averaging time of: 600.00 s  
Plume Width and Height are calculated at an averaging time of: 1,800.00 s  
and a Concentration of Interest of: 68,770.00 ppm  
Concentration at Height calculated at a Height of: 0.00 m

For instantaneous releases (and if present in this report) the Mass Flowrate is the Mass

## Annex 7: Comparison between PHAST 6.6.0 and PHAST/DRIFT

Storage Pressure	Weather	50 te		200 te		1000 te	
		PHAST 6.6.0	PHAST/DRIFT	PHAST 6.6.0	PHAST/DRIFT	PHAST 6.6.0	PHAST/DRIFT
20 barg, 15°C	D5						
	F2						
20 barg, -17°C	D5					85	375
	F2					81	324
20 barg, -30°C	D5	32	71	54	131	101	227
	F2	28	55	48	88	91	168
25 barg, 15°C	D5			46	227	83*	385
	F2			44	185	79	330
25 barg, -30°C	D5					101	227
	F2					91	168
30 barg, 15°C	D5					83	375
	F2					79	323
100 barg, 15°C	D5	29	93			90	249
	F2	27	68			84	209

\* Indicates release temperature reduced to 14°C to obtain result.

## Annex 8: Comparison between PHAST 6.6.0 and PHAST/DRIFT with PHAST/DRIFT hazards based on average concentration from PHAST output

Storage Pressure	Weather	50 te		200 te		1000 te	
		PHAST 6.6.0	PHAST/DRIFT	PHAST 6.6.0	PHAST/DRIFT	PHAST 6.6.0	PHAST/DRIFT
20 barg, 15°C	D5						
	F2						
20 barg, -17°C	D5					85	263
	F2					81	254
20 barg, -30°C	D5	32	43	54	89	101	176
	F2	28	No result	48	No result	91	121
25 barg, 15°C	D5			46	179	83*	303
	F2			44	137	79	262
25 barg, -30°C	D5					101	176
	F2					91	126
30 barg, 15°C	D5					83	282
	F2					79	256
100 barg, 15°C	D5	29	57			90	179
	F2	27	48			84	157

\* Indicates release temperature reduced to 14°C to obtain result.

# Annex 9: Scoping calculations for the hazard range of CO<sub>2</sub> (inventories below 100 te)

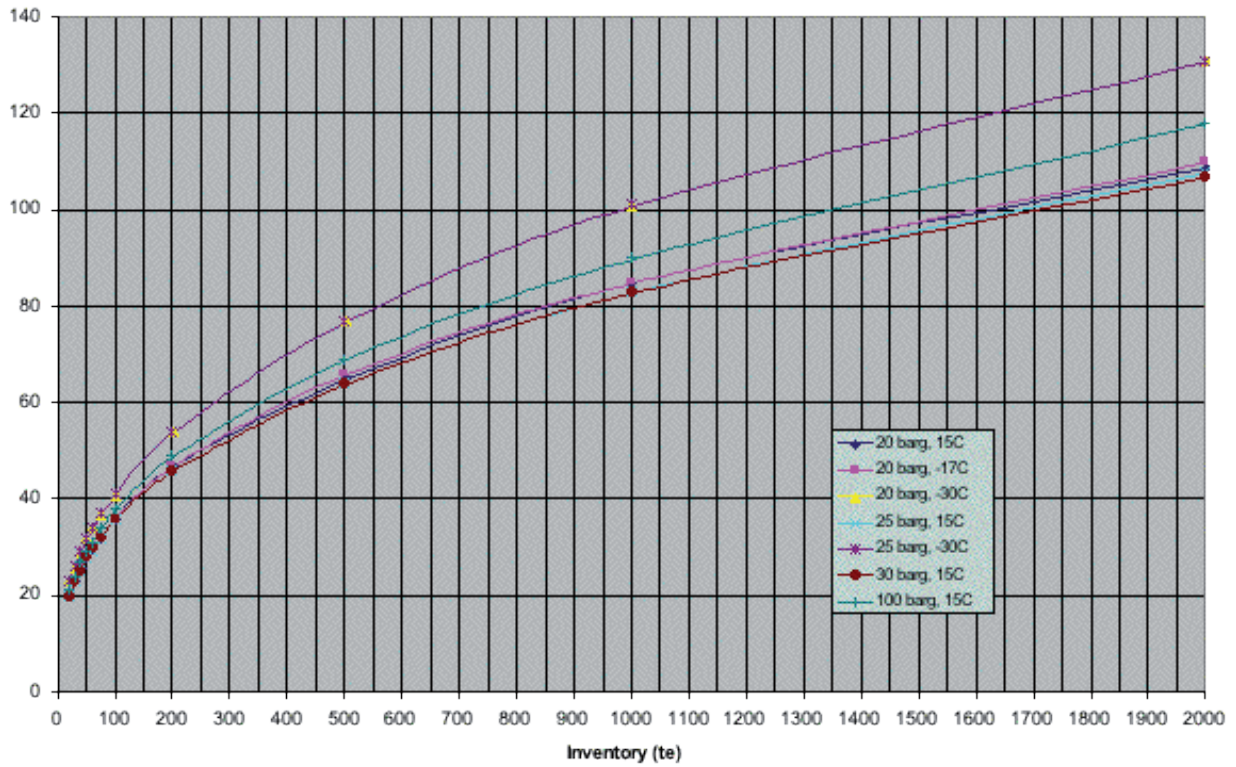
## Catastrophic, single vessel failure (50 mm holes)

Storage Pressure	Weather	20 te	30 te	40 te	50 te	60 te	75 te	100 te
		Distance to SLOT (m)	Distance to SLOT (m)	Distance to SLOT (m)	Distance to SLOT (m)	Distance to SLOT (m)	Distance to SLOT (m)	Distance to SLOT (m)
20 barg, 15°C	D5	20	23	26	28+	30	32	36
	F2	-	-	-	-	-	31	34
20 barg, -17°C	D5	20	23	26	28+	30	32	36+
	F2	-	-	-	-	28	31	34
20 barg, -30°C	D5	23	26	29	32	34	37	41
	F2	20	23	26	28	31	33	37
25 barg, 15°C	D5	20	23	25	28	29	32	36
	F2	-	-	-	-	-	-	34+
25 barg, -30°C	D5	23	26	29	32	34	37	41
	F2	20	23	26	28	31	33	37
30 barg, 15°C	D5	20	23	25	28	30	32	36
	F2	-	-	-	-	-	-	34
100 barg, 15°C	D5	21 (50)	24 (53)	27 (56)	29 (58)	31 (59)	34 (62)	38 (65)
	F2	- (52)	- (55)	25 (58)	27 (60)	29 (62)	32 (64)	35 (67)

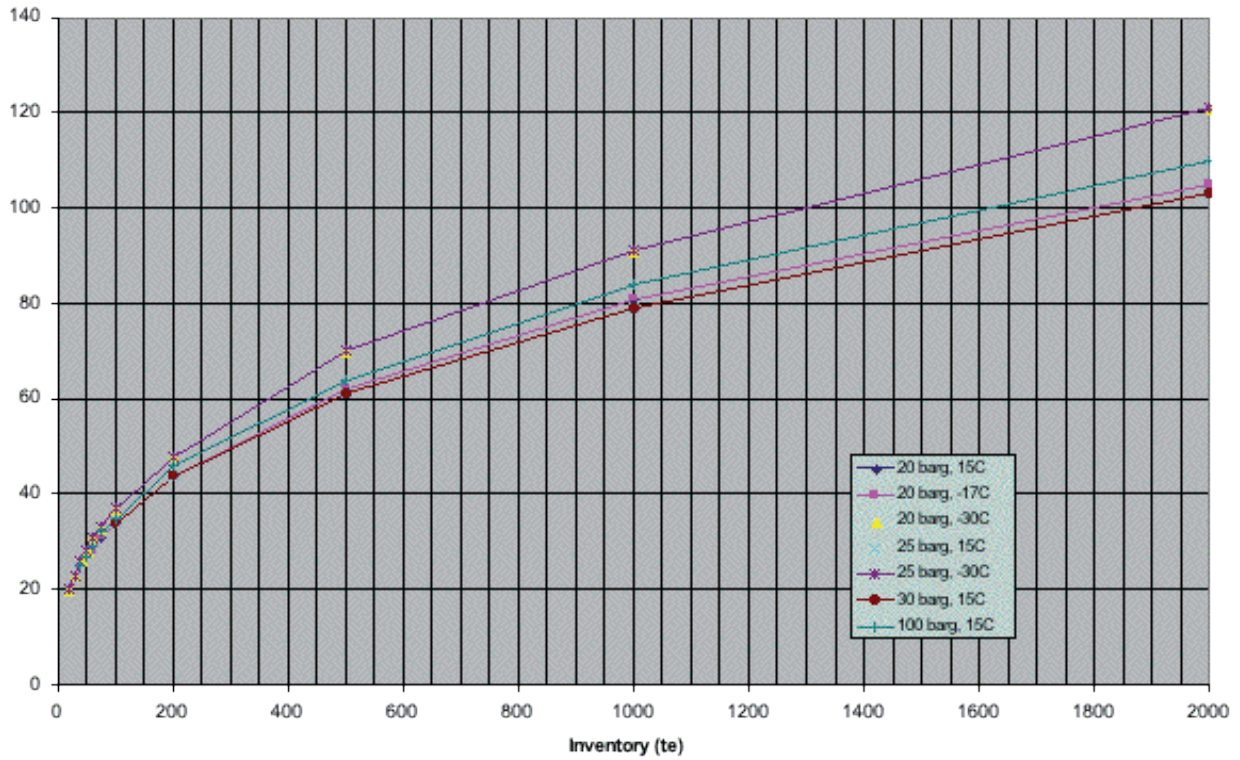
Dispersion calculations carried out using PHAST V6.6.0 Build 406

- Indicates release temperature could not be reduced to obtain result
- + Results obtained using larger dispersion calculation tolerance

# Annex 10: Results for D5 weather (catastrophic failure)



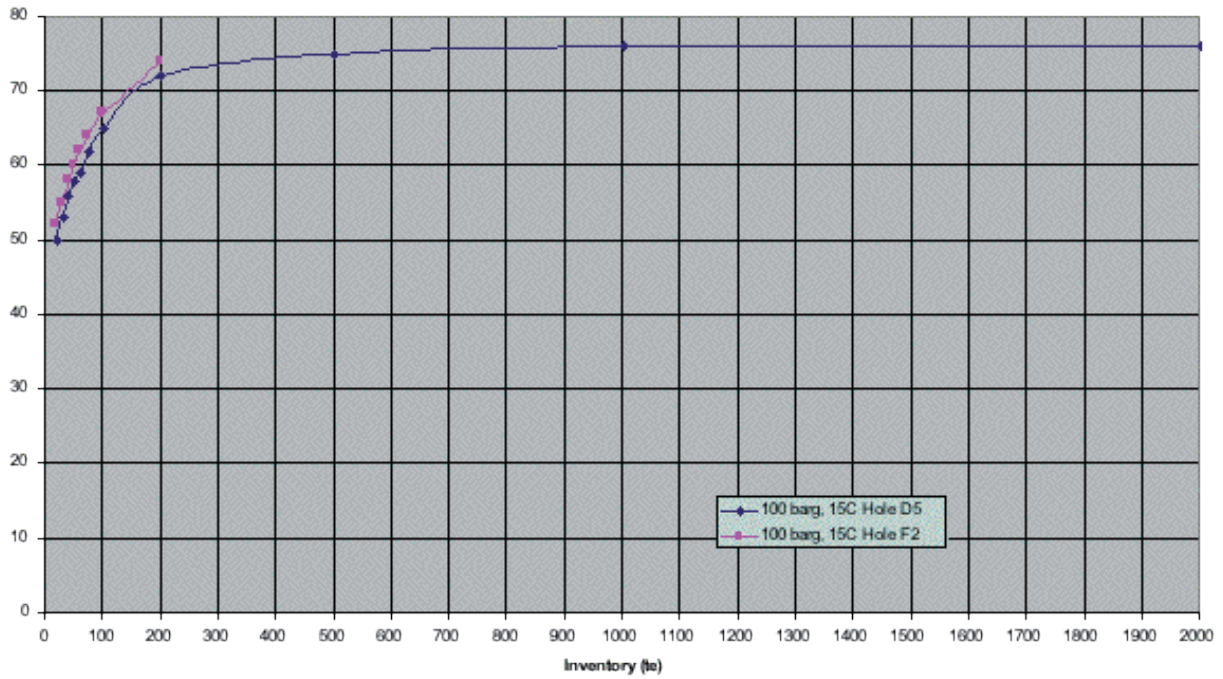
# Annex 11: Results for F2 weather (catastrophic failure)





# Annex 12: Results for 50 mm holes

100 barg, 15C Holes



## Further information

For information about health and safety, or to report inconsistencies or inaccuracies in this guidance, visit [www.hse.gov.uk/](http://www.hse.gov.uk/). You can view HSE guidance online and order priced publications from the website. HSE priced publications are also available from bookshops.

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