PHILLIPS 66 – HUMBER ZERO

CO_2 Venting & Dispersion Report

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215005-00857 – Humber Zero – CO_2 Venting & Dispersion Report

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		Andrew Dickinson	Paul King	Paul King			

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1. Executive Summary

The scope of this report is to evaluate the various concentrated CO_2 venting scenarios and impacts to the local population associated with the new post combustion FCC Carbon Capture Unit (CCU) to be installed at the Phillips 66 Humber Refinery.

The requirement for the direct venting of concentrated CO_2 has been minimised as far as possible through the recycling of CO_2 vent streams to the CCU absorber. Where this is not feasible for some plant shutdown activities and process upsets there is a requirement to vent concentrated CO_2 to atmosphere.

Through assessment of the various plant modes of operation, the following scenarios for the venting of concentrated CO_2 have been identified. These form the basis for dispersion modelling to establish the potential impacts upon plant personnel and the local population.

	Start-Up	Shutdown		CO_2 Off Specification
		Solvent Stripping	HP/ LP- De Pressuring	@ HP
Dispersion Modelling Scenario Reference	N/A	HP01	HP02	HP03
Venting Rate	N/A	62,845 lb/hr	62,845 lb/hr	22,050 lb/hr
Discharge Temp	N/A	46 °F	44 °F	40 °F
5,000 ppm Dispersion Radius		33 m	33 m	37 m
15,000 ppm Dispersion Radius		9 m	9 m	15 m
Distance to Nearest Offsite Receptor		630 m	630 m	630 m

Table 1.1 Summary of Dispersion Modelling Results

Dispersion modelling has assessed concentrations of 5,000 and 15,000 ppm based upon the Long-Term Exposure Limit (LTEL) and Short-Term Exposure Limit (STEL) for CO_2 respectively. Venting due to off spec CO_2 within the HP system provides the worst case maximum dispersion radius. Associated dispersion modelling results show a concentration of 5,000 ppm is not exceeded beyond the site boundary or at any offsite receptor locations.

The impact upon adjacent plant structures has also been assessed and dispersion results show no 'slumping' of the CO_2 plume below the stack elevation. A stack height of 40m x 200mm diameter has been specified to ensure sufficient elevation above pipe racks and structures within the direct vicinity. Some local structures including the wet gas scrubber, absorber and amine regeneration column are elevated above the 40m stack height, however all are sufficient distance from the vent to ensure adequate dispersion, ensuring concentrations are less than 5,000 ppm at all accessible locations across the site.

2. Introduction

Under the Humber Zero suite of projects, Phillips 66 intend to install a post combustion Carbon Capture Unit (CCU) on the Humber Oil Refinery downstream of the existing Fluid Catalytic Cracker (FCC) unit. As part of the proposed plant operation, the venting of concentrated CO_2 to atmosphere can occur during shutdown and upset operating scenarios. Dispersion modelling has been conducted against associated planned and unplanned venting scenarios to assess the impact upon the environment and local population.

This report presents the modelling basis and venting scenarios along with results and conclusions from dispersion modelling.

3. Modelling Software & Validation

3.1 Modelling Software

The Det Norske Veritas (DNV) Germanischer Lloyd (GL) consequence modelling software Process Hazard Analysis Software Tool (PHAST) version 8.7 shall be used to determine extents of the worst-case events in terms of CO_2 concentration. PHAST is an industry standard consequence modelling software which examines the progress of a potential incident from the initial release (source term) to far-field dispersion analysis, together with gas dispersion, jet fire thermal radiation modelling, flash fire and explosion effects calculation.

The current versions of PHAST software are capable of modelling CO_2. The Peng-Robinson equation of state is used for CO_2 releases for more accurate and robust behaviour particularly for temperatures closer to critical temperature. There are several validations for leak scenario which indicate that flowrates are predicted better with Peng-Robinson compared to the default equations of state. DNV recommends using the Peng-Robinson equations of state for CO_2 modelling.

Vertical concentration contours were generated covering the concentrations of concern at different weather conditions as stated below. DNV recommended using release angles slightly less than 90° for vertical releases such as from the vent stack. See PHAST 8.71 Release notes below:

67975	Dispersion results for vertical releases
Description	The dispersion calculations for vertical releases can be problematic, particularly when determining downwind concentrations. The algorithms are based on tangents to the centreline, and therefore vertical or near vertical clouds can run into difficulties that require special handling. In some cases, it has become apparent that this can lead to concentration predictions that are generally over-conservative. In most cases these problems can be solved by reducing the release angle, so it is just off vertical, e.g., to 85 degrees from the horizontal.

Figure 3-1 PHAST 8.7 release notes

3.2 Modelling Uncertainty

The PHAST software includes a large number of mathematical models. The theory, verification and validation of these models is included in the technical documentation provided with PHAST and in various technical publications. References to detailed validation analysis are provided rather than repeating the information here. For CO_2 (and other materials), an overview of key verification and validation is given in Witlox et al., (2018) and provides a good general introduction.

	BP	Shell	CO2PIPETRANS: Pipe releases	CO2PIPETRANS: Orifice releases	COSHER
Scenario	Orifice, horizontal	Orifice, horizontal	Long pipe, horizontal	Orifice, horizontal	Buried long pipe
Pressure [bar]	82 – 158	80 - 152	98 - 105	26 - 78	152
Temperature [°C]	5 – 149	0 - 71	3 - 14	-10 - 14	13.1

	BP	Shell	CO2PIPETRANS: Pipe releases	CO2PIPETRANS: Orifice releases	COSHER
Fluid phase	Dense liquid, super-critical	Dense liquid, super-critical	Dense liquid	Liquid, dense liquid	Dense liquid
Hole diameter [mm]	6 – 26	6 - 25	10 – 50	25 - 150	219.1 (full-bore rupture)
Year	2006-07	2010-11	2012-13	2013	2013
Location	Spadeadam	Spadeadam	Spadeadam	Spadeadam	Spadeadam
Reference	(Witlox, et al., 2014) [14]	(Witlox, et al., 2014)[14]	(Holt, et al., 2015)[10]	(Witlox, et al., 2015)[11]	(Ahmad, et al., 2015)[12]

Table 3.1 List of CO_2 experiments used for PHAST model validation

Over the past 10 years there have been several improvements in PHAST CO_2 modelling. These relate to the modelling of solid-vapour equilibrium calculations and solid properties, and special considerations for some physical properties (particularly density). This affects models from discharge through to dispersion. There is also a crater model which, while more generally applicable, was derived based on CO_2 buried pipeline experiments. The toxic effects of CO_2 are taken into account by using probit values derived from the HSE.

3.3 Modelling Confidence

The PHAST Model has been validated against BP and Shell experimental data made available via the CO2PIPETRANS JIP8. The experiments were of pressurised CO_2 releases involving steady-state and transient dense liquid phase releases, and time-varying supercritical releases. Initial pressure ranged from 80 bar to 158 bar, initial temperatures from 0°C to 149°C, and orifices diameters from 6 mm to 26 mm. The releases were horizontal and not impinged.

The releases were all modelled by the UDM as steady-state releases, with 20-seconds averaged flow rates applied for the time-varying BP releases and with the initial maximum flow rate applied for the time-varying Shell releases. For all cases the solid carbon dioxide was found to sublime rapidly, and no fallout was predicted, which was in line with experimental observations. The concentrations were found to be predicted accurately, as indicated in the figures below, where the vast majority of predicted concentrations are well within a factor of two.

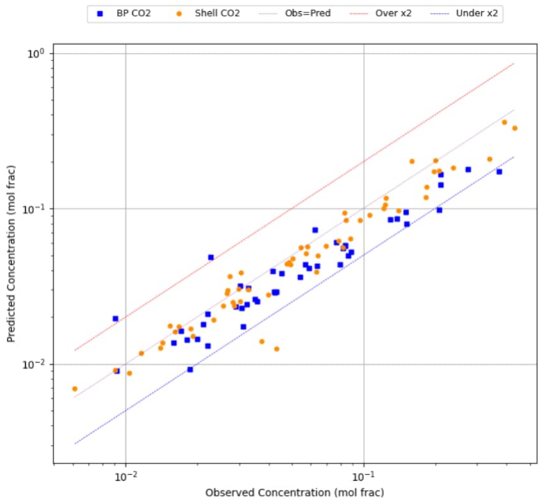


Figure 3-2 PHAST validation of Shell and BP CO_2 dispersion experiments

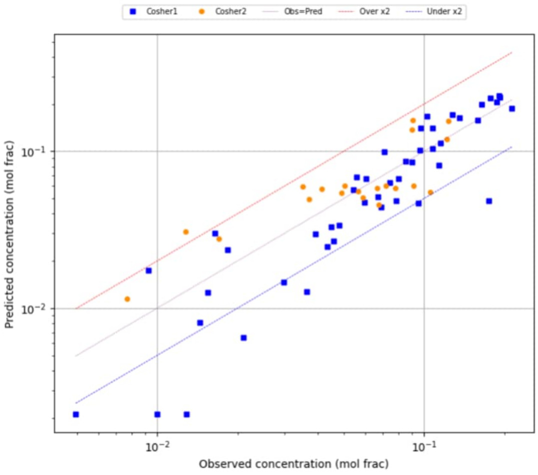


Figure 3-3: Pointwise observed vs predicted maximum concentrations for COSHER experiments.

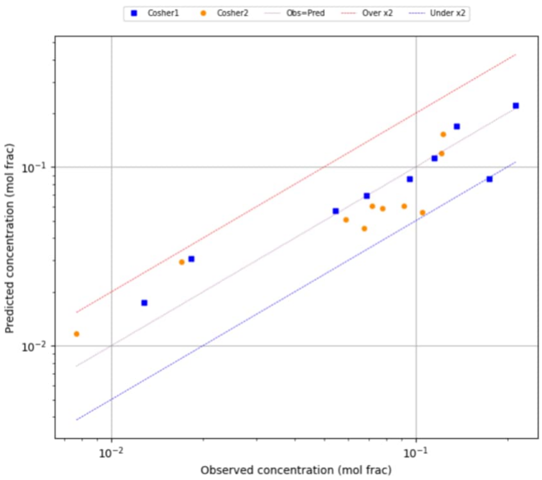


Figure 3-4: Arcwise observed vs predicted maximum concentrations for COSHER experiments.

The findings from this experimental data show that the Peng-Robinson equation of state (PR EoS) more accurately predicts CO_2 density in some regimes than the default method in PHAST. Vent modeling within PHAST will be completed using the ‘short pipe’ method to obtain similar results to those completed during the experiments mentioned above.

4. Modelling Basis and Assumptions

4.1 Concentration Exposure Limits

Concentration exposure limits are based on HSE Workplace Exposure Limit guidance (EH40) and HSE's Dangerous Toxic Load Assessment:

- 5,000 ppm (concentration of CO_2 of 0.5 % v/v in air): The Long-Term Exposure Limit (LTEL, based on an 8-hour time weighted average period)
- 15,000 ppm (concentration of CO_2 of 1.5 % v/v in air): The Short-Term Exposure Limit (STEL, based on a 15-minute time weighted average period)

It is noted that the HSE's Dangerous Toxic Load assessment for CO_2 shows a significant danger to humans if they inhale CO_2 at concentrations above the following:

- 14% in air (i.e. > 1400,000 ppm) for 1 min and;
- 8.4% in air (i.e. > 84,000 ppm) for 60 mins.

These concentrations correlate to the significant likelihood of death figures shown within Table 4.1. SLOD is defined as causing 50% lethality from a single exposure over a known amount of time.

Inhalation Exposure Time (min)	SLOT:1-5% Fatalities CO_2 Concentrations in air		SLOD: 50% Fatalities CO_2 Concentrations in air	
	%	ppm	%	ppm
60	6.3	63,000	8.4	84,000
30	6.9	69,000	9.2	92,000
20	7.2	72,000	9.6	92,000
10	7.9	79,000	10.5	96,000
5	8.6	86,000	11.5	115,000
1	10.5	105,000	14	140,000

Table 4.1 HSE Toxic Load Assessment - Concentration vs time consequences for CO_2 inhalation

For the purposes of this assessment we will solely focus on the STEL and LTEL as these are the lower limits prescribed by HSE for CO_2 concentration exposure.

4.2 Weather Data

Three weather conditions assessed for the study have been selected based on annual weather conditions for the Immingham area using the wind rose data (Figure 4-1) and are assumed typical for assessment of all installations.

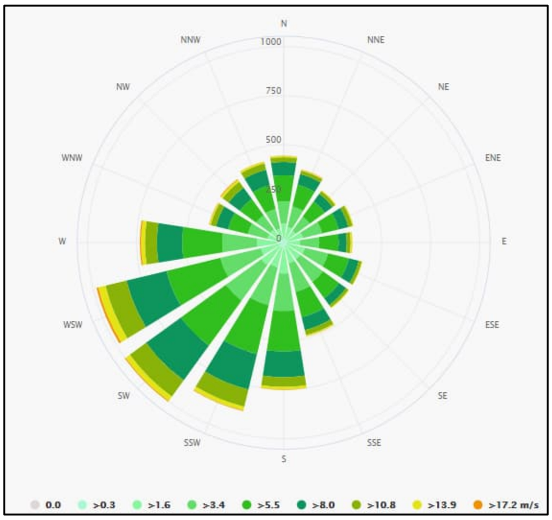


Figure 4-1 Wind rose data for Immingham (meteoblue)

Weather parameters within PHAST are designated using letters. The letter (ranging from A to F) associated to a Pasquill Stability Class refers to how stable an environment is in terms of atmospheric turbulence. The number (ranging from <2 to >13) associated to a Pasquill Stability Class refers to the surface wind speed (in m/s) measured at a 10 m height.

The following conditions were considered:

Pasquill Stability Classes:

- D: Neutral conditions, with wind speeds of 5 m/s (“5D”) This class represents the conditions for weather condition for day time.
- F: Moderately stable conditions, with wind speeds of 2 m/s (“2F”) This class represents the conditions for weather condition for night time.
- F: Moderately stable conditions, with wind speeds of 1 m/s (“1F”) This class represents the conditions for weather condition with poor visibility, e.g. fog and / or mist.

Ambient Air temperature = 50°F

Relative Humidity = 80%

4.3 Vent Location & Arrangement

All concentrated CO_2 vents shall be routed via a common atmospheric vent (NGR grid reference 515601, 416926) referred to in this document as the CO_2 vent stack. Table 4.2 provides a summary of proposed vent sources into the CO_2 vent stack.

Source	Location	Controlled	Vent Heating
LP Vent	Downstream of the Deoxy and Dehydration units	Flow	
HP Vent	Discharge of HP compressor	Flow	Yes
Export Vent	Export line downstream of HP analysis	Flow	Yes
Relief	Various relief devices to be specified in subsequent design phases.	No	

Table 4.2 Summary of vent sources into CO_2 vent stack

With the exception of relief vents, flowrates shall be regulated across a flow control valve to ensure specified venting flowrates are maintained. For HP vents on the compressor discharge and export line, venting shall be via an inline knock out drum and heater to ensure liquids/ solids formed from the high pressure let down are vaporised prior to venting to atmosphere.

The elevation of adjacent pipe racks and structures is ~ 25m. Dispersion modelling is based upon a proposed stack height of 40m x 200mm diameter to ensure personnel working on adjacent structures are not at risk from excess CO_2 concentration levels against the identified venting scenarios.

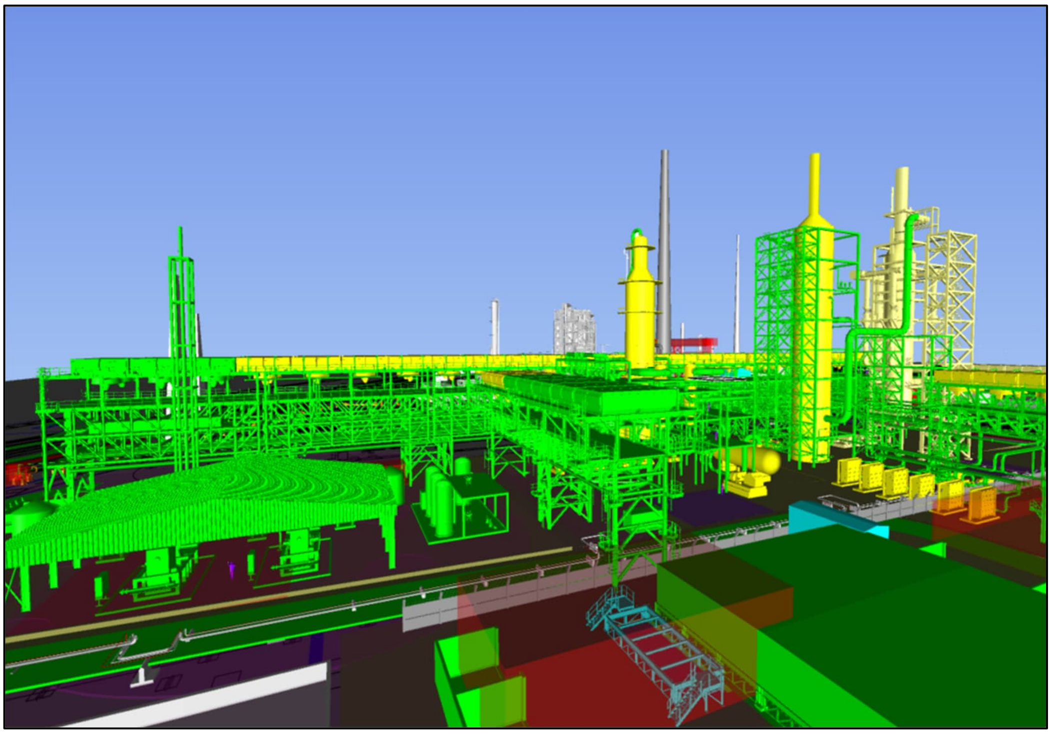


Figure 4-2 Model Screenshot showing location of vent.

4.4 Receptor Locations

4.4.1 Offsite Receptors

Receptors potentially affected by the emissions from the installation, including local residential and amenity receptors, have been identified through site knowledge and desk study of local mapping. Isopleth figures of pollutant dispersion have been examined to identify the receptors that will receive the highest point source contributions and these receptors have been included in the model set up as discrete receptors.

The receptors are selected to be representative of residential dwellings and recreational areas around the installation and are shown in Table 4.3. The nearest receptor to the CO_2 vent stack is taken as Melrose, South Killingholme.

Receptor I.D	Receptor	Distance from Stack	NGR Grid Reference
CO_2 Vent Stack			515601 , 416926
R1	Hazel Dene, Marsh Lane	1780 m	517330, 417311
R2	Station House, Station Road	2300 m	517333, 418345
R3	Fairfield House, North Garth	2160 m	514687, 418769
R4	Old Vicarage, North Garth	1820 m	514428, 418197
R5	Manor Farm, North Killingholme	1380 m	514515, 417653
R6	Church Lane, North Killingholme	990 m	514763, 417331
R7	Westfield Farm, North Killingholme	900 m	514708, 416785
R8	Melrose, South Killingholme	630 m	515115, 416417
R9	Town St/ Humber Road, South Killingholme	690 m	515516, 416120
R10	South Killingholme Primary School	1000 m	514880, 416120
R11	East End Farm	1120 m	515935, 415730
R12	Immingham	2640 m	517765, 415255

Table 4.3 Offsite receptors

Figure 4-3 Map of offsite receptors

4.4.2 Local Plant Receptors

The following provides a summary of all adjacent elevated plant equipment and horizontal distance from the CO_2 vent stack. Dispersion modelling shall consider the impacts of operatives accessing adjacent structures.

Plant Item	Distance from Stack
Compression Building	35 m (1)
Fin Fan Coolers	54 m
Solvent Stripper Column	70 m
Absorber Column	110 m
Wet Gas Scrubber	140 m

Table 4.4 Local plant receptors

(1) Although within max dispersion radius, compression building is elevated below 40m so concentration is < 5,000 ppm.

5. Venting Scenarios

Venting scenarios associated with start-up, shutdown and off specification have been assessed. The following provides a summary of all scenarios where concentrated CO_2 is vented via the CO_2 vent stack. Where identified venting activities can be planned as necessary to minimise any potential disruption associated with excess noise levels.

Vent discharge conditions have been derived using UniSim process simulation software using the Peng-Robinson equation of state, and are calculated upon letting down to atmospheric conditions from defined upstream operating temperatures and pressures. Upstream and discharge conditions are identified within Table 5.1 below.

	Start-Up	Shutdown		CO2 Off Specification
		Solvent Strip	HP/ LP- De Pressuring	@ HP
Source	N/A	LP Vent	LP + HP + Export	Export
Discharge Location	N/A	CO_2 vent stack	CO_2 vent stack	CO_2 vent stack
Vent Stream Composition		100% CO_2 (1)	100% CO_2 (1)	100% CO_2 (1)
Venting Mass Flow	N/A	62,845 lb/hr	62,845 lb/hr	22,050 lb/hr
Vent Tip Diameter	N/A	0.656 ft	0.656 ft	0.656 ft
Velocity @ Vent Tip	N/A	430 ft/s	428 ft/s	149 ft/s
Upstream Pressure	N/A	534 psig	100 psig	116 psig
Upstream Temperature	N/A	118 °F	59 °F	58 °F
Discharge Temp	N/A	46 °F	44 °F	40 °F
Planned	N/A	Yes	Yes	No
Release Frequency	N/A	0.2 /yr	0.2 /yr	(2)
Duration	N/A	< 8hrs	~ 8 hrs	~ 8 hrs

Table 5.1 Venting scenarios

(1) Composition of vented vent stream is taken as 100% CO_2 for the purposes of PHAST modelling. Actual vent stream likely to contain trace levels of H_2O (30 ppm)

(2) Release associated with unplanned plant deviation

5.1 Start Up

The proposal for all phases of plant start up is to recycle off specification CO_2 back to the absorber inlet. Excess CO_2 will be discharged along with the flue gases to atmosphere via the absorber vent. At this point it shall be a diluted stream and no venting of concentrated CO_2 will occur.

5.2 Shutdown

Venting of concentrated CO_2 shall take place as part of a planned operation when the CCU is shutdown. This is required to 'strip' CO_2 from the solvent prior to being sent to storage and to de-pressurise the LP and HP systems prior to purging and maintenance. Shutdown shall coincide with the FCC outage once every 5 years (0.2/yr).

During shutdown, flue gases from the FCC shall be vented to atmosphere via the wet gas scrubber and the flow to the CCU stopped. As the CO_2 flow reaches the minimum turn down for the Deoxy and Dehydration units there is potential the CO_2 will go off specification. At this point concentrated CO_2 would be discharged to the CO_2 vent stack via the LP & HP vents until stripping of CO_2 from the solvent has ceased. Under this scenario CO_2 would be vented at a rate equivalent to the minimum turndown of the Deoxy and Dehydration units (62,845 lb/hr). Refer to Appendix 9.1 for associated venting diagram.

On completion of solvent stripping the final phase of the CCU shutdown is to de-pressurise the HP and LP stages of the compressor. Venting rates shall be controlled to ensure peak discharge rates are within those for CO_2 stripping and do not exceed 62,845 lb/hr. Refer to Appendix 9.2 for associated venting diagram.

5.3 CO_2 Off Specification

Continuous analysis is provided in both the LP and HP systems. Where possible this would provide early indication of material going out of specification, and allow corrective action to be taken ensuring atmospheric venting is minimised. It shall be necessary however to vent CO_2 if off specification CO_2 is detected.

In the event of LP going out of specification, flow to the HP system is stopped and flow to the LP system is reduced to the minimum turndown for the Deoxy and Dehydration units and recycled back to the absorber inlet. CO_2 is then vented along with the flue gases via the absorber vent as a diluted stream and no venting of concentrated CO_2 will occur.

In the event of HP going out of specification, flow to the HP system is stopped and flow to the LP system is vented to the absorber as per LP out of specification. De pressuring of the HP system would however be through the HP vent to atmosphere as a concentrated CO_2 stream via the CO_2 vent stack. Depressuring of the HP line would occur at a flow of 22,050 lb/hr governed by the capacity of the HP vent heating system. Refer to Appendix 9.19.3 for associated venting diagram.

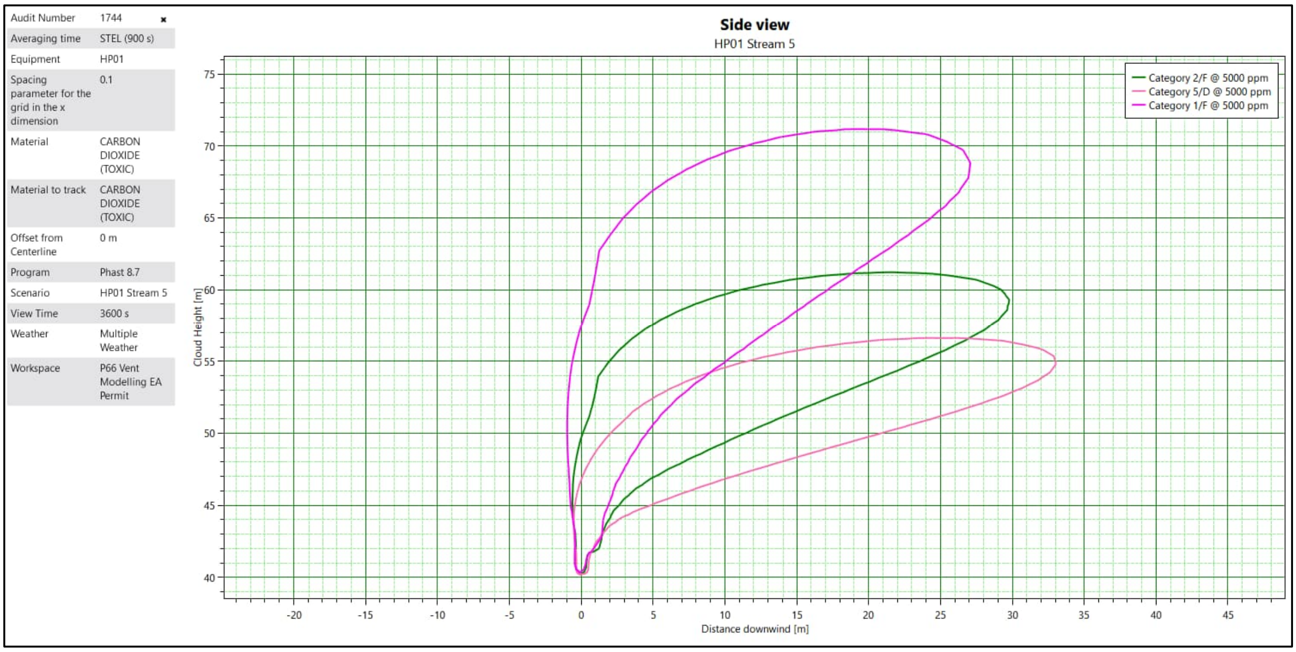
5.4 Relief Valve Discharges

Relief valves including those identified on the LP and HP compressor suction drums shall discharge concentrated CO_2 to atmosphere via the CO_2 vent stack. Relief venting shall however be infrequent and only in the event of plant upset. Determination of required relief provisions and sizing will be conducted at detailed design along with dispersion modelling as necessary to ensure discharged CO_2 concentrations are acceptable.

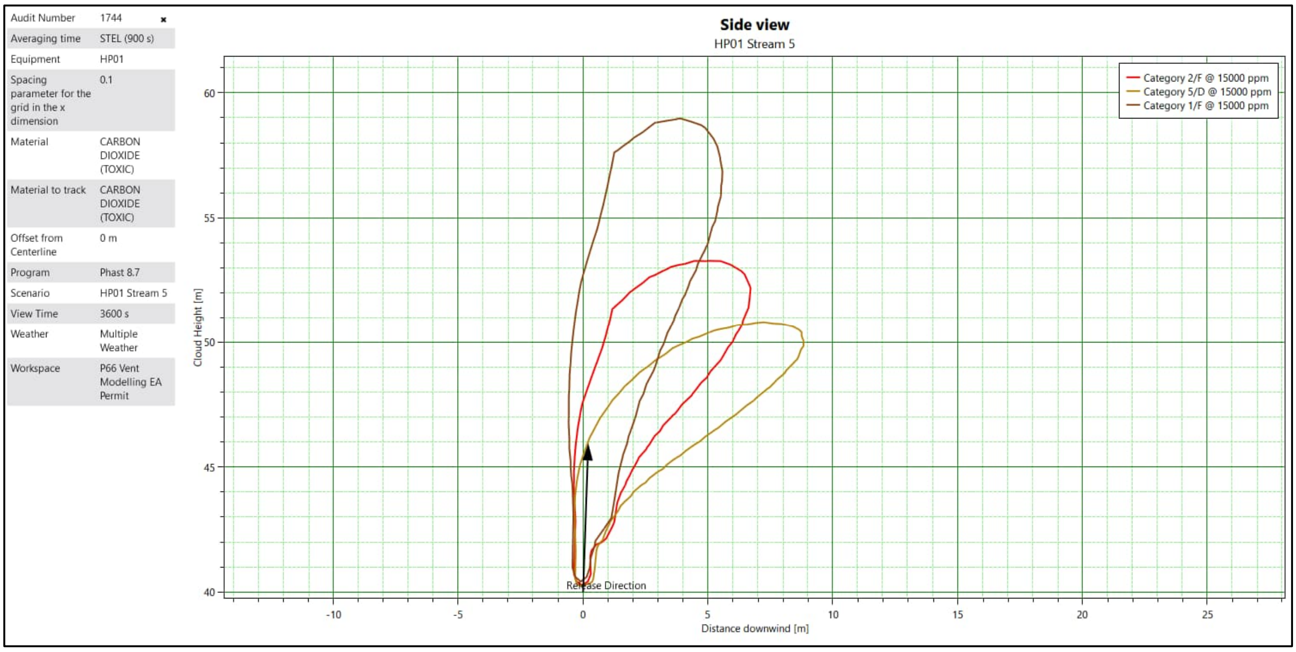
6. Results Summary

Consequence Model Contours for each scenario, associated with all weather conditions are shown below for 5,000 ppm and 15,000 ppm respectively.

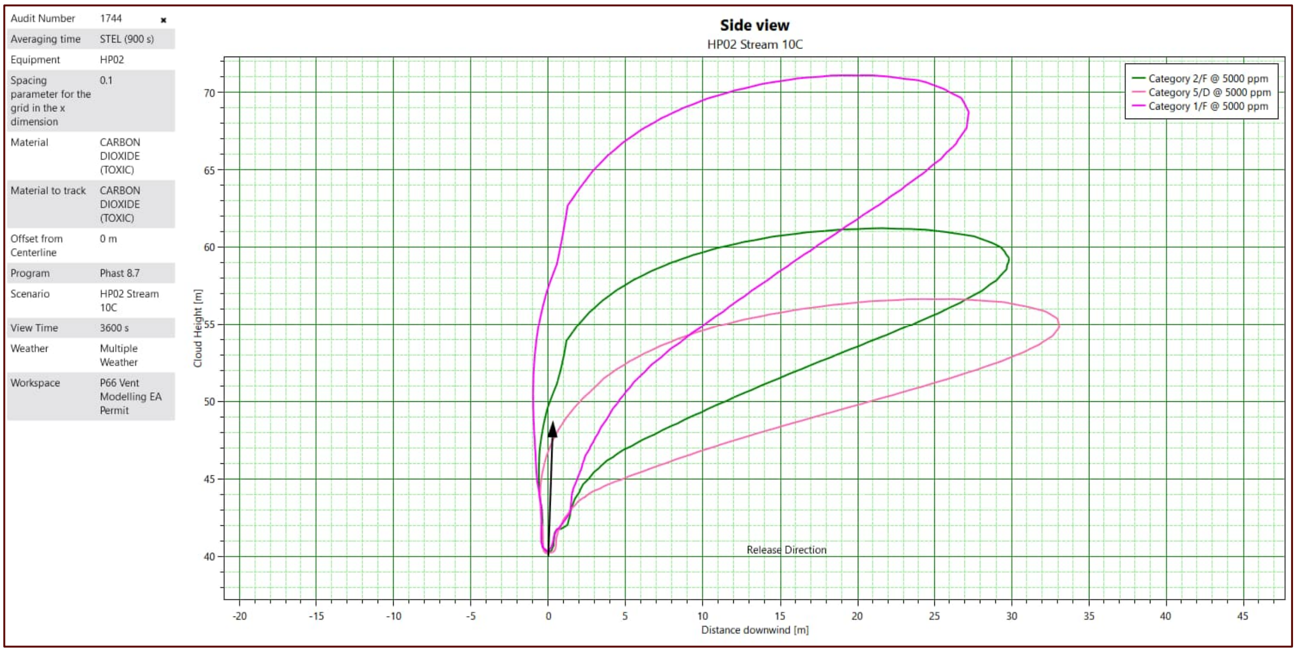
6.1 HP01 5,000 ppm



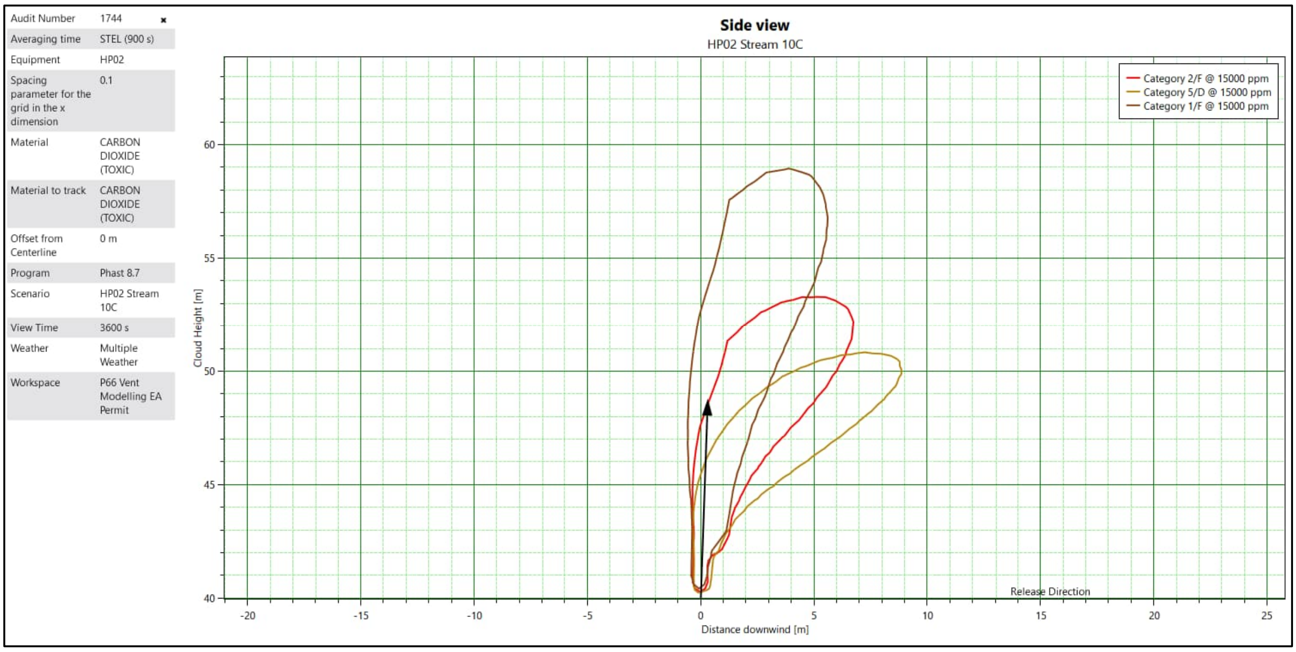
6.2 HP01 15,000 ppm



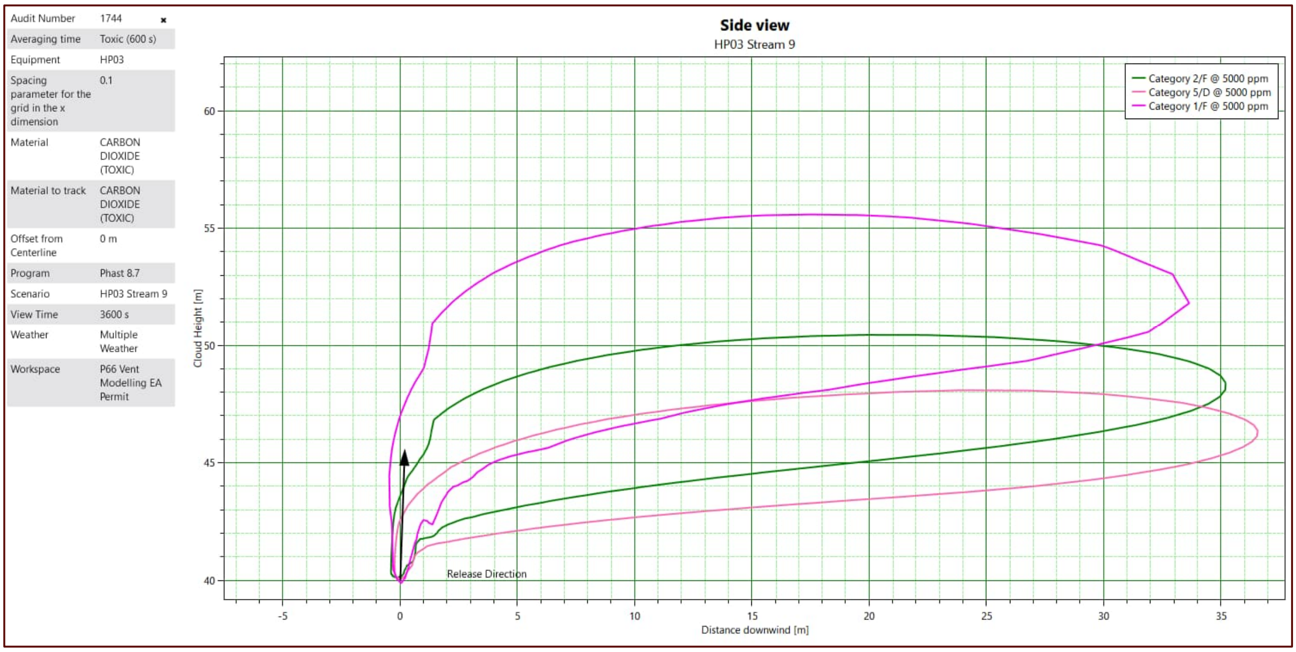
6.3 HP02 5,000 ppm



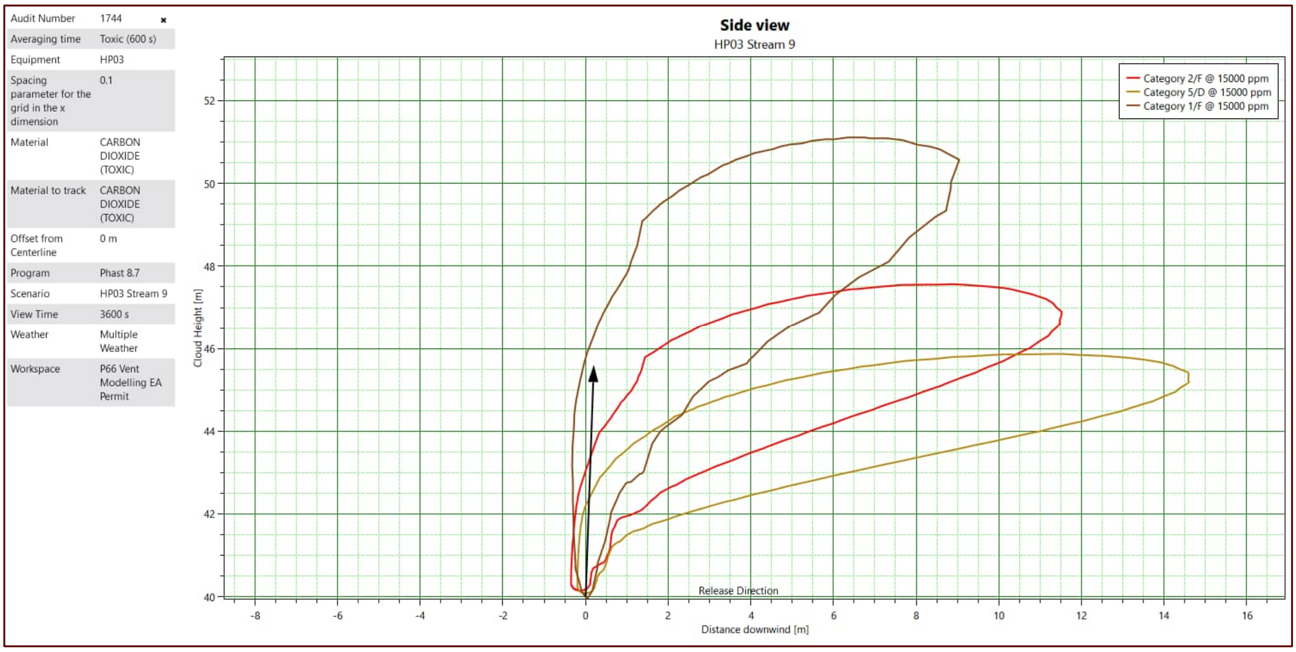
6.4 HP02 15,000 ppm



6.5 HP03 5,000 ppm



6.6 HP03 15,000 ppm



6.7 Vent Plume Extent

The following shows the extent of the CO_2 vent plumes from the CO_2 Vent Stack against a 5,000ppm CO_2 concentration.

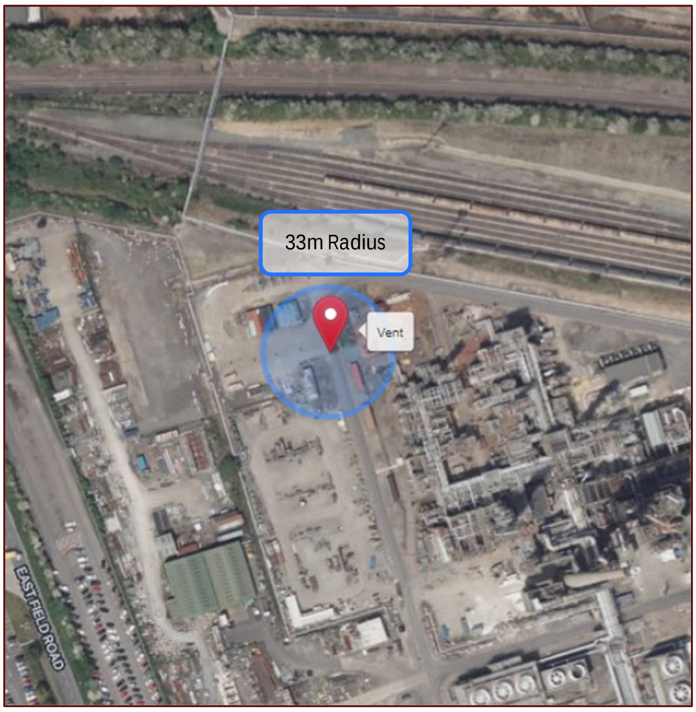


Figure 6-1 Case HP01 5,000ppm CO_2 extent at 40m elevation

Figure 6-2 Case HP02 5,000ppm CO_2 extent at 40m elevation

Figure 6-3 Case HP03 5,000ppm CO_2 extent at 40m elevation

7. Conclusions

The vent dispersion results presented within this report show the modelling results using DNV PHAST exhibit the type of behaviour observed from real time experiments conducted by others for the concentrations chosen. Concentrations of interest used within the model demonstrate that CO2 plumes do not touch down to grade and can be shown that venting of CO2 from the FCC will not create an adverse effect to people or animals.

The scenario representing the worst case dispersion impact is associated with controlled venting of the HP system in the event of CO_2 going out of specification.

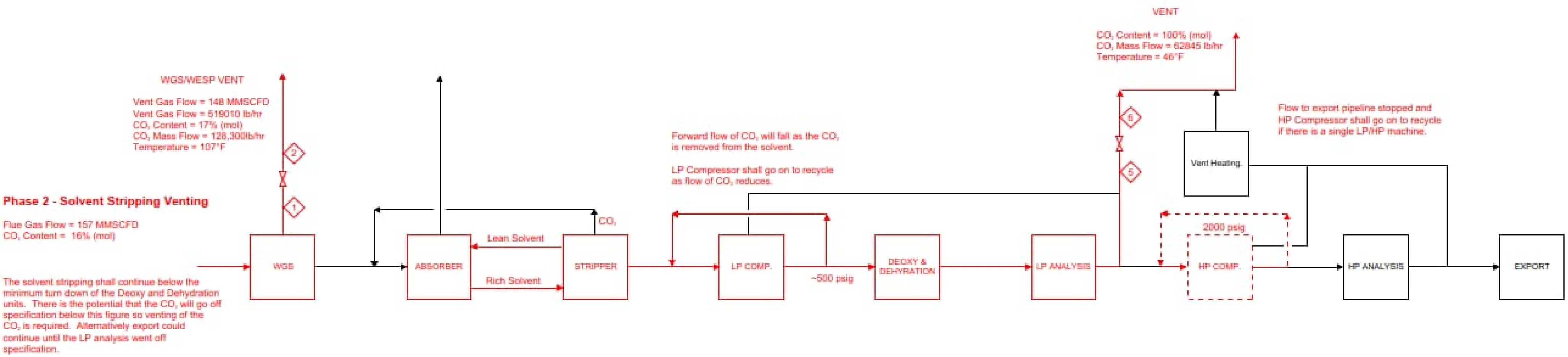
Against a specified stack height of 40m x 200mm diameter, the associated concentration does not exceed the LTEL (5,000 ppm) both offsite and at onsite elevated structures.

8. References

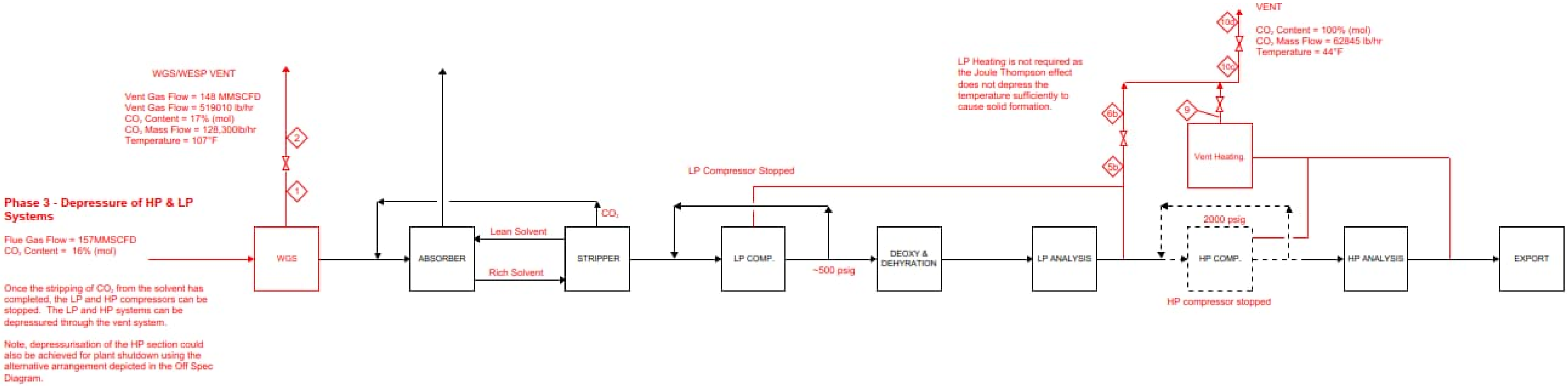
1. UK EA & DEFRA, 2014 – 2021, Guidance on Environmental permitting: air dispersion modelling reports (Environmental permitting: air dispersion modelling reports - GOV.UK (www.gov.uk))
2. UK EA & DEFRA, 2016 – 2023, Guidance on Air emissions risk assessment for your environmental permit (Air emissions risk assessment for your environmental permit - GOV.UK (www.gov.uk))
3. Dr Peter Harper, UK Health and Safety Executive (HSE), Assessment of the major hazard potential of carbon dioxide (CO_2).
4. UK Health and Safety Executive (HSE), Fourth Edition 2020, EH40/2005 Workplace exposure limits.
5. Energy institute, Rev. C Draft 2023, EI123/013, Hazard Analysis for Onshore and Offshore Carbon Capture Installations and Pipelines
6. C.M. Dixon Et Al, 2012, Validation of Dispersion Models for High Pressure Carbon Dioxide Releases, Hazards XXIII Symposium Series no 158
7. DNV, Rev. 3 (June 2023), Application of Phast and Safeti to carbon dioxide consequences and risks.

9. Appendix

9.1 Venting Diagram Case HP01, Shut Down - Solvent Stripping



9.2 Venting Diagram Case HP02, Shut Down - Depressure of HP & LP Systems



9.3 Venting Diagram Case HP03, Shut Down – De Pressure HP & LP