SAFETY IN CARBON DIOXIDE CAPTURE, TRANSPORT AND STORAGE

Technical Study

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ACKNOWLEDGEMENTS AND CITATIONS

This report describes upgrade of a computer programme for calculating the cost of CCS systems sponsored by the IEA Greenhouse Gas R&D Programme. This report was prepared by:

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SAFETY IN CARBON DIOXIDE CAPTURE AND STORAGE

Background

Within the next few years it is expected that an increasing number of commercial scale demonstrations of CO_2 capture and storage technology will be built and brought into operation. Many aspects of the design of such facilities including issues relating to engineering design, environmental impacts, standards and permitting have been the subject of studies undertaken for the IEA GHG. So far no study has been dedicated specifically to the issue of safety in the above ground elements of CCS systems although such safety issues have been addressed to some extent in earlier studies[1]. This study was designed specifically to examine the safety issues which are likely to arise when preparing safety cases and planning emergency procedures for CO_2 capture and storage (CCS) projects.

Study approach

The study was contracted to the UK Governments main Health and Safety Laboratory (HSL) which has become involved in a number of issues relating to safety in CCS projects specifically in support of the DF1 project[2] and more generally in support of UK government policy development for CCS. The study has considered a generic CCS system consisting of power plant with CO_2 capture, transport by trunk line to an on or offshore injection site. The safety of all surface facilities was considered but not the risks associated with underground reservoirs or the below ground sections of wells. The most established forms of the three leading processes (pre- post- and oxy-combustion) for CO_2 capture at power stations were all considered.

The study started by collecting basic information in the form of flow schemes, material balances and layouts as well as safety information on CO_2 and other materials, such as absorption solvents, which might be encountered. Once this was done a group of experts drawn from the oil and gas, power, pipeline and industrial gas industries were assembled complemented by staff from the UK health and safety executive and IEA GHG. HSL lead this group through a series of 4 structured hazard analysis sessions with the aim of identifying all possible causes of hazards and means of their mitigation when CCS systems are introduced. The study differentiated between those hazards which are already present in conventional power generation, pipeline transport and underground injection activities thus singling out new hazards which might arise when CO_2 capture is added.

The results of the Hazard identification sessions were documented and used to construct cause and consequence diagrams (often referred to as Bow tie diagrams) showing what factors and

[1] PH4/23, Barriers to Overcome in Implementation of CO_2 Capture and Storage (2): Rules and Standards for Transmission and Storage of CO_2, 2006/03, Permitting Issues for CO_2 Capture and Geological Storage, 2007/01, Environmental Assessment for CO_2 Capture and Storage,

[2] DF1 was BP's first proposed "Decarbonised Fuel" project to be located at Peterhead in Scotland

events could precede key "top events" and those which could mitigate their immediate consequences and later recovery.

Results and Discussion

Hazard identification sessions
The four sessions examined safety in CCS systems from different perspectives. The first concentrated on defining the facilities which would be examined and on assessing the information which was available on CO_2 safety and handling. An important outcome of this session was the realisation that as yet there is not a great deal of detailed information about the design of CCS systems. This will become available only when detailed engineering designs are prepared during the first large scale projects. Even then this information may be proprietary. During this meeting information was generated as to what the non-capturing baseline design was and which additions and changes would be introduced by adding CCS.

In the second meeting a structured top down HAZID (Hazard identification) was conducted to brainstorm top events, such as major CO_2 release, fire, explosion, relevant to CCS. Brainstorming was carried out using keywords which represented possible top events and/or consequences.

In the third meeting CCS was examined from a completely different angle. Participants were asked to focus, again using keywords, on what changes to existing practices CCS might bring particularly in terms of layout, interfaces and organisation.

In the last meeting draft bow-tie diagrams which had previously been constructed based on the information from meetings 1-3 were considered The structure of the bow-ties was analysed and possible barriers to the realisation of the top events and mitigation of their consequences were brainstormed

Bow tie diagrams
The information generated during the sessions was encapsulated in a set of bow tie diagrams which effectively describe all of the factors which could contribute to causing incidents in CCS systems and the subsequent handling of the consequences. The diagrams have been transferred to an interactive Excel spread sheet which makes them easier to navigate. It is anticipated that they can be used in the first phases of safety management in future CCS projects.

Identification of new hazards and knowledge gaps
To raise awareness of the potential hazards emerging from the HAZID sessions a list of 23 avoidable accidents was formulated which illustrate all of the significant generic factors which were identified. These were formulated on the basis of the following list of potential hazards which could be used as part of a safety check list at various stages of a CCS project. It must however be emphasized that this is no substitute for timely application of a full safety management program during the design, construction, operation and maintenance of CCS facilities.

The teams identified potential for:-

1. New low points to be subject to CO_2 asphyxiation hazard
2. Parts of pigs exposed to HP CO_2 to explode when depressurised
3. Increased risk of running pipeline fractures
4. New enclosed spaces to be subject to CO_2 asphyxiation hazard
5. HP CO_2 leaks to be a potential source of static discharge
6. Undetected formation of low level clouds of CO_2 even when there are no low points
7. Persons to move to less safe places following a CO_2 release due to inappropriate emergency training
8. Cold burns from CO_2 releases
9. Toxic hazards due to mercury accumulation
10. Changes in abundance and toxicity of scales and sludges co-produced with oil from reservoirs where CO_2 storage is combined with EOR
11. Fires in oxygen enriched atmospheres
12. Pyrophoric material formation in lines and equipment exposed to H_2S contaminated CO_2 streams
13. Inappropriate training and qualifications for staff designing, operating and maintaining CCS systems
14. Oxygen burning of steel in oxygen systems due to inadequate standards of equipment cleanliness
15. Enhanced risk of brittle failure during depressurisation of CO_2 containing equipment
16. Increased explosion overpressures due to congestion
17. New places to be subject to nitrogen asphyxiation
18. Fires involving new solvents used for CCS because they are more flammable than they appear
19. Formation of water from O_2 and H_2 and subsequent corrosion when certain CO_2 streams are mixed
20. New solvents used for CCS to contain toxic components
21. Ergonomic problems caused by revamping sites with old control systems
22. Inadequate dispersal of CO_2 from large vents
23. Incomplete coverage when advanced CO_2 pipeline leak detection systems are deployed

Those responsible should ask, for each of these in turn, whether this potential has been introduced and if so whether it has been adequately addressed, understood and controlled.

Through working in the diverse group it became apparent that industry in its totality has sufficient experience, some of it very extensive, to conduct CCS operations safely. However unless this information can consistently be made freely available and accessible where it is needed, the safety of CCS systems may be jeopardized. A few areas where further research and development are needed were noted namely:-

1. Consequence modeling of CO_2 releases, particularly the development of the source term.
2. Pipeline failure criteria in terms of validation of models predicting conditions under which running failure could occur.
3. Understanding the propensity of dense phase CO_2 to dissolve heavy metals and other toxic or radioactive contaminants from rock formations. Experience from EOR is limited to a relatively small number of reservoirs.
4. Design and operational standards for CO_2 pipelines and other equipment are still in development. Issues include suitable CO_2 specification (particularly water content); avoidance of hydrate formation; suitable non-metallic materials for seals etc.; suitable

design and operating regime for intelligent pigs; flow modeling of CO_2 with impurities which impacts on leak detection systems.

5. Aspects of emergency response planning such as recommendations for those in cars.

General recommendations for industry

The report made a number of general recommendations which would need to be taken up by industry. These in summary are

- The hazard lists and bow-tie diagrams produced by this project should be used as an input to hazard identification and design studies for CCS projects

- Work should continue to be carried out to develop design standards for CCS and to resolve knowledge gaps which have been identified.

- Particular attention should be paid to layout and interface issues when CCS is retrofitted into existing power stations. Control system compatibility and ergonomic studies should be considered.

- Training and competency issues should be considered at the outset of a project, including setting competency and training requirements for key staff and providing a hazardous substances training module for all staff destined to work on a new CCS plant.

- An international CCS system incident database should be set up with free access to all.

- An emergency response plan should be developed, particularly for incidents involving major loss of containment of CO_2.

Expert Reviewers Comments

Expert reviewers had few comments. It was pointed out by several that that the good US experience with 4000 miles of supercritical CO_2 trunk lines was being under played and that perhaps too much concern was expressed about safety of large CO_2 pipeline systems. The main report was modified to better acknowledge this. However it was felt that concerns relating to the different and more densely populated environment, very large scale and lack of established local experience remain valid. One reviewer pointed out a new hazard which could be caused by a minor leak in a buried CO_2 pipe namely that this would acidify the ground water and potentially accelerate external corrosion. A further comment was that more detailed information on the effects of CO_2 and absorption solvents and their degradation products on humans would be valuable in this report. Some additional information and references were added.

Conclusions

Industry has wide experience in the handling of CO_2 which can be used to ensure the safety of above ground CCS operations.

The extensive hazard analysis performed during this study did not find any fundamental safety issues which could not be fully managed although some new considerations were identified. Nevertheless there are numerous hazards associated with CCS surface operations which will have to be addressed if the industry is to develop without incident.

The CCS industry is in its infancy and as such is starting with a clean record. However, it is acknowledge that there have been a number of fatalities due to the use of CO_2 in other industry sectors over the years.

Sharing of information and expertise is expected to contribute significantly to safety in the industry in its early years. Additional efforts and mechanisms to ensure that this exchange occurs would be beneficial.

Recommendations

Some of the general recommendations to industry made in the report could be actively encouraged or supported by IEA GHG. In particular:

- IEAGHG could make the generic bowtie diagrams available as an additional tool through its website

.

- IEA GHG could also support the setting up of a centralized incident database for the CCS industry. However, it is considered that the task of running such a database could be quite onerous for IEA GHG. Therefore it is considered the newly formed Global CCS Institute would be a more suitable organization to do this rather than IEA GHG..

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Safety in Carbon Dioxide Capture, Transport and Storage

FP/09/17

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DISTRIBUTION

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EXECUTIVE SUMMARY

Objectives

The International Energy Agency Greenhouse Gas R&D Programme (IEA GHG) was established in 1991 to evaluate technologies that could be used to avoid emissions of greenhouse gases, particularly from the use of fossil fuels, and identify targets for useful R&D. IEA GHG commissioned this study specifically to examine the safety issues which are likely to arise when preparing safety cases and planning emergency procedures for carbon capture and storage (CCS) projects.

The following steps were required within the study:

1. Establish baseline of non-CCS facilities and activities;
2. Identify CCS additions/changes to this baseline;
3. Identify the exposure to new hazards which these bring;
4. Identify the major incidents which might result;
5. Assess the consequences of major incidents and the methods available for doing so;
6. Analyse where change from established practices could be a significant additional factor in causing incidents;
7. Propose measures available for eliminating or minimising risk of incidents and their after effects, and identify needs for additional measures;
8. Identify gaps in ability to quantify risks and evaluate consequences;
9. Propose emergency response measures.

Main Findings

1. A series of hazard studies have been carried out for the elements of the carbon capture and storage chain. These have used different perspectives to help brainstorm hazards. The perspectives included new substances, equipment and activities, potential types of major accident scenario, and changes introduced by CCS to layout, interfaces and organisation. It is hoped that the results of these HAZID studies will be of use to those carrying out CCS projects, but should never be a substitute for them carrying out a full suite of integrated hazard management processes.

2. The level of information available about the different stages in a CCS chain was found to be fairly high level. This limited the depth of HAZID which was possible but good progress was still able to be made, particularly by making use of the knowledge of experts who attended the HAZID meetings. Lack of detailed design information would not, of course, be an issue for design teams carrying out a CCS project.

3. No absolute showstoppers have been found; rather a number of potential hazards have been identified which will require the adoption of safe design principles to eliminate, prevent, control or mitigate them. Some possible barriers have been identified as a starting point in this process. Death or injury to a person or persons could result from any of the following example events, unless they are identified and addressed in the design, operation and/or emergency response.
    - (a) They entered a tunnel under a power station unaware that CO_2 had accumulated there.
    - (b) A component in a pig exploded in their faces when it was removed from a pig trap.
    - (c) A pipeline leak turned into a running fracture whilst the crew were preparing to deal with it.

(d) They were inspecting the inside of CCS power station ducting which had not been properly isolated and purged of CO_2.

(e) A spark caused by static from a CO_2 discharge started a fire in a place where it was thought no ignition source existed.

(f) They tried to rescue some one who had been overcome by CO_2unaware that the area was blanketed by a cloud of low lying CO_2.

(g) They didn't realise that it would be a good idea to move upstairs or to a higher point following a CO_2 release incident.

(h) They didn't know that they could suffer cold burns near a CO_2 release.

(i) They didn't know that equipment might be contaminated with mercury.

(j) Toxic scale had been transported selectively from underground into equipment they were working on.

(k) An oxygen-enriched atmosphere started a fire which would otherwise not have happened.

(l) Scale collected from equipment carrying CO_2, supposedly an inert gas, was pyrophoric.

(m) A chemical process was being run by staff who had no chemical process training or background.

(n) Equipment exposed to oxygen had not been properly cleaned.

(o) A vessel or pipe in CO_2 service suffered a brittle failure because it was depressured too quickly.

(p) A detonation occurred in a power plant, which was very congested following conversion to make and burn hydrogen and capture CO_2, because more equipment had to be fitted in than anticipated.

(q) Nitrogen leaked into a turbine hood and no-one realised that there was a supply of nitrogen as well as hydrogen.

(r) An amine solvent caught fire when everyone thought it was not flammable.

(s) Hydrogen and oxygen present in different CO_2 streams combined and formed water which corroded high pressure equipment.

(t) A toxic solvent was chosen when a non-toxic alternative was available.

(u) The revamp to CCS introduced such a mixture of old and new control systems that an incident occurred which would normally have been easily avoided.

(v) CO_2 was vented during an upset and did not adequately disperse/dilute before coming down to the ground.

(w) Sophisticated monitoring for a pipeline was omitted at a road crossing because modern 'laid alongside pipe systems' detection cannot be pulled under crossings.

4. Retro-fitting CCS into existing plant introduces space constraints and raises issues such as:
   - Switch gear tends to be separately owned and not easily relocated, so its location may introduce inflexibility when modifying layout to add CCS to an existing site.
   - It may not be practical to build ASUs on sites of power plant considering space constraints, but having them on a separate site raises some new safety issues.
   - If the ASU is separate, should the CO_2 be cleaned up on the same site? It could be transported wet at moderate pressure in plastic pipe.
   - A wider range of specifications will be required for spare parts, and more comprehensive materials and maintenance systems may be needed.
   - Decisions on the space required for a power plant to be capture-ready should be based on a full understanding of the layout issues.

5. CCS will introduce increased complexity and risk into power generation plants. This may introduce additional requirements for safety management systems and staff competence.

6. Knowledge gaps which have been identified by this study include:
   - Consequence modelling of CO_2 releases, particularly the development of the source term.
   - Validation of fracture control models for CO_2 pipelines.
   - Understanding the propensity of dense phase CO_2 to dissolve heavy metals and other toxic or radioactive contaminants from rock formations. While most general types of formation have been subjected to CO_2, flooding the specific response of the wide range of different mineral combinations has not been tested. Confirmation is needed that solution of contaminants is not a problem.
   - Design and operational standards for CO_2 pipelines and other equipment are still in development. Issues include: suitable CO_2 specification (particularly water content); avoidance of hydrate formation; suitable non-metallic materials for seals etc; suitable design and operating regime for intelligent pigs; and flow modelling of CO_2 with impurities which impacts on leak detection systems.
   - Aspects of emergency response planning such as recommendations for those in cars.
   - A suitable stenching agent for CO_2 may need to be developed.

Recommendations

1. The hazards and bow-tie diagrams produced by this project should be used as an input to hazard identification and design studies for CCS projects. (Electronic copies of the bow-tie diagrams in Excel format will be provided to IEA GHG members with this report so that they can be modified and extended for specific projects.)

2. Work should continue to develop design standards for CCS and to resolve knowledge gaps that have been identified; some such work is already in progress.

3. Particular attention should be paid to layout and interface issues when CCS is retrofitted into existing power stations. A control system compatibility and ergonomic study should be considered.

4. Training and competency issues should be considered at the outset of a project, including setting competency and training requirements for key staff; providing a hazardous substances training module for all staff destined to work on a new CCS plant.

5. An international CCS system incident database should be set up with free access to all.

6. An emergency response plan should be developed, particularly for incidents involving major loss of containment of CO_2.

1 INTRODUCTION

1.1 OBJECTIVES

CO_2 is handled extensively in industry in many applications such as brewing, gas reforming and gas processing. It has a host of small-scale applications and is used as an inerting gas and fire extinguishant. It is also routinely manufactured and transported by industrial gas companies. Its properties are well understood in these industrial settings for the quantities and under the conditions involved.

Whilst there has been some use of CO_2 for enhanced oil recovery (e.g. 40 years experience of transporting CO2 in pipelines in the US), with the advent of carbon dioxide capture and storage (CCS) technology the scale and extent of its handling will increase dramatically. Much larger inventories are envisaged as well as much higher pressures, possibly in combination with other toxic materials such as H_2S and SO_2. CCS may also introduce routing of pipelines through more densely populated areas. Furthermore, other substances such as hydrogen, oxygen and chemical absorbents are likely to be used in large quantities. The processing plants are expected to be situated at power plants and other industrial facilities such as steel and cement works, which may be inexperienced in handling such materials or operating the equipment required for CO_2 capture. CO_2 is likely to be transported through pipeline systems that may run through non-industrial areas and cross/follow major features of the transport network, such as roads and railways.

Finally there will be operations at the storage site that will involve site investigations and monitoring, including seismic and other surveys, drilling of wells, operation of injection equipment, maintenance and well closure. All of these will be based on established practices used by the oil/gas and water extraction industries, but with some differences that may have safety implications. The above raises issues relating to the safety of equipment and operations throughout the CCS chain.

The International Energy Agency Greenhouse Gas R&D Programme (IEA GHG) was established in 1991 to evaluate technologies that could be used to avoid emissions of greenhouse gases, particularly from the use of fossil fuels, and identify targets for useful R&D. IEA GHG is an international organisation, presently supported by 20 countries worldwide, the European Commission and 18 industrial organisations.

IEA GHG commissioned this study specifically to examine the safety issues which are likely to arise when preparing safety cases and planning emergency procedures for CCS projects. An objective was to help maintain the accident-free status of the emerging CCS industry. The scope of the work was safety, i.e. threats to humans but not to the environment.

The following steps were required within the study:

1. Establish baseline of non-CCS facilities and activities;
2. Identify CCS additions/changes to this baseline;
3. Identify the exposure to new hazards which these bring;
4. Identify the major incidents which might result;
5. Assess the consequences of major incidents and the methods available for doing so;
6. Analyse where change from established practices could be a significant additional factor in causing incidents;
7. Propose measures available for eliminating or minimising risk of incidents and their after effects, and identify needs for additional measures;

8. Identify gaps in ability to quantify risks and evaluate consequences;
9. Propose emergency response measures.

It is intended that the hazards and possible safeguards identified in this report should be useful to those undertaking CCS projects. However, considerations should not be limited to those given in this report. It is expected that those carrying out CCS projects undertake a full suite of integrated safety management processes, including hazard identification and risk assessment for the design and operations. Some examples of relevant guidance are references 24-27.

1.2 METHODOLOGY

The methodology adopted was to organise HAZID brainstorming meetings with participants from varied industry sectors. A list of participants along with their organisations is provided at the beginning of the report.

Possible experts who could help with the study were identified via IEA GHG, the Carbon Capture and Storage Association (CCSA) and the Health and Safety Executive (HSE). They were requested to provide information about carbon capture and storage processes. Experts were also invited to assist the project by attending and participating in HAZID meetings. Prior to each meeting, information was circulated in terms of draft flowsheets/block diagrams of parts of the CCS chain and information about their operating conditions. This information was refined by means of comments from the experts and is presented in this report. The information was also used as the basis for the HAZID meetings. Particularly for meeting 3, information was also supplied by meeting participants about layout for typical CCS projects. Such information was provided in confidence and has not been included in this report.

It was surprising how little information was available, and this reflects the current stage of development of CCS. This may affect early high level hazard identification of proposed projects. HAZID may need to be repeated later in a project if the quality of information is lacking at early stages in the design.

The following HAZID meetings were carried out.

Meeting 1
This meeting confirmed the process block diagrams for the different stages in the CCS chain. It also identified new substances, equipment and processes that would form part of a CCS chain. Meeting 1 provided information on baseline of non-CCS facilities and activities, and identified what changes may arise to this baseline as a result of CCS being introduced.

Meeting 2
A structured top down hazard identification study was used to brainstorm top events relevant to CCS. Brainstorming was carried out using keywords that represent possible top events and/or consequences.

Meeting 3
This meeting focused on the changes introduced by CCS, particularly in terms of layout, interfaces and organisation.

Meeting 4

This meeting considered draft bow-tie diagrams that had previously been constructed based on the information from meetings 1-3. The structure of the bow-ties was analysed and possible barriers to the realisation of the top events were brainstormed.

On the basis of proceedings and discussions in these meetings, the following were analysed or developed:

- The safety hazards which CCS introduces;
- The potential top events which are possible with an analysis of what would be the main causes of such events;
- The consequences of such potential top events and the capability to model and predict outcomes using approved techniques;
- Identification of research needed to support formulation of effective safety cases for all the main elements of CCS projects;
- Proposals to eliminate or minimise the occurrence of events and to reduce the severity of consequences; and
- Outline recommendations as to the emergency procedures that should be in place to support CCS projects.

These are described in detail in subsequent sections of this report.

2 CO_2 HAZARDS AND ISSUES

2.1 SAFETY

2.1.1 CO_2 toxicity

In addition to the hazard of asphyxiation due to released CO_2 displacing oxygen in the air, the inhalation of elevated concentrations of CO_2 can increase the acidity of the blood triggering adverse effects on the respiratory, cardiovascular and central nervous systems. CO_2, like nitrogen, will displace oxygen but unlike nitrogen, which does not have a neurological impact on humans, people would be at severe threat from increasing CO_2 concentrations well before they were from the reducing oxygen concentrations.

After several hours' exposure to a concentration of 3%, CO_2 begins to affect the human respiratory system, with headaches and restricted breathing becoming noticeable. Increasing the concentration to 7% can result in unconsciousness within a few minutes and exposure to 17% CO_2 can result in coma and death within one minute[30].

Some criteria for harmful exposure to CO_2 include:

- The UK occupational exposure limit is 0.5% for an 8 hour time-weighted average and with a short-term explosure limit (STEL) of 1.5% for 15 minutes.
- The US Immediately Dangerous to Health (IDLH) is 4% for 30 minutes exposure
- US submarine contaminants guidance levels are 0.8% for (continuous) normal operations and 2.5% (1 hour) emergency situations.

The UK Health and Safety Executive (HSE) has produced criteria, in terms of two levels of Dangerous Toxic Load (DTL)[31]. The Specified Level of Toxicity (SLOT) causes severe distress to almost everyone in the area; a significant number of the exposed population to require medical attention; serious injury that requires long term treatment in some people; and death for highly susceptible people. The SLOT DTL is based on approximately 1% likelihood of death. Another level of toxicity used by HSE is Significant Likelihood of Death (SLOD), which corresponds to a 50% likelihood of death. For CO_2, the SLOT DTL is 1.5×10^{40} ppm^{40}.min and the SLOD DTL is 1.5×10^{41} ppm^{41}.min. Table 1 gives the relationship between concentration and exposure time leading to the SLOT and SLOD DTL.

Table 1: SLOD and SLOT DTL for CO_2

Exposure period (minutes)	CO_2 concentration (%) producing the	
	SLOT	SLOD
0.5	11.5	15
1	10.5	14
10	8	11
30	7	9
60	6	8

2.1.2 Other properties of CO_2

Dense phase CO_2, i.e. liquid and/or at supercritical pressure, has properties very different from gaseous CO_2 at ambient conditions. Due to most CO_2 capture projects being in the conceptual or pilot stage at the moment, the effects of these properties on selection of equipment, design and operation of power plants is not well known or documented. It is therefore necessary to understand these properties before we proceed to the risk assessment. Connolly and Cusco[6] highlighted some of the issues with dense phase CO_2. These are listed below:

- CO_2 is a known asphyxiant;
- Zero surface tension and near zero viscosity, tendency to creep or wet surfaces (sealing difficulties);
- Forms acid solution in aqueous phase (corrosion issues);
- Release may lead to low temperatures in plant (embrittlement);
- Degradation of sealing compounds and seals; the literature lists CO_2 among other contaminants as H_2S, which can degrade seals and sealing compounds in hydrocarbon processing;
- No significant initial human sensory response to pure CO_2 release.

The scarcity of risk-based reference points in handling high pressure CO_2, against which estimated risk to persons can be established, was also highlighted.

The above properties of dense phase or supercritical CO_2 will raise issues such as[6]:

- Scale of thermal cooling envelope from a supercritical release;
- Issues with containment of supercritical $CO_{2;}$
- Explosive decompression: Elastomer seals having absorbed gas at high pressures following sudden pressure drops;
- Powerful solvent: toxic contamination effects on release;
- Dry ice ‘grit blasting’ effects;
- CO_2 detection (methods quite different from ‘lighter than air’ methane);
- Plant and temporary refuge integrity issues;
- Changes to existing fire and explosion profile of hydrocarbons. The presence of CO_2 will reduce the mixture’s flammable limits, but its effects on a flammable mixture need to be established with some confidence if credit is given for its extinguishing properties.

A study done by HSL for Mr Stephen Connolly, inspector at HSE, on incidents related to carbon dioxide worldwide is provided in Appendix A, for appreciation of hazardous effects of carbon dioxide.

2.1.3 Other considerations for CO_2

The importance of risk assessment in carbon capture and sequestration is also highlighted through the following conclusions suggested in a Newcastle University presentation[12]:

1. Design and operation of CO_2 pipelines requires careful consideration due to the unique properties of supercritical CO_2 both with and without impurities. The type, combination and quantity affects the physical and transport properties of CO_2 (density

and compressibility - product metering, compression, water solubility and flow assurance affected etc).

2. Recompression distance, compressor power and pipeline capacity are directly affected by the type, combination and quantity of impurities, with H_2 having the greatest impact. Offshore is costly. Generally, 2-phase region, Tc and Pc increase with increasing amount of impurities thus reducing operating margin of pipeline. Initial inlet pressure needs to be increased to reduce the number of pumps and compressors.

3. Constraints are placed on CO_2 pipeline infrastructure by the requirement to minimise cost, maintain reliability, and sustain flexibility of operation with changing composition, upsets, sales and supply. The capture of CO_2 for sequestration could possibly introduce high levels of impurity to optimize between CAPEX and OPEX.

4. Network analysis, transient flow (particularly from variable sources), flow assurance due to the cyclic operation of power plants and risk assessment will also have to be addressed if CCS is going to be implemented.

5. The infrastructure development varies between scenarios. This also highlights the need for developing homogeneity in risk control measures.

2.2 SAFETY CONSIDERATIONS FOR OTHER RELEVANT SUBSTANCES

Key substances which are likely to be used in CCS are:

- **Amines.** As described below the formulation of suitable amines or other solvents is an important aspect of the development of capture technologies. Depending on the solvent chosen, hazardous properties may include flammability and toxicity of the solvent itself and degradation products. In some cases such degradation products may be carcinogenic.

- **Oxygen** is toxic to humans and can greatly enhance the ignition and combustion of any flammable or combustible material.

- **Hydrogen** is a flammable gas with a high propensity to detonation.

3 AVAILABLE TECHNOLOGIES TO SEPARATE CO_2 FROM FLUE GASES

3.1 OVERVIEW: THREE WAYS TO CAPTURE CO_2

There are three possible types of process for the capture of CO_2. These are:

- Post-combustion capture (PCC);
- Pre-combustion capture;
- Oxy-fuel combustion.

Some further information is given below.

3.2 POST-COMBUSTION

Post-combustion capture (PCC) is basically CO_2 capture from plants of conventional pulverised fuel technology by scrubbing of the flue gas for CO_2 removal[1]. This involves the removal of CO_2 from the exhaust gas following normal air combustion. Typical air-fired combustion plants for power generation, produce exhausts with CO_2 concentrations in the 4 – 14 % volume range, with nitrogen being the dominant diluents.

PCC captures CO_2 at atmospheric pressure with low CO_2 partial pressure and thus uses a moderately reactive chemical solvent. Typically amine-based solvents are used in this process, and a large amount of energy is required to regenerate the solvent[1] (about 80 % of total energy of process).

The schematic representation of the PCC process is shown in Figure 1. Some options are given below. Amine-based systems are the technology currently available and have been considered in this study. Some emerging technologies are also discussed.

3.2.1 Amine-based system

Amines react with CO_2 to form water-soluble compounds. Because of this compound formation, amines are able to capture CO_2 from streams with low partial pressures, but capacity is equilibrium-limited. Amines can thus be used for capture from existing pulverised coal power plants, however at a significant cost and efficiency penalty[5].

Amines are NH_3 molecules in which one or more H atom is replaced by –CH group.

COS (Carbonyl sulphide) degrades Methyl Ethyl Amine, MEA as well as Di-Ethyl amine, DEA but Methyl Di-Ethyl Amine, MDEA, is stable to degradation and is less corrosive than the other amines, but it has lower relative CO_2 absorption capacity. MDEA however has high selectivity to H_2S over CO_2 and can be used as the H_2S removal step.

A material safety data sheet for Methyl Ethyl Amine is included in Appendix B.

3.2.2 Emerging technologies

Several emerging technologies are briefly described here but were not considered during the HAZID process.

Carbonate based systems[5]
These are based on the ability of soluble carbonate to react with CO_2 to form a bicarbonate which, when heated, releases CO_2 and reverts to a carbonate. Significantly lower energy is required for regeneration, compared to amines. At the University of Texas, Austin, a K_2CO_2 based system has been developed which uses Piperazine, (PZ) as catalyst. A benefit is that oxygen is less soluble in K2CO3/PZ solvents. This system has adsorption rate 10-30 % faster than a 30 % solution of MEA and has favourable equilibrium characteristics. PZ is more expensive than MEA so economic impact of oxidative degradation is about the same. However, higher loading capacity, structured packing and multi-pressure stripping can give more savings.

Aqueous Ammonia[5]
Ammonia-based wet scrubbing is similar to amine system in operation. Ammonia and its derivatives react with CO_2 via various mechanisms, one of which is reaction of water, CO_2 and Ammonium Carbonate to form Ammonium bi Carbonate. The reaction has significantly lower heat of reaction (energy savings) than amine-based systems, provided the adsorption-desorption cycle is limited to this mechanism. Other advantages are potential of higher CO_2 capacity, lack of degradation during absorption/regeneration, tolerance to oxygen in flue gas, low cost, and potential for regeneration at high pressure. There is also a possibility of reaction with SOx and NOx-components in flue gas to form fertiliser as saleable by-product. There are concerns related to ammonia’s higher volatility, the need to be cool to 15–25 °C to enhance CO_2 absorptivity and minimise ammonia emissions during absorption steps. Also, there are concerns about ammonia losses during regeneration, which occurs at higher temperatures.

Chilled Ammonia Process[5]
This uses the same Ammonium Carbonate (AC)/Ammonium Bi Carbonate (ABC) absorption chemistry as the aqueous system described above, but differs in that a slurry of aqueous AC and ABC and solid ABC is circulated to capture CO_2. The process operates at near freezing temperatures (32–50 °F), and the flue gas is cooled prior to absorption using chilled water and a series of direct contact coolers. Concerns associated with this process include cooling the flue gas and absorber to maintain operating temperatures below 50 °F (required to reduce ammonia slip, achieve high CO_2 capacities, and for AC/ABC cycling), mitigating the ammonia slip during absorption and regeneration, achieving 90 % removal efficiencies in a single stage, and avoiding fouling of heat transfer and other equipment by ABC deposition as a result of absorber operation with a saturated solution.

Membranes[5]
In one concept, flue gas will be passed through a bundle of membrane tubes and amine will flow on the shell-side. CO_2 would pass through and be absorbed in amine while impurities will be blocked. It should also be possible to achieve high loading differential between rich and lean amine. After leaving the bundle, amine would be regenerated and recycled in the normal way. Another concept is use of inorganic membranes.

CO_2 Capture sorbents[5]
These are prepared by treating high surface area substrates with various amine compounds. Immobilisation of amine groups on high surface area material significantly increases the contact area between CO_2 and amine. The Research Triangle Institute is developing another process ideally suited for retrofit application in non-power and power generation sectors.

Metal Organic Frameworks (MOFs) [5]

Through this method high storage capacity may be possible and heat required for recovery of adsorbed CO_2 is low. Over 600 such frameworks have been developed. UOP is leading DOE efforts in this area and has developed a screening modelling tool.

Enzyme Based systems[5]

An enzyme-based system, which achieves CO_2 capture and release by mimicking the mechanism of the mammalian respiratory system, is under development by Carbozyme. The process utilises carbonic anhydrase (CA) enzyme in a hollow fibre contained liquid membrane and has demonstrated the potential for 90 % CO_2 capture in laboratory. The process has shown to have very low heat of absorption that reduces energy penalty typically associated with absorption process. The rate of CO_2 dissolution is limited by the rate of aqueous CO_2 hydration and the CO_2-carrying capacity limited by buffering capacity. Adding CA to the solution speeds up the rate of carbonic acid formation. The ability of CA to make turnover faster (catalyse hydration of 600,000 molecules of CO_2 per molecule of CA per second compared to max rate of 1,400,000). Technical challenges include membrane boundary layer, pore wetting, surface fouling, loss of enzyme activity, long-term operation and scale up.

Ionic liquids[5]

These can dissolve gaseous CO_2 and are stable at temperatures up to several hundred degrees centigrade. Their good temperature stability offers the possibility of recovering CO_2 from flue gas without having to cool it first. Also, since these are physical solvents, little heat is required for regeneration. At the same partial pressures they have shown SO_2 solublity 8-25 times higher than that for CO_2. Hence they can be used for SO_2 step as well. Their high viscosities may be limitation in application. Capacity still needs to be significantly improved, however, to meet cost targets.

3.3 PRE-COMBUSTION CARBON CAPTURE: EXISTING AND EMERGING SEPARATION OPTIONS

This involves Integrated Gasification Combined Cycle (IGCC) with a shift reactor to convert CO to CO_2 followed by CO_2 capture[1]. IGCC produces H_2 and can use a high pressure of 2-8 MPa, enabling the CO_2 to be captured using physical wash processes and then delivered at pressure. The physical solvents exhibit best capacity at low temperatures; the syngas needs to be cooled down before capture which causes a compromise on the efficiency of IGCC[5]. The physical wash processes using Rectisol or Selexol are further discussed below.

The gasification process is an alternative to coal fired combustion. The process produces syngas - a mixture of carbon monoxide and hydrogen. The CO can be further 'shifted' with steam to produce a hydrogen rich stream for subsequent combustion in a gas turbine. In this case the CO_2 is removed before the final combustion process, i.e. from the syngas stream where its composition is around 35 % volume [(2)].

Schematic representation of IGCC without and with pre-combustion capture process is given in Figures 2 and 3.

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Two widely used physical solvents are:

- **Selexol :** The Selexol solvent is a mixture of the dimethyl ethers of polyethylene glycol. It is widely used presently in applications as selective removal of H_2S and COS in IGCC, refineries or fertilizer industry. The product specifications achievable depend on the application and can be anywhere from ppmv up to percent levels of acid gas.

- **Rectisol:** Rectisol is a physical acid gas removal process using an organic solvent (methanol) at sub-zero temperatures. It can purify synthesis gas down to 0.1 vppm total sulphur (including COS) and CO_2 in ppm range. Rectisol wash units are operated worldwide for the purification of hydrogen, ammonia, and methanol syngas, and the production of pure carbon monoxide and oxo-gases.

3.4 OXY-COMBUSTION CARBON CAPTURE

This is combustion in oxygen rather than air. Oxygen is diluted with recycled flue gases to reduce combustion temperature and is also needed to carry the combustion energy through the convective heat transfer equipment employed in current first generation technology[1].

Since nitrogen is the main diluent in the products of air combustion, using pure oxygen readily allows the generation of a high purity CO_2 exhaust stream, removing the need for any subsequent separation stage[2]. Consequently, the oxy-fuel process does not require CO_2 capture prior to compression. The idea behind recycling flue gas prior to combustion in a boiler is to maintain combustion conditions similar to an air-fired configuration. This is necessary, as currently available material of construction cannot withstand high temperatures resulting from coal combustion in pure oxygen.

A schematic representation of the oxy-combustion process with and without the capture process is given in Figure 4.

4 HAZARD IDENTIFICATION

4.1 MEETING 1: ESTABLISHING BASELINE OF NON-CCS FACILITIES AND ACTIVITIES AND IDENTIFYING CCS ADDITIONS/CHANGES

The first meeting looked at features of existing power plants and the new activities, substances or equipment that will be needed as a result of introducing carbon capture options were discussed. Table 1 below lists these additional changes at a high level. The detailed information/discussions captured were used to inform the team members taking part in HAZID brainstorm Meeting 2 and are presented in the section below.

It should be noted that Table 1 might not be an exhaustive list. Lack of information in the column for a particular capture option does not necessarily mean that the least changes will be needed if that particular option is selected. Caution and professional experience should be exercised as this could be due to knowledge gaps or experience gap of participants in this particular area. Also, changes listed for one option can be applicable to another as well, so it is a good idea that boxes should be read in conjunction. An earlier study by HSL for HSE on the incident history of CO_2, attached in Appendix A was also used as informative background for the first meeting.

4.1.1 Flowsheets

It is important that HAZID be based on as reasonably detailed schematics of the processes as are available. It proved difficult to obtain schematics with much detail or process conditions and the following flowsheets resulted from information brought to the meetings by the various contributors. There is a need to document basic flow schemes and layouts in more detail for effective hazard identification to take place. Despite considerable work done to source information, this sort of information was not readily available.

The final versions of the flowsheets are presented below (Figures 1 to 6).

Figure 1 shows carbon capture by flue gas scrubbing (post-combustion capture). The section in black is the existing power plant and the one is red is the additional module needed for the capture of carbon dioxide.

Figures 2 and 3 show pre-combustion capture by means of IGCC with and without carbon capture, respectively. They were provided by Andy Brown of Progressive Energy. In Figure 2, for an existing IGCC facility without a CO_2 capture option, the modules shown in red are those which will be removed if the IGCC facility has to implement a CO_2 capture option. In Figure 3 the modules shown in red are those which will be new to an existing IGCC, as a result of implementing carbon capture.

Figure 4 is the schematic representation of the oxy-combustion processes with units different from an existing power plant highlighted in red.

Figure 5 is the schematic representation of the pipeline transport of dense phase CO_2 obtained from various capture modes.

Figure 6 is the schematic representation of injection of captured $CO_{2.}$

In this meeting, some initiating events were also identified and were used to inform brainstorming in Meeting 2.

Table 1 New substances, equipment and activities as a result of introducing carbon capture to existing facilities

Post-combustion capture	IGCC/ Pre-combustion Capture	Oxy-combustion Capture
SUBSTANCES Fuels Sox, NOx, Mercury ROx – particulates. Intermediate salts Amine (purge) Discrete sorbant – ammonia Promoters Corrosion inhibitors Range of amines Sulphuric acid CO_2 phases Free water Ey glycol Emulsives Hydrate CO_2 Impurities Hydrogen Oxygen Nitrogen Bacteria from O2 Carbonyls	**SUBSTANCES** If air-fired then too much nitrogen, if Oxy-fired then huge oxygen requirements Physical solvents, e.g Selexol, Rectisol Ethylene glycol (e.g. selexol) – 550ppm/v water – some unshifted CO, >95% CO2, ppm H2, N2/argon/H2 > 4%) H2S Hydrogen Saturated syngas for shift CO_2 drying CO_2 phases Free water Ethylene glycol Emulsive Hydrate formation	**SUBSTANCES** Large inventories of Oxygen SOx NOx So_x oxidation catalysed to sulphur trioxide Mercury, not all contained in solid phase as ash Condensed steam Recycled flue gas Inhibitors. CO_2 drying CO_2 phases Free water Ethylene glycol Emulsion breakers Hydrate formation
EQUIPMENT High pressure-dense phase CO_2pipelines Booster stations Additional compressors Isolation valves Metering Amine absorption and separation columns	**EQUIPMENT** High pressure-dense phase CO_2pipelines Booster stations Additional compressors Isolation valves Metering Huge air separation units (ASUs)	**EQUIPMENT** High pressure-dense phase CO_2pipelines Booster stations Additional compressors Isolation valves Metering ASUs; may be cryogenic Oxygen quantities would be limited by column diameter
ACTIVITIES Amine absorption and separation Disposal issues of the ash; ash becomes hazardous waste CO_2 compression- may be multistage	**ACTIVITIES** CO_2compression Acid gas removal Shift conversion	**ACTIVITIES** CO_2 purification/ compression

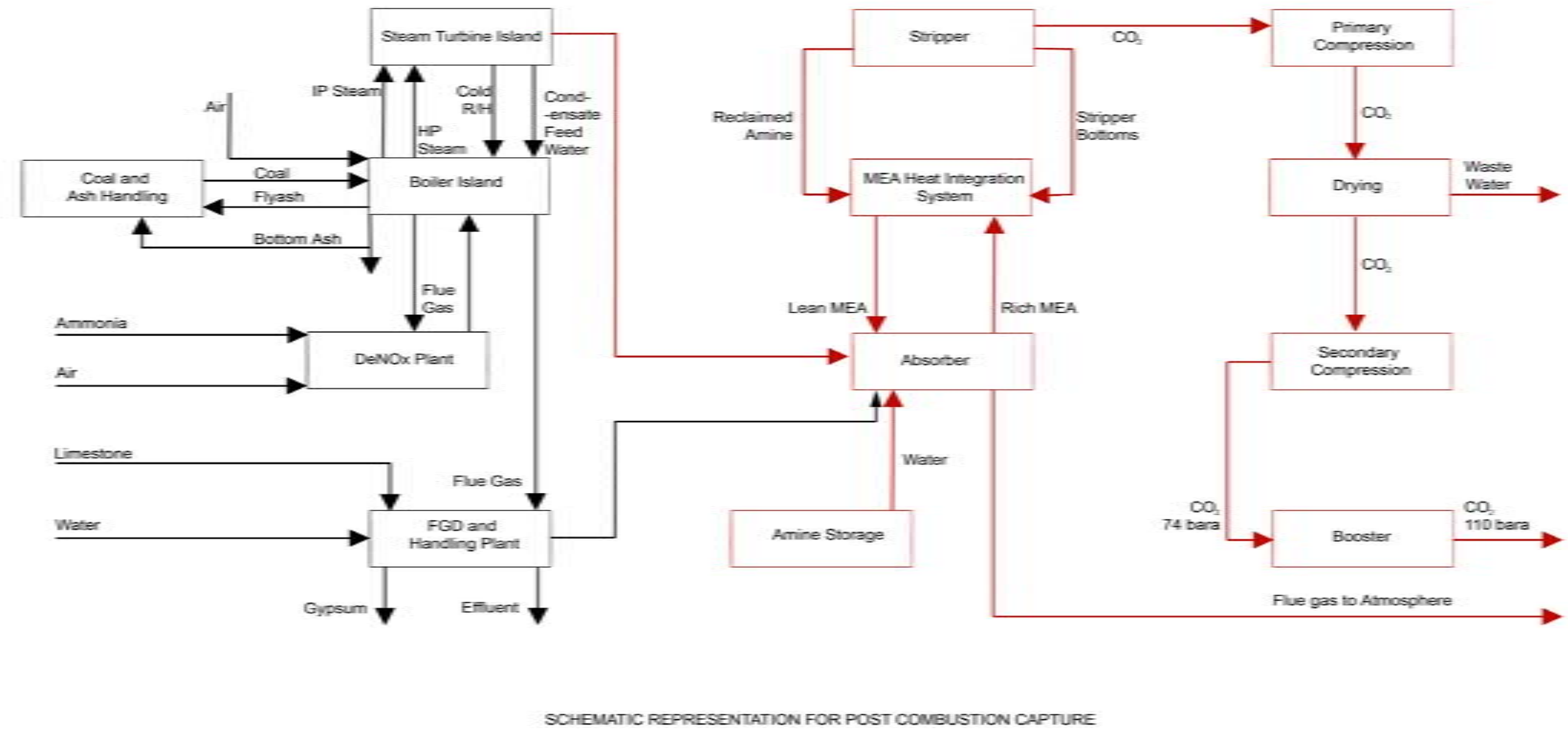

Figure 1 Schematic representation of post-combustion capture

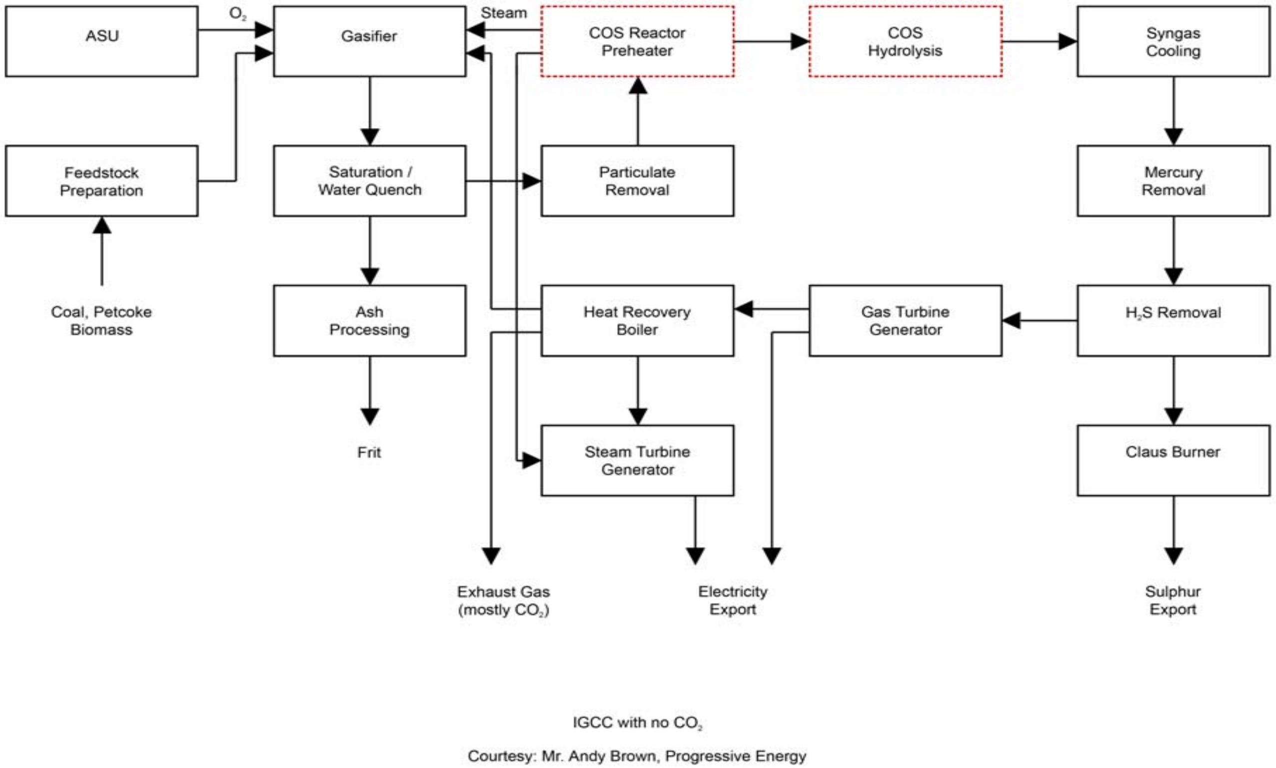

Figure 2 Schematic representation of IGCC without (pre-combustion) capture

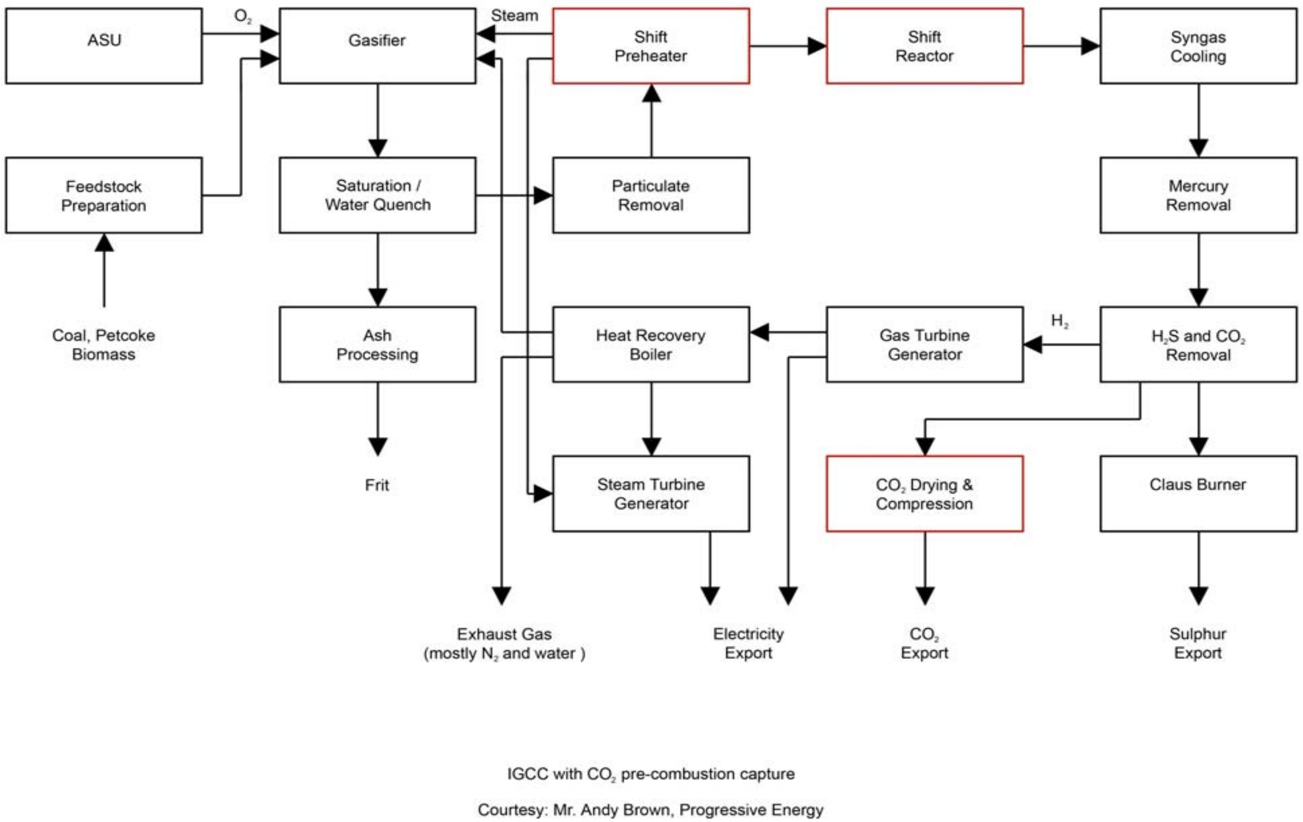

Figure 3 Schematic representation of IGCC with (pre-combustion) capture

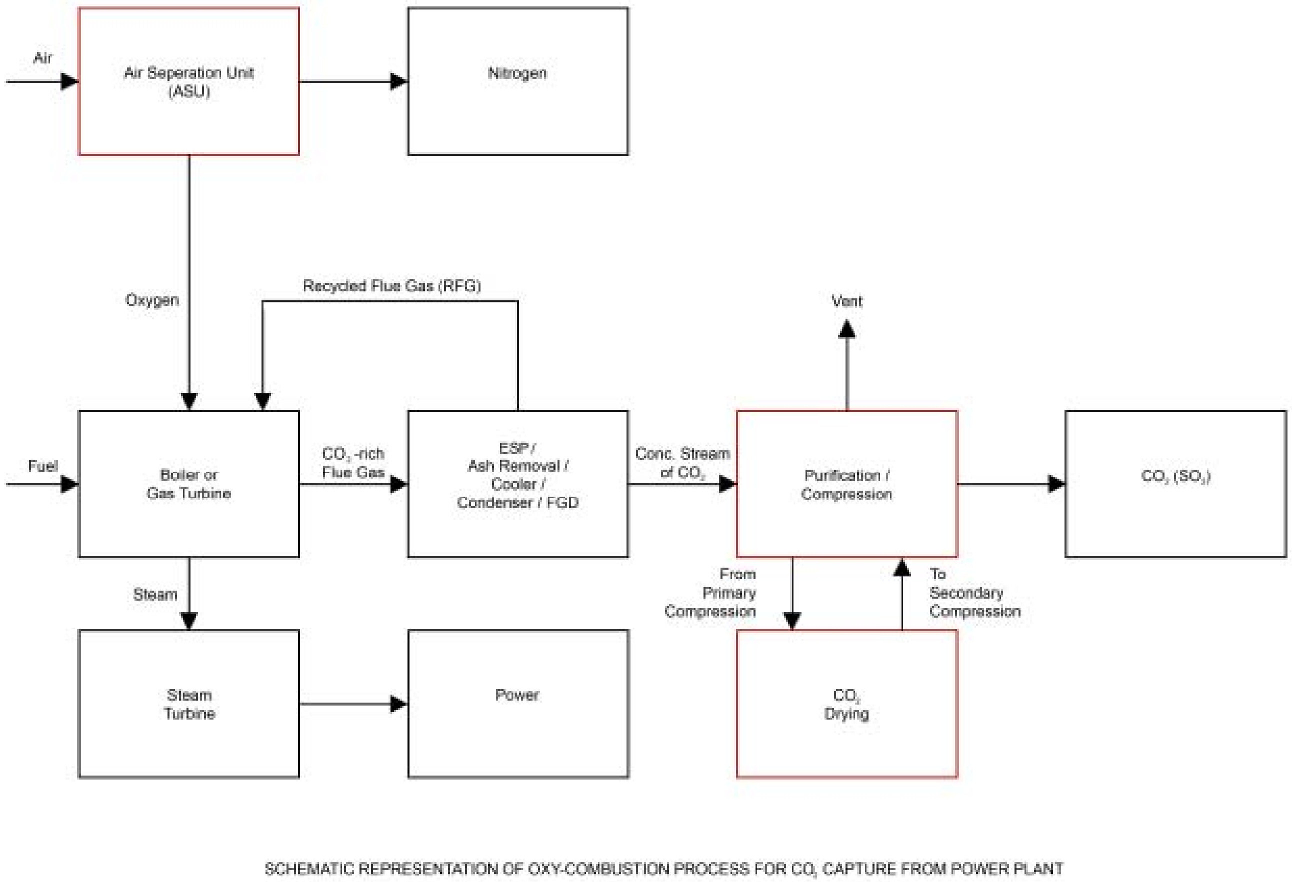

Figure 4 Schematic representation of oxy-combustion capture

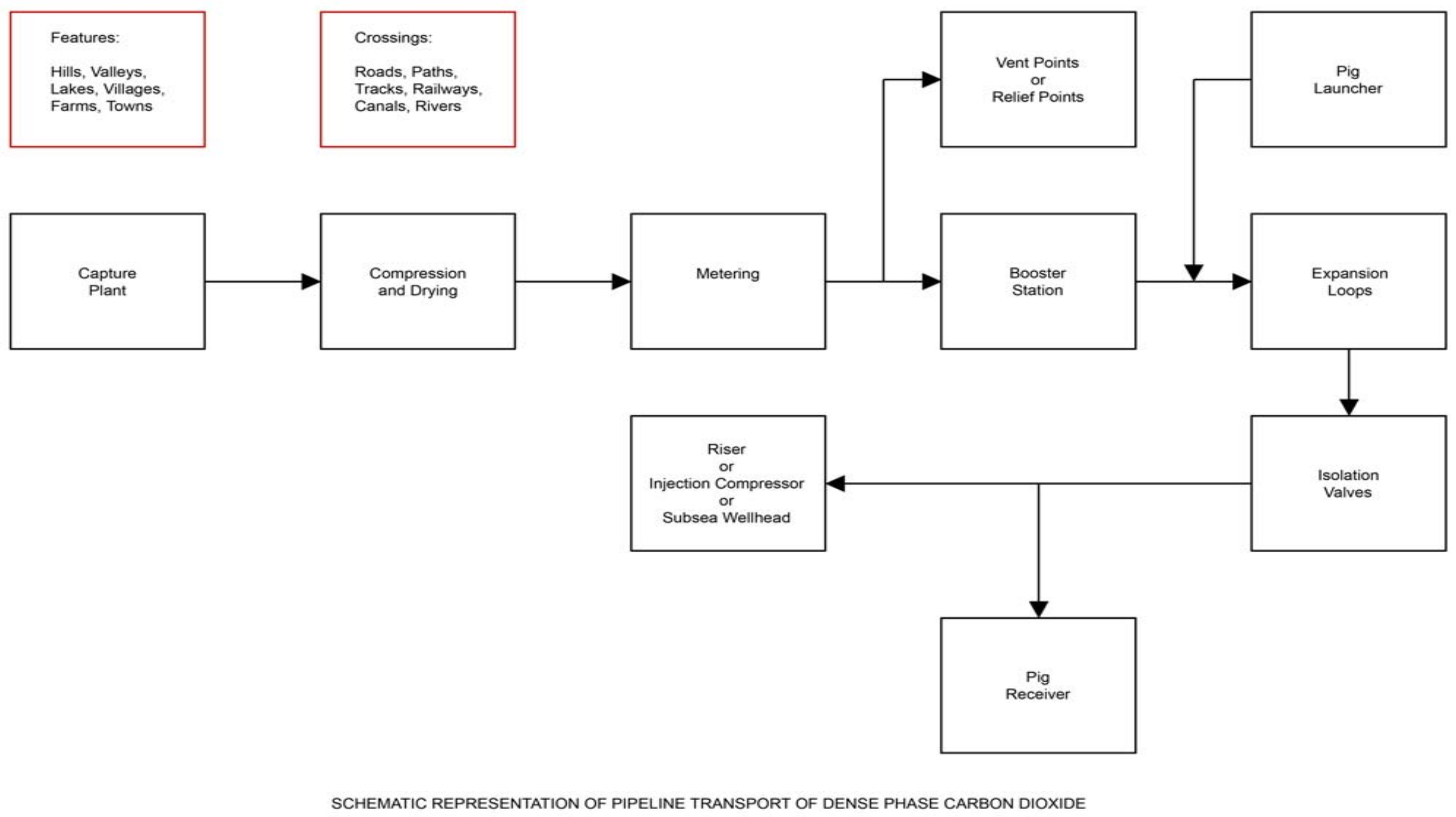

Figure 5 Schematic representation of pipeline transport

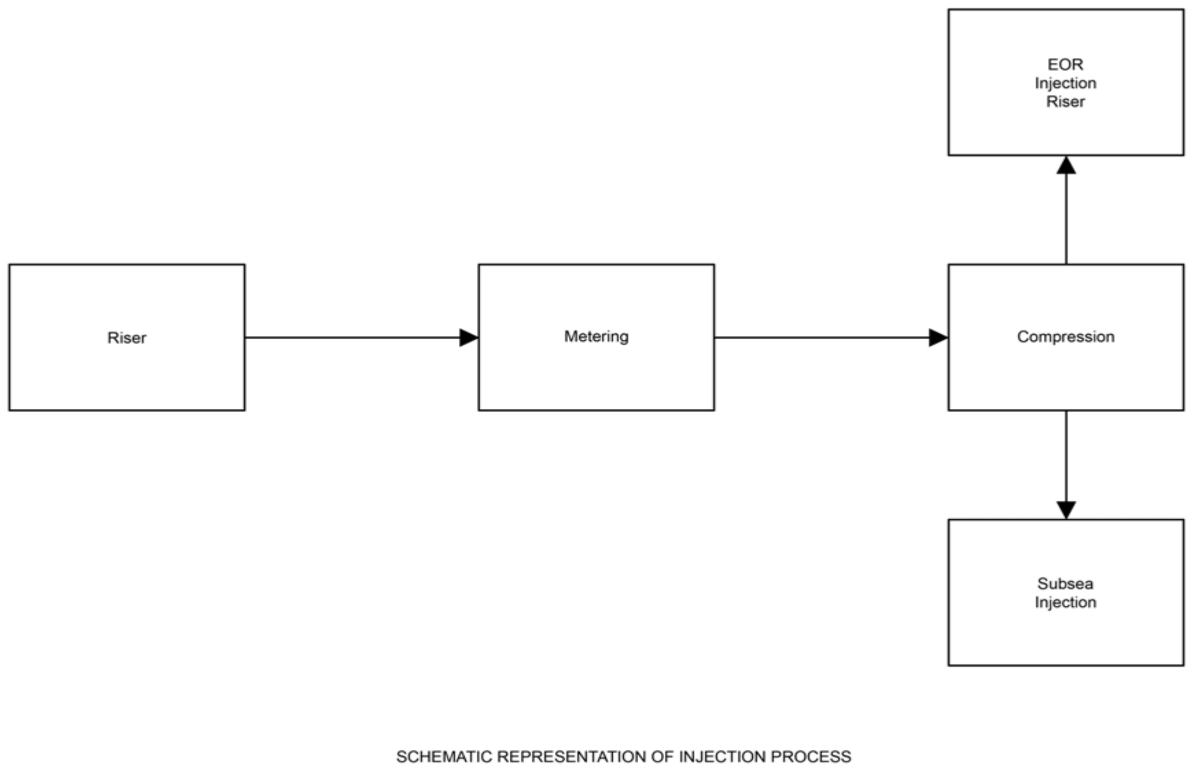

Figure 6 Schematic representation of CO_2 injection

4.2 MEETING 2: IDENTIFYING NEW HAZARDS WHICH CCS INTRODUCES AND POTENTIAL MAJOR INCIDENTS

The additional potential hazards, identified in the first meeting, were further discussed in the second meeting. The second meeting carried these further for a detailed brainstorm using keywords.

The following keywords chosen for brainstorming:

- Fire;
- Explosion;
- Toxicity;
- Electrical;
- Mechanical.

The study was then broken down into following segments for applying the keywords:

- Post-combustion capture;
- Pre-combustion capture;
- Oxy-combustion capture;
- Transport;
- Injection.

A structured hazard identification (HAZID) study was used to brainstorm top events relevant to CCS and to populate the bow-tie accident model for each top event. A bottom-up HAZID approach (such as HAZOP or FMEA) in which deviations from normal operation or failures are used to brainstorm possible incidents was not used. Bottom-up HAZID is relatively time-consuming and requires a greater level of detail of information about the process than was available.

Events identified were recorded including the relevant segment(s) of the CCS chain and whether the event should be considered a top-event comprising the knot of a bowtie, or a consequence in one or more bowties. Any initiators, which came up in the discussion, were also recorded to be systematically analysed later.

These results were then used to identify the different bow-ties requiring further analysis. At a later stage, the results from the brainstorming sessions in Meeting 3, which focused on changes introduced by CCS, were also used in this process. As was expected, loss of containment of CO_2 in each segment of the CCS chain comprised a good number of the top events requiring consideration. Other top events identified were the loss of containment of oxygen, loss of containment of toxics, and fire and explosion. Several consequences of the top-events or potential accidents were also identified. The information from the first meeting about some initiating events was used to inform the team members taking part in this stage of the brainstorming session.

The output from this meeting were tables with key top safety events, and a high level analysis of the main causes (initiating events), consequences and mitigation/control barriers. The output top-down HAZID tables are presented in Appendix C. Emergency response has been discussed further in Section 6 below.

4.3 MEETING 3: IDENTIFYING CHANGE AS A CAUSE OF INCIDENTS AND MANAGEMENT/CONTROL OF HAZARDS

A similar HAZID session was carried out for identifying ‘changes to existing ways of hazard management and control’ as initiators of incidents. The keywords used for this HAZID brainstorming were:

- Layout;
- Interfaces;
- Organisational factors.

As well as the schematic diagrams in Figures 1-6, some layout drawings of power stations and CCS projects were also available to the team. The segments of the CCS chain were considered systematically and the changes introduced by CCS were brainstormed. For each change, possible hazards/safety implications were further brainstormed and documented.

Consideration was given to whether the additional hazards identified should be considered as new top events or whether they can be included in the existing top events/bow-ties identified in Meting 2.

The barriers for various issues identified here were also discussed. The output tables are presented in Appendix D. This meeting contributed extensively to emergency response and strategy for CCS scenarios, discussed further in Section 6 below.

4.4 MEETING 4: IDENTIFYING POTENTIAL MAJOR INCIDENTS (TOP EVENTS) AND DRAFTING THE BOW-TIE DIAGRAMS

The initiating events, consequences and mitigation barriers for the identified top-events were presented in the form of bow-tie diagrams. Appendix E provides a short introduction to bow-tie diagrams. These bow-tie diagrams are discussed below. The top-events identified for developing bow-tie diagrams were:

- loss of containment of $CO_{2;}$
- loss of containment of oxygen;
- loss of containment of toxics;
- explosion; and
- fire.

Tables were compiled from the results of the previous HAZID meetings to be used as a precursor to the development of the bow-tie diagrams. These tables are provided in Appendix F.

Each initiator or consequence which came up during the brainstorming was considered in turn for possible mitigation barriers using the following hierarchy:

- Elimination;
- Protection;
- Reduction;
- Separation;
- Emergency response.

The output from this brainstorming study was reviewed by HSL staff using an existing database of possible risk reduction measures, which was developed to aid assessors of COMAH safety reports and, if applicable, additions were made.

Bow-tie diagrams are provided below along with Tables giving brief descriptions of the barriers. The bow-tie diagrams are also available separately and electronically in Excel format. The Excel versions give barrier descriptions as comments. These bow-tie diagrams could be used as a starting point for the development of diagrams for developing CCS projects.

4.4.1 Bow-tie diagram for loss of containment of carbon dioxide

The bow-tie diagram is shown as Figure 7. The descriptions for the barrier codes shown on the bow-tie diagram are given in Table 2.

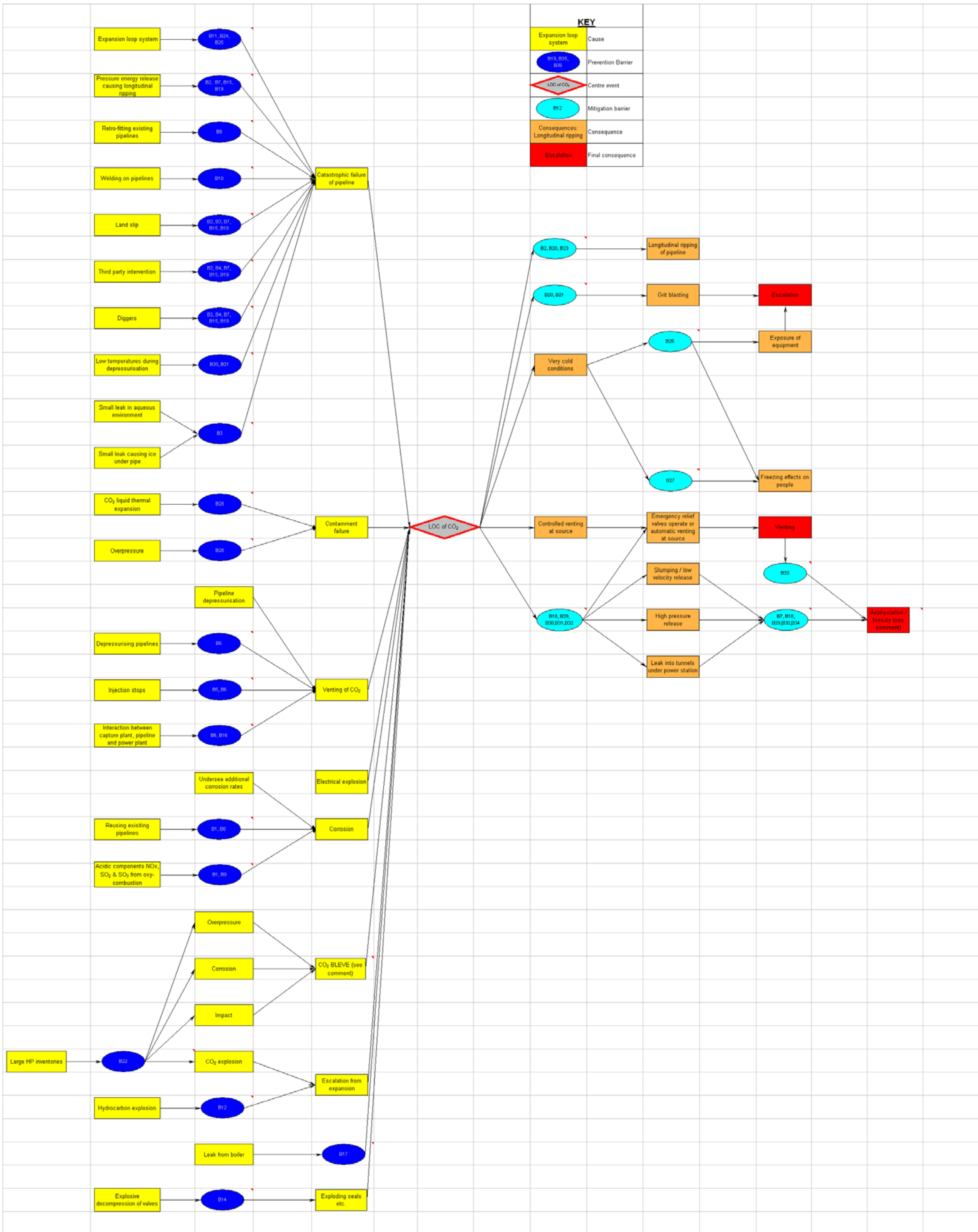

Figure 7 Bow-tie diagram for loss of containment of carbon dioxide

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Table 2 Description of barrier codes for bow-tie diagrams for loss of containment of carbon dioxide

Barrier code	Description
B1	Prevent free water and hydrates
B2	Metallurgy solutions, extra wall thickness above 19 mm, concrete slab coverage
B3	Design, identify and monitor vulnerable locations
B4	Control systems to shut pipeline off
B5	Line pack and/or cut back production
B6	Dilutes vent stream by up to 20 times at source
B7	CO_2might go straight up in air. Also, this will be mitigated by the pipe being buried. Even if the cover material at the surface is ejected, the jet will still be diffused to some extent by the surrounding ground
B8	All equipments and ancillary parts suitable for the service range
B9	CO_2, needs to be super-dry and very pure to prevent free water or hydrate formation
B10	Procedures and standards for hot tap and similar operations
B11	Design
B12	Existing hydrocarbon explosion reduced by CO_2
B13	Choice of operating conditions
B14	Improvement in technology
B15	Decompression procedures at pig receiver
B16	Flexibility in CO_2transmission grid system to absorb temporary production/injection imbalances
B17	Boiler designed to operate at slight negative pressure (this applies specifically to oxy-combustion, all other PF boilers operate under negative pressure anyway)
B18	Leave H_2S in CO_2as stenching agent
B19	Route and crossing point selection and additional washout protection
B20	Select steel with right low temperature impact properties
B21	Avoid low temperatures by correct depressurisation procedure
B22	Select conditions and inventories which preclude CO_2BLEVE
B23	Crack arrestor
B24	Eliminate from design
B25	Choose non-vulnerable locations
B26	Procedures to avoid cold exposure
B27	Effective early treatment for cold injuries
B28	Pressure relief
B29	Monitoring of CO_2 Levels
B30	Emergency response/evacuation/public awareness/visual or audible warnings
B31	Isolation
B32	Blowdown
B33	Design of vent stack
B34	Understanding and being able to predict the visible cloud (important for emergency response)

4.5 BOW-TIE DIAGRAM FOR LOSS OF CONTAINMENT OF OXYGEN

The bow-tie diagram is given as Figure 8. A key to the barriers is given in Table 3.

Table 3 Description of barrier codes for bow-tie diagram for loss of containment of oxygen

Barrier code	Description
B1	Layout: Separate fuel, e.g. coal pile, from ASU
B2	Emergency shutdown of ASU
B3	Competence
B4	Training
B5	Design standards
B6	Human factors study of interface issues
B7	Remotely Operated Shut-Off Valves (ROSOVs)
B8	Safety culture
B9	Control of ignition sources
B10	Separation of flammable inventories
B11	Shutdown of power/capture plants
B12	Layout: separate vulnerable equipment
B13	Layout. Separate people from locations in which oxygen release is possible

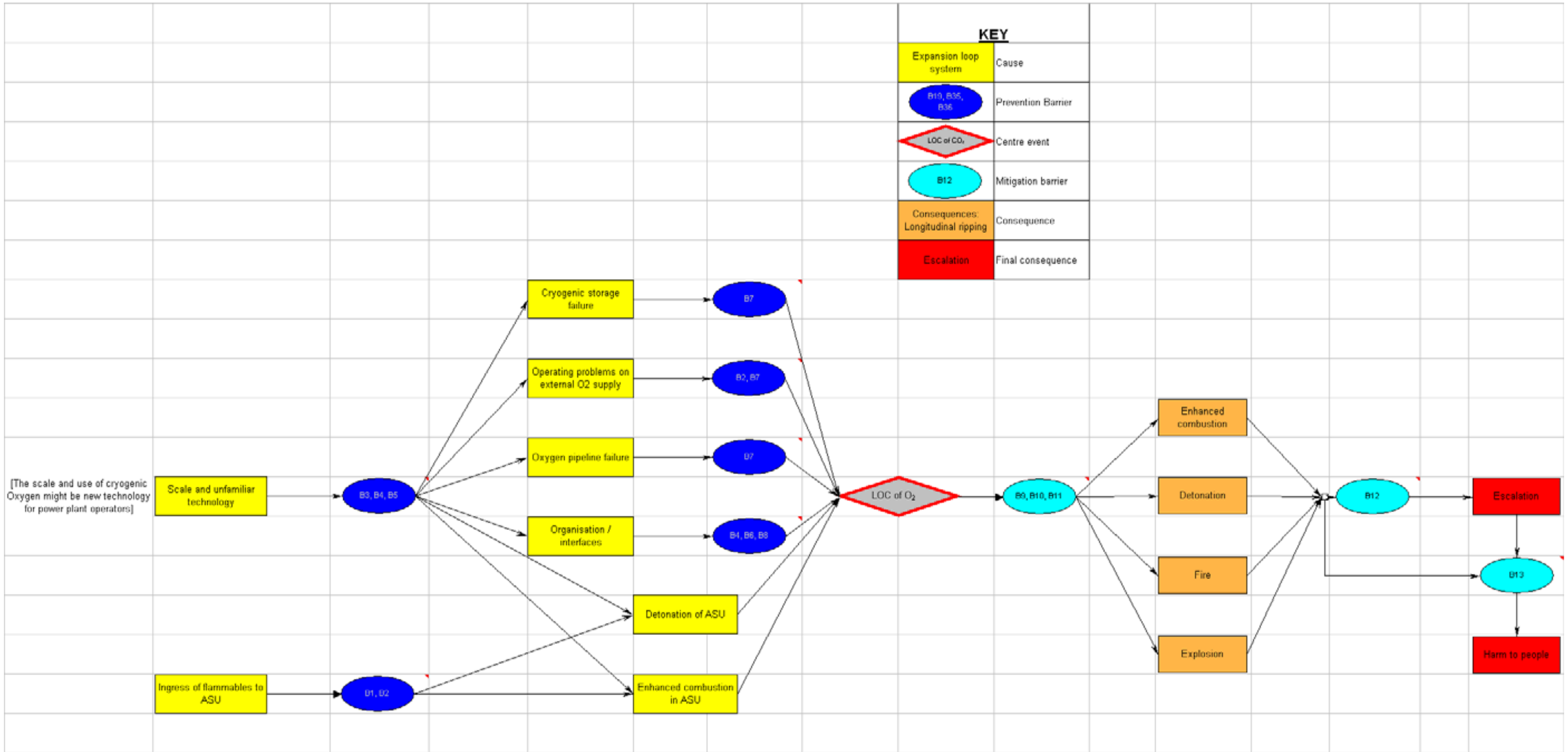

Figure 8 Bow-Tie diagram for loss of containment (LOC) of oxygen

4.5.1 Bow-tie diagram for fire scenarios

The bow-tie diagram is given as Figure 9. A key to the barriers is given in Table 4.

Table 4 Description agree of barrier codes for bow-tie diagrams for fire

Barrier code	Description
B1	Hot tapping procedures
B2	Flame detection device
B3	Alternative methods of fire detection
B4	Layout: separate ASU from HC
B5	Design for containment, bunding
B6	ROSOVs
B7	Ignition control
B8	Inerting systems
B9	Operative with excess O_2
B10	Gas detection and ventilation (note detector and air intake locations different for H2 than most flammable gases)
B11	Selection of solvent composition that has low or preferably no flammability
B12	Fire suppression
B13	Active fire protection: sprinklers/deluge system
B14	Emergency response procedures
B15	Emergency services
B16	Evacuation of personnel
B17	Separation of equipment
B18	Segregation of fire zones with fire walls

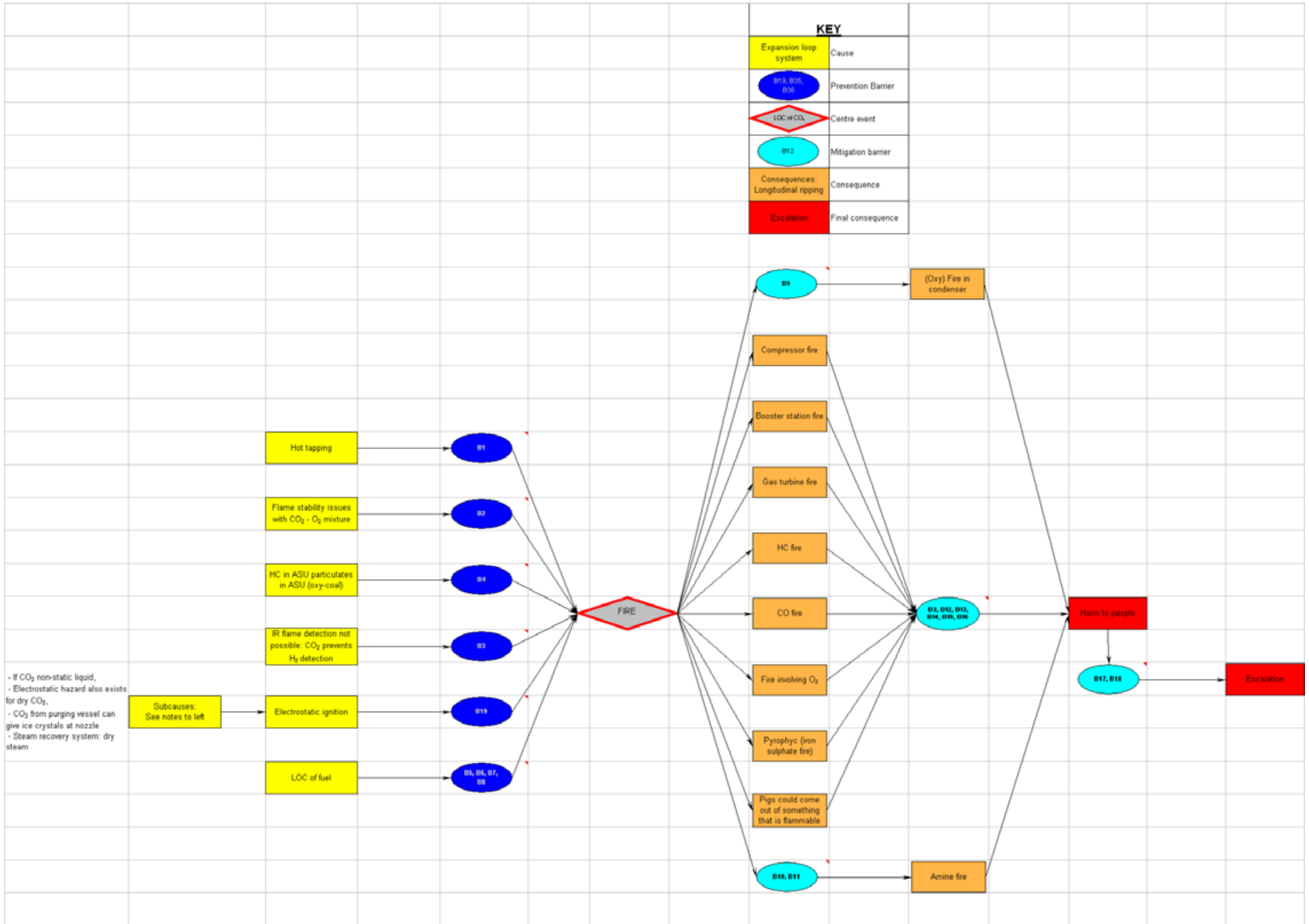

Figure 9 Bow-tie diagram for fire scenarios

4.5.2 Bow tie diagram for explosion scenarios

The bow-tie diagram is given in Figure 10. A key to the barrier codes is given in Table 5.

Table 5 Description of barrier codes for bow-tie diagrams for explosion

Barrier code	Description
B1	Layout/separation
B2	Design inspection
B3	Layout to prevent containment/congestion
B4	Pulverise coal at inlet to burner to minimise coal dust
B5	Burner control system
B6	Keep operating conditions outside envelope where CO_2 BLEVE is possible
B7	Explosion suppression
B8	Explosion venting
B9	Separation of equipment
B10	Make use of the natural dispersion tendency of hydrogen in design
B11	Choose non-flammable refrigerant e.g. CO_2, not propane or ammonia
B12	Keep boiler away from open flames
B13	Keep ASU and O_2 apart
B14	Design and control
B15	ASU Emergency Shut-Down System (ESDS)
B16	Prevention of depressurisation

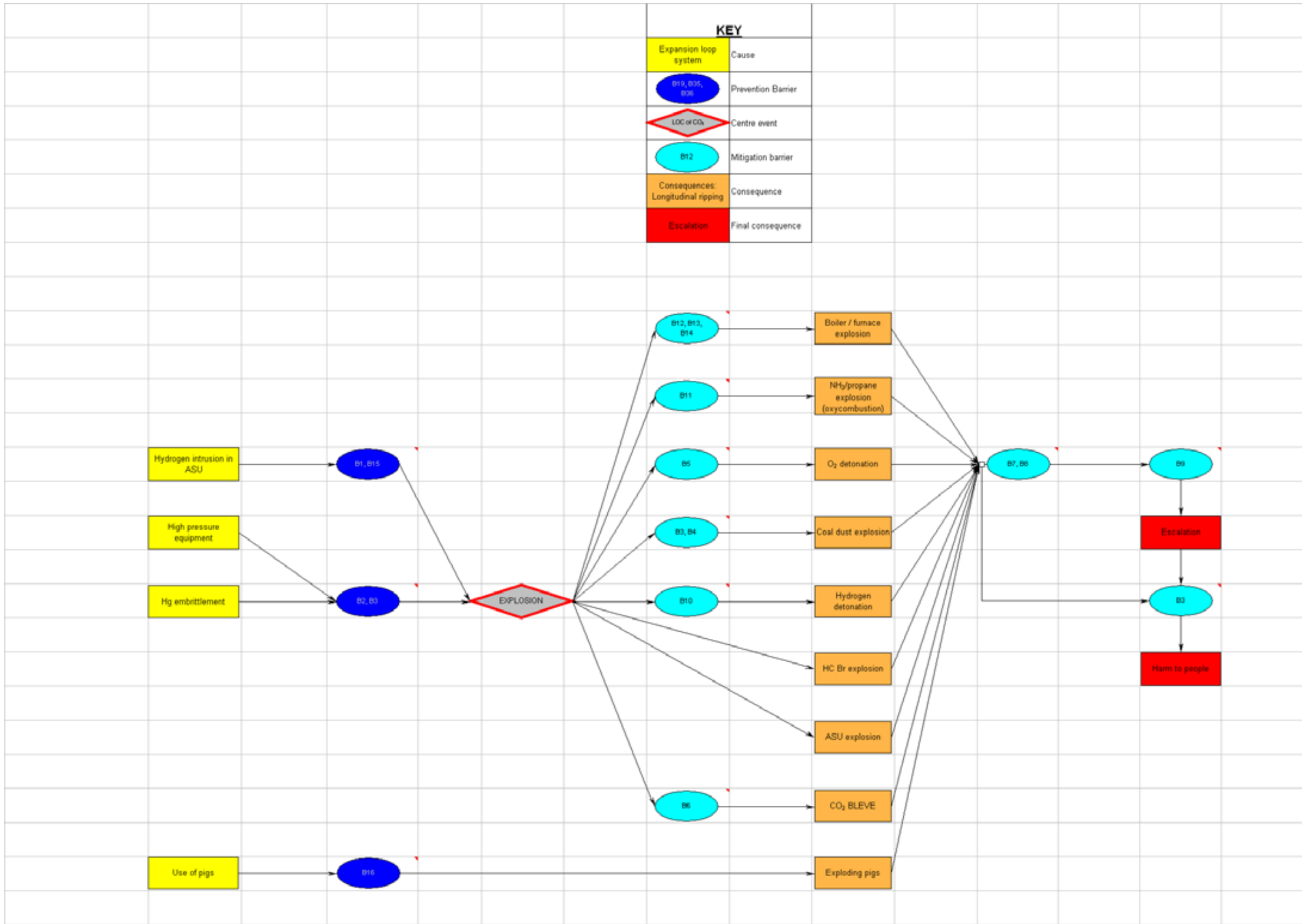

Figure 10 Bow-tie diagram for explosion scenarios

4.5.3 Bow-tie diagram for release of toxics scenarios

No bow-tie diagram has been constructed for toxics scenarios as the consideration possible in Meeting 4 was too high level. Table 6 presents a summary of the toxics scenarios which were identified, including the part of the CCS chain which they relate to, the hazard and possible barriers.

Table 6: Summary of identified toxics scenarios

Toxic Material	**Source of Toxic**	**Hazard**	**Barriers?**
H_2S	Concentrated H_2S at inlet to Claus?	Release	Pigging? Same issues as usual FGD
SO_2	Produced during combustion. Levels higher due to concentration of SO_2 caused by the flue gas recycle	Release Corrosion	
SO_3	Reaction of NO and SO_2 in purification system to give SO_3	SO_3 mist in compressor will be fatal to compressor	
Sulphur	Lime slurry, wet Line FGD?		
CO	In pre-combustion capture process e.g. pipe fracture between quench of gasifier and shift would emit large amounts of CO	Release	Venting/flare stack design. Designing for low ground level. Monitoring and detection
COS/carbonyls		Toxic particulates	Well understood from oil refineries, ammonia plants
Hg	Fuel	Aluminium components downstream- packing in absorber beds; may get disintegrated	In normal coal fired plants about 85-90% captured
Amines		Release	Steel spade damper
NO_x			Low concentration as lowered by recycle

5 CONSEQUENCE ASSESSMENT CAPABILITY

5.1 INTRODUCTION

The modelling of the consequences of release of CO_2 requires the following stages:

(a) Identification of the release scenario, e.g. release from a pipeline failure; release during injection into geological storage. This scenario implies the pressure/temperature/phase conditions from which the release occurs.

(b) Determine a hole size through which the release occurs. Alternatively a range of hole sizes up to catastrophic failure may be modelled. For pipelines, an important aspect will be whether a propagating failure/running crack could develop (see 5.3 below).

(c) Calculate the release rate through the hole or crack. This will reduce over time and it will need to be determined whether the time dependence is significant and needs to be modelled. The time dependence will be most significant for large/catastrophic releases.

(d) Take account of phase changes as the pressure falls from that at the release point to atmospheric pressure. This may result in the formation of solid CO_2 and may cause some flashing/sublimation to CO_2 vapour. Assumptions may need to be made about the thermodynamic path to determine the final temperature and phase.

(e) It may be necessary to model the initial dispersion in terms of jet entrainment of air due to the momentum of the release (depending on whether this is included in the chosen dispersion model). This will include making assumptions (or considering different cases) about whether the jet impinges and loses some or all of its momentum.

(f) Estimate how much liquid or solid drops out of the cloud. This will depend on the droplet/particle size. Estimate the rate of sublimation of particles which have dropped out of the cloud. Alternatively, it may be possible to make conservative assumptions such as that all the CO_2 solid remains with the cloud (but this may not always be conservative, e.g for emergency planning close to the release point where solid CO_2 may be deposited.

(g) It may be necessary to model the initial mixing with sufficient air to sublime CO_2 solid which remains in the cloud (depending on whether the dispersion model can handle a two-phase solid/vapour mixture).

Aspects of the source term formulation which give rise to the key uncertainties for CO_2 are discussed below.

5.2 SOURCE TERMS

5.2.1 CO_2 Thermodynamics

The phase diagram for carbon dioxide is shown schematically in Figure 12. The thermodynamic critical point of CO_2 is at 31 ^oC and 72 bar; the triple point is at –56 ^oC and 5.1 bar.

Many pipelines are likely to operate in the ‘dense phase’ region which comprises the liquid region and the part of the supercritical region which is roughly above the liquid region. Loss of containment from these dense phase conditions will result in the thermodynamic state entering the two-phase vapour/liquid region as the pressure falls. When the pressure reaches approximately 5 bar, this will become vapour/solid. It is therefore important that source term models for consequence assessment are capable of handling the transition to solid CO_2 (also known as dry ice).

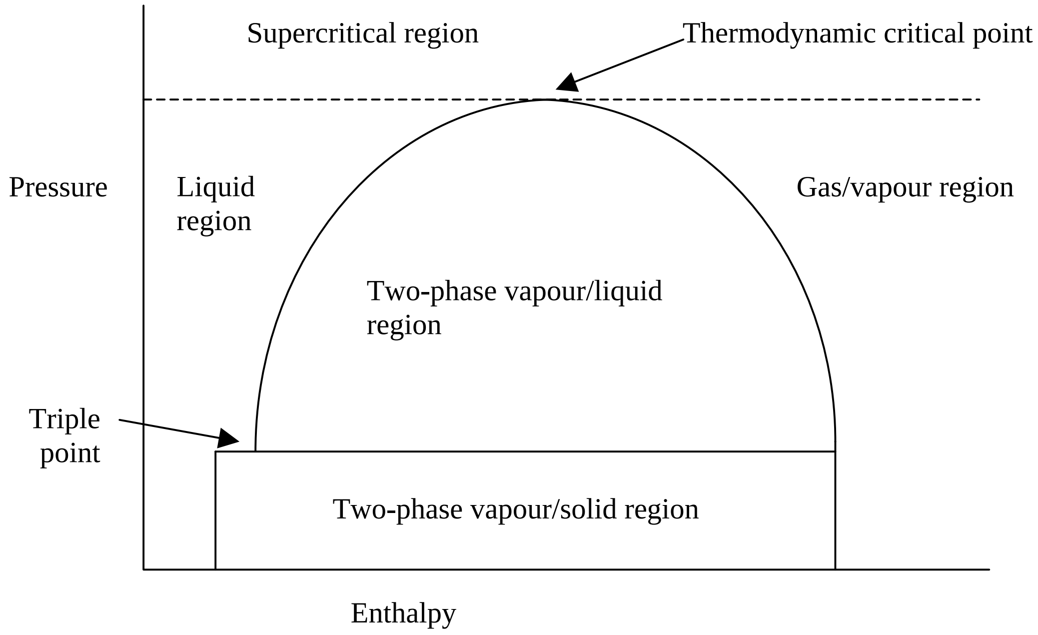

Figure 11 Schematic representation of thermodynamic chart for CO_2

5.2.2 Source term modelling

The gap in consequence modeling for CO_2 applications relates primarily to the ability of models to handle source terms for dense phase CO_2 releases which would give rise to CO_2 solid formation. Current models do not include the formation of solid and therefore the energy balance is not correct. Also the fate of the solid CO_2, including the timescale for its subsequent sublimation and the effect on the temperature of the cloud, needs to be modelled. There is also the issue that particularly around or above the thermodynamic critical point, physical properties will be non-ideal.

It is likely that many of these issues can be resolved by incorporating a suitable equation of state (EoS) into the calculation procedures. The Span and Wagner EoS for CO_2 is a better alternative for CO_2 to more usual EoSs such as Peng Robinson or Redlich Kwong Soave. Span and Wagner is the most comprehensive equation of state available for CO_2. In the region up to 200 bara and 32^o Centigrade, encompassing the supercritical region, the equation produces remarkable accuracies (plus/minus 0.03 % to plus/minus 1 %) in density, speed of sound and specific heat predictions. This EoS should get the energy balance correct when solid rather than liquid is produced.

It is understood that a version of the DNV PHAST consequence modelling software is to be released which incorporates the Span and Wagner EoS. For pipeline releases, the PIPETECH model[21] is to be modified to incorporate this EoS with funding from HSE.

DNV PHAST can be used for subsequent dispersion/consequence modelling using the unified dispersion model (UDM), which is a well-respected integral model. Alternatively PHAST or PIPETECH could be used to obtain release rate information. This is likely to require further analysis to obtain a suitable source term for CFD dispersion modelling. The output from both models, describing the discharge rate, will give information at the exit of the pipeline or hole and this will be at a pressure above atmospheric, due to choking. Further solving of momentum and energy balance equations is required to give a source term at atmospheric pressure for CFD (or other integral dispersion models which cannot handle the non-ideal physical properties to self-calculate discharge conditions).

There are remaining uncertainties in terms of how to model solid particle size and hence whether or not the solid will remain with the cloud or drop out. The particle size will also affect the rate of sublimation if the solid particles remain with the cloud. This will have a large effect on the cloud temperature.

Any solid which drops from the cloud will subsequently sublimate; there are no available models for this process. Again this can give rise to a very cold dense cloud. Anecdotal reports suggest that this sublimation process may be very slow. Also that it is associated with fairly low pressure releases and impingement. The BP experiments at Spadeadam (high pressure) showed rapid sublimation/dispersion and no significant drop out of CO2 even for impinging releases. However the experiments were short duration and may not have cooled the impingement plate/ground sufficiently. It also may be possible that hydrate could be formed at the very cold conditions following a release.

Available pipeline models treat the discharge modelling using the homogeneous equilibrium model (HEM). If solid is present then this model may be inadequate as significant slip may occur between the phases.

5.2.3 Data for validation

Given the issues raised above, validation of source term models for CO_2releases is important. However, data for such validation is sparse.

BP and Scottish and Southern Energy had experiments conducted by Advantica at Spadeadam during the DF1 project. The results are confidential but BP presented the result that models gave good agreement. However the modelling assumptions required to obtain good agreement were not provided. The results of these experiments are now the property of Hydrogen Energy who have expressed interest in forming a JIP to share costs and disseminate the results more widely. The version of the DNV PHAST code incorporating a revised equation of state (see above) was validated against these experiments, as were some CFD models, e.g. reference 22.

In the UK, an Energy Institute JIP is planning release experiments from refrigerated CO_2 storage. This will be at lower pressure than a pipeline but should provide relevant data for validation of modelling assumptions.

5.2.4 Other factors

The high propensity of supercritical CO_2 to be a solvent, particularly if CO_2 is used for EOR, could lead to the solution of heavy metals etc from the rock formation. Loss of containment would then tend to deposit the heavy metals (or other toxic or radioactive contaminants) in relatively large quantities. Deposition in CO2 recycling facilities could then cause a hazard during maintenance or disposal of equipment. Exposure could cause acute toxicity or longer term health effects. There is little current understanding of this issue. The development of this hazard is likely to be highly dependant on the reservoir formation. Experience of EoR is limited to a relatively small number of rock types.

5.3 PIPELINE FAILURE CRITERIA

A study using the PIPETECH model[23] developed possible criteria for running failures of CO_2 pipelines. This paper raises interesting issues for emergency response as isolation of a pipeline can contribute to the onset of running failures. There is a need to understand the factors that could cause running failures and thereby develop strategies for prevention or mitigation. For consequence modelling, this is important in terms of whether releases from a running failure need to be modelled. Understanding where the release could occur will also be important for the development of emergency response procedures. Reference 23 suggests that closing of emergency shut down valves could increase the risk of a running failure occurring and this also needs to be taken into account in developing emergency response plans, e.g. evacuation might need to occur before pipeline isolation.

5.4 CO_2/ HYDROCARBON FLAMMABILITY

CO_2 may be present with hydrogen in some capture technologies, and may also be present in hydrocarbons if CO_2 is used for enhanced oil recovery (EOR) as part of the storage strategy. Work by HSL[24] suggests that the concentrations of flammable gas and CO_2 that will not support combustion can be estimated by calculation. It further showed that very high CO_2concentrations are required to fully prevent combustion, e.g. 88 % CO_2, 12 % propane. However, scale effects were identified and further investigation at larger scale would be required unless conservative assumptions are made.

6 IMPROVEMENTS IN HAZARD ANALYSIS AND CONTROL

6.1 HAZARD ANALYSIS

It is hoped that this report will assist those undertaking CCS projects in their hazard identification. However, it should not be seen as a substitute for carrying out thorough hazard identification studies for the specific project. The hazard identification carried out for this report was necessarily fairly high level and used only high level block diagrams of the constituents of a CCS chain. Nevertheless, hazards have been identified here which should be considered for relevance to any specific project.

There are current gaps in consequence assessment modelling for carbon dioxide releases and data for model validation, which have been discussed in the previous section. While better models are developed and validated, it will be necessary to make conservative assumptions about inputs to existing models. This may have to result in very precautionary decisions. Conservatism in assumptions will be able to be reduced as better models are developed and validated, as discussed in section 6.

Better understanding is also needed of the tendency of supercritical CO_2 to dissolve contaminants which could be concentrated as the CO_2 flashed/sublimed following a release. This is needed to assist emergency response and safe escape. While most general types of formation (sandstones and carbonates) have been subjected to CO2 flooding the specific response of the wide range of different mineral combinations has not been tested.

In addition to hazards from CO_2, hazards associated with other parts of the capture process also need to be analysed. These include:

- Loss of containment of oxygen leading to enhanced combustion of any potential fuels and very large potential flow rates.
- Loss of containment of nitrogen, produced as a by-product by the Air Separation Unit, again at very large flow rates, giving an asphyxiation hazard.
- Fire and explosion hazards associated with hydrogen or syn gas.
- Possible flammability or toxicity of amine or equivalent used to capture CO_2.

6.2 CONTROLS IDENTIFIED DURING HAZIDS

The Tables presented for the bow-tie diagrams and for the top-down and change HAZIDs (Appendices F, C, and D respectively), summarise improved hazard control. Some measures have been pulled out and are again presented in this section to underline their importance.

Some hazard control measures which came out of the brainstorming in the HAZID meetings are as follows.

6.2.1 Inherent safety

Layout

Layout of the facility will be an important factor to mitigate as much risk as possible, in the design stage. Space will certainly be a new significant issue. There will be huge cryogenic oxygen requirements along with the need to move and transport columns and other equipment, which are anticipated to be much larger than those in use at any existing power plant.

Oxygen could be produced/stored remotely and supplied there from. However, pressurising/compressing of Oxygen for transport (especially when it is to be used at 1atm) will impose energy penalties and there might be new safety issues with cross-country oxygen lines. When the oxygen is produced at the power station, there are well understood layout issues involving separation of the ASU from the fuel, particularly the coal supply.

Pipelines should be routed so as to minimise proximity with populations including transport routes.

Congestion should be minimised at the capture plant/power station to minimise explosion effects in the event of loss of containment of hydrogen.

Low points which have potential to accumulate CO2 e.g access tunnels, should be identified. Also power stations often have chemicals (e.g ammonia) stored at site and these could be a significant factor when making decisions on layouts particularly for retrofits. Broad brush layout decisions should be made taking these into account otherwise designers could be left with intractable problems when detailed layouts have to be made for sites with restricted space.

Other

As sufficient CO_2 can inert hydrogen or hydrocarbons, the CO_2 should be kept mixed with these fuels as long as possible before separation to reduce fire and explosion hazards. Although a very high inert concentration is required to prevent combustion, the consequences can be much reduced by the inert, including reducing the propensity of hydrogen to detonate.

6.2.2 Prevention and control

- Suitable materials for seals need to be identified and specified for supercritical CO_2 which will tend to become dissolved in seal materials. Some further information about such materials has recently been provided[28, 29].

- Including too many **valves** from the compressor to the injection or storage point can be a problem. Although more legs can be isolated and vented, extra valves produce additional leakage paths at the flange connections and past the stem packing.

- All pipelines have both operating and emergency pressure-relief systems. With CO_2 pipelines, however, care must be taken to ensure that **extreme cooling** does not take place during pressure relief as this will be detrimental to the valves. Attention to the “small things” is especially important in CO_2 pipeline design[18]. If low ductile to brittle transition temperature (DBTT) steel is specified, it will also be necessary to ensure that welding procedures are suitable.

- Water content of CO_2 being transported in pipelines will be crucial to prevent corrosion of pipelines. When CO_2 is under high pressure and with traces of water, second acidic phases can form in presence of water and reactive substances such as SO3, HF, HCl etc. An understanding will be needed of how these substances will behave in a pressurised CO_2 atmosphere. This might involve the requirement to model the formation of a free water phase, or perhaps a direct test of corrosivity, e.g. copper strip, could be used. There is a current knowledge gap in terms of the ability to model this, particularly for high pressure CO_2. This will need to be addressed if general standards for the water content of CO_2 are to be set. Some data has recently been made available[28,29] which addresses some of the knowledge gaps. However some of the corrosion tests were carried out for CO_2 containing both water and H_2S and this may be less corrosive than water alone.

- Suitable design standards are required for isolation valves within pipelines. As they will need to be above ground (valve pits could fill with CO_2), they are most likely to be at booster stations. However, inventory requirements may make them necessary more frequently. It will certainly be safer to always bring the line above ground to install such block valves and possibly cheaper than building pits. Some form of screening may be needed to avoid spoiling the landscape but not anything which creates enclosure.

6.2.3 Operability

- Hydrate formation is an issue. This is not just for cold climates but hydrate formation is an issue when the pipe is sub-sea (assumed to be at 4°C) or buried. Hydrate formation might not lead to any primary hazard but causes equipment blockages. Such operability issues can often be the source of secondary hazards.

- The CCS chain needs to be designed to address possible **variable operation**, particularly as wind and other renewables start to provide a greater fraction of the total energy mix. This can be partly at least addressed by allowing the pipeline to act as a buffer (line pack). Another possible strategy would be to provide equipment and controls which can respond quickly to demand changes without becoming unstable. Having variable capacity could potentially increase the chance of upsets leading to trips and the possible need to vent. Design should minimise any need for venting under upset conditions and vents should be designed to give proper dispersion of the maximum quantity of CO_2 under all atmospheric conditions.

6.2.4 Maintenance and inspection

- Suitable inspection and maintenance regimes need to be developed. For pipelines, the development of intelligent pigs which are suitable for CO_2 service is in its infancy. Facilities need to be provided to prevent depressurisation of pigs as this could lead to explosive decompression due to CO2 dissolved in seals etc.

- There needs to be provision for addressing the **ageing** of the CCS infrastructure, particularly injection and the geological store following injection. This may be a challenge without revenue from the production of hydrocarbons. Mechanisms to adequately fund activities vital for safety need to be put in place at an early stage.

- Isolation for maintenance of large ducts containing CO_2, in the capture plant, needs to be considered. Flaps and dampers used for flow control will leak to some extent and so will not be suitable. Spades will need to be provided. Gas freeing of large equipment for entry also needs to be considered. E.g in Oxycombustion there may not be the luxury of a large airblower to clear out the system. It will also be necessary to think about flushing out recycle loops.

6.2.5 Mitigation

Leak detection

- CO_2 is odourless, so, given its dangerous qualities, there may be advantages to using a **odour-additive strategy** for CO_2 transmission and leak detection, particularly if the CO_2 pipeline is routed near human population centres. It may be that a low level of H_2S could be left in the CO_2 as a stenching agent. Alternatively a stenching agent suitable for CO_2 would need to be developed.

- **Aerial pipeline surveys** are a common approach to checking pipelines. A release of pressurized CO_2 is accompanied by a temperature transient, typically a drop in temperature. This property presents an opportunity to inspect for CO_2 releases or leaks using thermal imaging. A low-level aerial survey would allow high-resolution thermal images to be obtained that could help detect releases on an aboveground pipeline and possibly from buried pipelines depending on the magnitude of the CO_2 release[18].

Emergency response

This is discussed further in section 7.

6.2.6 Interfaces and Organisational factors

There will be a number of new organisational interfaces which need to be managed. These include:

- Between the different aspects of the capture plant and the power station. The capture plant and powerplant might be operated by different companies, as might the oxygen supply (where relevant).

- Between the capture plant, pipeline operator and injection operator. The pipeline may well be a network needing to manage inputs from many diverse sources. Organisational interfaces for pipelines may also include local authorities, landowners, other service providers, construction companies, rail companies, regulators etc. Network control will be needed.

- Between construction team for new capture plant, possibly being retrofitted into an existing (and operating) power plant. This will create significant challenges, particularly given the large size of equipment to be installed. Fabrication adjacent to live plant may introduce issues with lifting over live equipment. A decision might have to be made to shut down the power plant during critical stages of construction. There will be a possible need to relocate large items of equipment

Effective communication between different interfaces is an important aspect of effective hazard control. Activities like welding at heights (of the new boilers/columns) with potentially new substances like liquid oxygen on the same site need adequate controls.

Contract conditions, e.g. for an uninterruptible oxygen supply with cost penalties, may have undesirable implications in terms of safety, such as the possibility of storing oxygen.

Technical interfaces, which need to be addressed, include control systems for the capture plant which may need to interface with much older non- IEC61508 control systems at older power stations.

Competence

The training and competency assurance arrangements for the new and modified facilities need to be adequately recognised and addressed. For example, control systems, which might be entirely new to a power plant's existing staff, may be used. Also, the staff should be well trained in handling of new chemicals on site. Also, now there might be need for chemical engineers, rather than just mechanical engineers traditionally, on power plants. The resource requirements and availability should be foreseen and planned.

Training courses need to be available. In the longer term, university courses, e.g. chemical engineering, need to include CCS processes. Professional development courses will also be required. Demonstration projects could have a role to play, for instance by allowing short placements for operators to gain experience**.**

Some training and competency issues which require early action include:

- Set competency and training requirements for key staff at an early stage
- Conduct a control system compatibility and ergonomic study where CCS is retrofitted
- Provide a hazardous substances training module for all staff destined to work on a new CCS plant
- Set up an international CCS system incident database with free access to all.

Relative inexperience in design teams working on CCS projects might be mitigated by a design review by a more experienced competent person, e.g. with experience of EOR projects in the USA.

6.3 STANDARDS AND GUIDELINES FOR CO_2 PIPELINES

It would be best in interest of hazard control to apply good practise at the design stage. However, depending on the level of risk and complexity involved, it is possible the adoption of good practice alone may not be sufficient. The principle of reducing the risk as low as reasonably practical (ALARP) should also be considered.

There is a current lack of relevant standards. For improved hazard control it is necessary to integrate current knowledge and work towards developing best practise guidelines for pipeline transmission of dense phase carbon dioxide. In recognition of the fact that the current operating experience of dense phase carbon dioxide, on the scale anticipated for CCS, is not substantial HSE UK has provided Interim guidance[20] on conveying CO_2 in pipelines in connection with carbon capture, storage and sequestration projects.

HSE UK has adopted a cautious approach and for the purposes of the UK CCS Demonstration Competition, pre-bidders / project developers have been required to give a health and safety compliance demonstration **as if** CO_2 was classified as a 'dangerous substance' or a 'dangerous fluid' under COMAH (Control of Major Accident Hazard Regulations, the UK enactment of the European Seveso II Directive) and Pipeline Safety Regulations (PSR) and for offshore installations as if all relevant offshore regulations applied, in order to satisfy the requirements of the Health and Safety at Work etc Act 1974.

Recognising the novel issues and that current industry standards do not adequately address the risks associated with the transmission of CO_2 in pipelines other initiatives are currently being undertaken by industry stakeholders working in partnership and with government agencies. For example, the Det Norske Veritas (DNV) has initiated a joint industry project (JIP) on pipeline transmission of CO_2, which will lead to a standard.

A review of CO_2 pipelines with relevance to future offshore Norwegian pipelines[29] includes information about effects of impurities, materials, the effect of free water, fracture propogation, flow assurance, metering and measurement, monitoring and control, operation and maintenance. The review is based largely on USA experience of CO_2 pipelines.

Additionally the UK Energy Institute has initiated a JIP which will produce guidelines on aspects of design for CO_2 which will promote technology transfer from the industrial gases sector. Presentations on aspects of pipeline design and operation were given at a recent workshop[28].

7 EMERGENCY RESPONSE

Conventional fuel systems have been designed diligently with support of good industry knowledge and experience gained over many years. Still however, emergency response teams in these facilities deal with some accidents. For upcoming CCS facilities, which will operate on unprecedented scale, the emergency planning might also need careful reworking to account for additional hazards brought in by high volumes of CO_2.

The difference with CO_2 is that neither small nor large leaks can be dispersed in the same way as for natural gas pipelines. Natural gas is buoyant and this will assist dispersion. As captured CO_2 is heavier than air (unlike the dilute hot combustion products which are currently vented from power stations without capture) it will tend to accumulate in depressions. CO_2 can stay there undetected for a very long time. Current process plant practices provide for operator testing for heavy hydrocarbons and CO_2 in low-lying areas in plants before they enter these potentially dangerous areas[18]. One example of areas at a power plant highly prone to this hazard will be the tunnels frequently found underneath for running cables and other services. Procedures for entering such places will need to be in place and may have to be revised once large quantities of CO_2 are present on site.

Emphasis on robust emergency planning and response is underlined by the fact that with CCS becoming acceptable and widely applicable pipelines might be running through not so sparsely populated areas.

A good dispersion study will be crucial for emergency planning as this would be needed to identify escape and access routes. This should take into account influencing factors as seasonal effects, routing, and terrain etc[18]. Emergency planning is therefore effected by uncertainties in the consequence modelling for CO_2 as discussed in section 5. It may be that a "live" model should be available to the emergency co-ordinator so that the dispersion pattern on the day of an event can be predicted. Live dispersion modelling for CO_2 would need to be developed.

A best practice emergency response plan for CO_2 should be developed. This should include information about where members of the public should go in an emergency, e.g. upstairs indoors with doors and windows closed and air-conditioning off. It may be possible to take advantage of CO_2 being a heavy gas when at high concentrations following a dense phase release but the position of air intakes for air conditioning systems would need consideration. A response plan for people in the open or in cars needs to be developed. Emergency response planning for sour gas/H_2S releases in Canada may be a relevant starting point and would include public consultation, communication and training of the public.

The emergency response should consider the potential impairment of human responses in CO_2 atmosphere because of its asphyxiant and physiological properties. Emergency responders will require appropriate breathing apparatus. It is important that anyone without breathing apparatus does not bend down to assist casualties as this could result in them being overcome themselves. Casualties should be moved to high level to promote the possibility of recovery.

The possibility of providing indicators/monitors for CO_2 should also be considered. For example: Is there a way to observe whether there are pointers to a low lying CO_2 layer having formed. Is there a simple CO_2 monitor which people could be provided with?

It should also be kept in mind that in case of larger releases, visibility would be drastically reduced due to CO_2 ice cloud and fog formation due to moisture in air. CO_2 releases will also cause significant local cooling and all equipment and components which could be impacted. The emergency response plan needs to consider their survivability and whether failure could be expected and might lead to escalation. Any valves or other equipment which are required for the emergency response need to be designed and/or protected so that they will still operate under such conditions.

Any incidents calling for an emergency response should be monitored and recorded in order to learn from experience.

8 INSIGHTS FROM EXPERT REVIEWERS COMMENTS

The following insights and additional hazards were identified as a result of comments from the expert reviewers:

Events requiring significant emergency response planning due to potential CO_2 releases were questioned by one reviewer. This highlights the very large scale of CCS projects such that current experience may not always be relevant.

The following additional hazards were identified by expert reviewers and have been included within the bow-tie diagrams:

- A small leakage (pinhole), due to corrosion or bad welding, in a aqueous environment. Such a leak will cause rapid and accelerating corrosion of the pipe, due to the forming of acid.

- Additionally or alternatively, a small leak might cause ice to form under the pipe, through which the pipe could be pushed up, influencing the integrity of the pipeline

Monitoring alongside the pipeline may not be necessary except at installations like booster stations with equipment and flanges, where employees may be working. Prevention of leaks is more effective than monitoring for leaks. This might include the detection of intrusion so as to prevent external interference as a cause of leaks.

H_2S as a stenching agent may not be practical. However, it might be useful to develop a new stenching agent specifically for CO_2 (although nowadays the trend is not to odorise the high pressure natural gas transmission pipelines).

9 CONCLUSIONS

1. A series of hazard studies have been carried out for the elements of the carbon capture and storage chain. These have used different perspectives to help to brainstorm hazards. The perspectives included new substances, equipment and activities; potential types of major accident scenario; and changes introduced by CCS to layout, interfaces and organisation. It is hoped that the results of these HAZID studies will be of use to those carrying out CCS projects but should never be a substitute for them carrying out a full suite of integrated hazard management processes.

2. The level of information available about the different stages in a CCS chain was found to be fairly high level. This limited the depth of HAZID which was possible but it was still possible to make good progress, particularly making use of the knowledge of experts who attended the HAZID meetings. Lack of detailed design information would not, of course, be an issue for design teams carrying out a CCS project.

3. No absolute showstoppers have been found. Rather a number of potential hazards have been identified which will require the adoption of safe design principles to eliminate, prevent, control or mitigate them. Some possible barriers have been identified as a starting point in this process. Death or injury to a person or persons could result from any of the following example events unless they are identified and addressed in the design, operation and/or emergency response:
   - (a) They entered a tunnel under a power station unaware that CO_2 had accumulated there
   - (b) A component in a pig exploded in their faces when it was removed from a pig trap
   - (c) A pipeline leak turned into a running fracture whilst the crew were preparing to deal with it.
   - (d) They were inspecting the inside of CCS power station ducting which had not been properly isolated and purged of CO_2
   - (e) A spark caused by static from a CO_2 discharge started a fire in a place where it was thought no ignition source existed
   - (f) They tried to rescue some one who had been overcome by CO2 unaware that the area was blanketed by a cloud of low lying CO_2
   - (g) They didn't realise that it would be a good idea to move upstairs or to a higher point following a CO_2 release incident
   - (h) They didn't know that they could suffer cold burns near a CO_2 release
   - (i) They didn't know that equipment might be contaminated with mercury
   - (j) Toxic scale had been transported selectively from underground into equipment they were working on.
   - (k) An oxygen enriched atmosphere started a fire which would otherwise not have happened
   - (l) Scale collected from equipment carrying CO_2, supposedly an inert gas, was pyrophoric
   - (m) A chemical process was being run by staff who had no chemical process training or background.
   - (n) Equipment exposed to oxygen had not been properly cleaned
   - (o) A vessel or pipe in CO_2 service suffered a brittle failure because it was depressured too quickly
   - (p) A detonation occurred in a power plant, which was very congested following conversion to make and burn hydrogen and capture CO_2, because more equipment had to be fitted in than anticipated.

(q) Nitrogen leaked into a turbine hood and no-one realised that there was a supply of nitrogen as well as hydrogen.
(r) An amine solvent caught fire when everyone thought it was not flammable.
(s) Hydrogen and oxygen present in different CO_2 streams combined and formed water which corroded high pressure equipment
(t) A toxic solvent was chosen when a non toxic alternative was available
(u) The revamp to CCS introduced such a mixture of old and new control systems that an incident occurred which would normally have been easily avoided.
(v) CO_2 was vented during an upset and did not adequately disperse/dilute before coming down to the ground
(w) Sophisticated monitoring for a pipeline was omitted at a road crossing because modern "laid alongside pipe systems" detection cannot be pulled under crossings.

4. Retro-fitting CCS into existing plant introduces space constraints and raises issues such as:
   - Switch gear tends to be separately owned and not easily relocated, so its location may introduce inflexibility when modifying layout to add CCS to an existing site.
   - It may not be practical to build ASUs on sites of power plant considering space constraints but having them on a separate site raises some new safety issues.
   - If the ASU is separate should the CO_2 be cleaned up on the same site? It could be transported wet at moderate pressure in plastic pipe.
   - A wider range of specifications will be required for spare parts; and more comprehensive materials and maintenance systems may be needed.
   - Decisions on the space required for a power plant to be capture-ready should be based on a full understanding of the layout issues.

5. CCS will introduce increased complexity and risk into power generation plants. This may introduce additional requirements for safety management systems and staff competence.

6. Knowledge gaps, which have been identified by this study, include:
   - Consequence modelling of CO_2 releases, particularly the development of the source term.
   - Validation of fracture control models for CO2 pipelines..
   - Understanding the propensity of dense phase CO_2 to dissolve heavy metals and other toxic or radioactive contaminants from rock formations. While most general types of formation have been subjected to CO2 flooding the specific response of the wide range of different mineral combinations has not been tested. Confirmation is needed that solution of contaminants is not a problem.
   - Design and operational standards for CO_2 pipelines and other equipment are still in development. Issues include suitable CO_2 specification (particularly water content); avoidance of hydrate formation; suitable non-metallic materials for seals etc.; suitable design and operating regime for intelligent pigs; flow modelling of CO_2 with impurities which impacts on leak detection systems.
   - Aspects of emergency response planning such as recommendations for those in cars.
   - A suitable stenching agent for CO_2 may need to be developed.

10 RECOMMENDATIONS

1. The hazards and bow-tie diagrams produced by this project should be used as an input to hazard identification and design studies for CCS projects. (Electronic copies of the bow-tie diagrams in Excel format will be provided to IEA GHG members with this report so that they can be modified and extended for specific projects.)

2. Work should continue to be carried out to develop design standards for CCS and to resolve knowledge gaps which have been identified. Some such work is already in progress.

3. Particular attention should be paid to layout and interface issues when CCS is retrofitted into existing power stations. A control system compatibility and ergonomic study should be considered.

4. Training and competency issues should be considered at the outset of a project, including setting competency and training requirements for key staff; providing a hazardous substances training module for all staff destined to work on a new CCS plant.

5. An international CCS system incident database should be set up with free access to all.

6. An emergency response plan should be developed, particularly for incidents involving major loss of containment of CO_2.

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11 APPENDICES

11.1 APPENDIX A: INCIDENTS RELATED TO CARBON DIOXIDE RELEASES

(Report by Moonis, M. and Hare, J., HSL, reproduced with permission of Mr Stephen Connolly, HSE, UK)

1. A delivery driver succumbed to carbon dioxide asphyxiation while dispensing CO_2 from his tractor-trailer [(1)].

2. On 24th May, 1994 a plant operator was fatally injured when he opened a pressure vessel which was still under pressure in near supercritical fluid process, which employed methanol and carbon dioxide at pressure of 2000 psi. Apparently believing the vessel to be depressurised, the victim attempted to remove the heavy steel cover. The pressure was released, throwing the victim 10 feet across the room. The victim was transported to a hospital where he was pronounced dead later that night [(2)].

3. On 14th November, 1998 high-pressure gas containing carbon dioxide and hydrogen sulphide rushed out of an oil well near Nagylengyel, Zala county (SW Hungary). Because of the huge gas cloud, which developed above the well and was blown by the wind, about 2,500 people had to be evacuated[(3)].

   This is a case of geothermal resource being used in oil production. Natural gas, with a high content of CO_2 (~81 %) is produced, transported, and re-injected to form an artificial gas cap above the depleted part of the oil reservoir. The technology operates without compressors; compressor power is provided by the thermal lift between the production and the re-injection wells. The higher the extracted geothermal heat from the produced gas, the stronger the thermal lift and the higher the gas mass flow rate. In this case, the fluid carrying the geothermal energy is CO_2 gas (Bobok et al, 1998).

4. In Cerro Fortunoso field in south of Mendoza province, Spain, an incident occurred in the drilling of a well. After reaching bottom hole at depth of 1500 m and before the final interval had been cased, a high pressure CO_2 eruption began from casing at 1200 m. The gas began to flow up around casing already in place and eventually found two paths to surface through natural fissures in subsurface and produced two large craters 70 m south of the wellhead. Even with excellent planning and help of specialised companies, it took 30 days to drill a relief well and control the blow-out.

5. Dieng Volcano Complex, 1979, Indonesia, diffusive CO_2emissions occurred prior to major accident. 200,000 tonnes of pure CO_2 was released and flowed from volcano to plain below as a dense layer causing asphyxiation to 149 people. This incident was associated with a 'phreatic explosion', an explosion in which ground water is explosively evaporated by hot magma. CO_2 was released at the same time. It was considered the pure CO_2 released must have accumulated in a shallow reservoir as high density fluid before the explosion and was then released through fractures as they opened up due to pressure build up in volcano prior to explosion (ex of leak from volcanic areas) [(4)].

6. Lake Monoun, Cameroon 1984, Lake Monoun overturned, causing sudden release of volcanic CO_2 leading to death of 37 people[(4)].

7. Lake Nyos, Cameroon 1986, 1.24 MT of CO_2 was released in few hours and asphyxiated 1700 people[(4)].

8. Yellowstone hydrothermal areas, USA diffuse degassing has been measured at about 16 MT CO_2 per year. In diffuse degassing, gaseous CO_2 can percolate to surface through porous zones on volcano flanks and through hydrothermal areas[(4)].

9. Horseshoe lake, Mammoth mountains California; 'treekill' was caused by CO_2 emerging through the ground along fault zones on the volcano's flanks, following a period of enhanced seismic activity. The enhanced concentrations of CO_2 in the soil killed a large number of trees[(4)].

10. Cava dei Sielci region, Alban Hills Volcanic Complex Italy, release resulted in deaths of more than 30 animals. This release too was associated with increased seismic activity in that area (ex of leak from volcanic areas) [(4)] .

11. Paradox basin, Colorado plateau CO_2 seepage along faults results in CO_2 charged groundwater in several springs and through old well bores. A crystal geyser, now a tourist attraction, first erupted in 1935 when well being drilled, intersected a charged aquifer. The geyser erupts every 4-12 hours as result of pressure changes in the aquifer (ex of leak from sedimentary basin) [(4)].

12. Matradrecske, Hungary, ex of leakage as result of presence of permeable cap rocks above fields. High levels of have been recorded for sometime in this area. In 1992, residents in two houses in village suffered from headache and since then control flushing system have been installed (ex of leak from sedimentary basin) [(4)].

13. S&N groups Berkshire Brewery, a contractor's employee died having been overcome by release of CO_2in carbon dioxide recovery plant at Berkshire brewery. A detailed HSE investigation is currently underway. (http://www.scottish-newcastle.com/snplc/rsp/environment/incidents/)

14. **INCIDENTS INVOLVING** CO_2 **AS FIRE SUPPRESSANT**

- Report presented by USEPA in 2000 searched various databases for CO_2-related incidents in fire scenarios. From 1975 till report was prepared, 51 cases of carbon dioxide incident records were located that reported a total of 72 deaths and 145 injuries resulting from accidents involving the discharge of carbon dioxide fire extinguishing systems.[12] All the deaths that were attributed to carbon dioxide were the result of asphyxiation[(5)].

  The Table A.1 below presents a breakdown of CO_2 related incidents and deaths/injuries[(5)].

Table A.1 Breakdown of CO_2 related incidents

Use Category		Number of Incidents	Deaths	Injuries
United States and Canada				
1975-Present	Military	9	10	15
	Nonmilitary	20	19	73
Before 1975	Military	3	11	0
	Nonmilitary	5	3	3
Total		37	43	91
International				
1975-Present	Military	1	4	5
	Nonmilitary	21	39	52
Before 1975	Military	0	0	0
	Nonmilitary[a]	3	33	4
Total		25	76	61
Total		**62**	**119**	**152**

[a] Included in the total international nonmilitary incidents, deaths, and injuries before 1975 are the 20 deaths resulting from the use of carbon dioxide as a fire suppressant in England from 1945 to the mid 1960s, for which the cause is unknown.

All the 13 military incidents were related to marine activities, compared to only 11 of 49 in civilian cases. Other civilian cases were from varied environments, airplanes, data processing centers, garages, mills, parking etc.

Different results show that accidental exposure to carbon dioxide during maintenance or testing was the largest cause. In some cases, non-compliance with safety procedures led to death/injury/exposure.

The reason was not solely asphyxiation in fire mitigating system atmosphere but comprised of different scenarios such as too much CO_2 released or escape of CO_2 to adjacent rooms during testing, accidental discharge or false alarm. The worst incident reported in this report is of an aircraft crash killing all 43 passengers onboard. The last transmission received indicated release of a CO_2 fire extinguisher in the forward cargo hold, minutes before the crash. However, it is not clear if any of the deaths can be attributed to CO_2 release **(this incident is from 1948**).

15. Northumberland, 11th Feb 1995, a 60 year old man and his dog were asphyxiated when they sucked in CO_2. This was due to stythe or choke-damp released under unusual weather conditions when the low pressure outside caused venting of CO_2 from an abandoned coal mine[(6)].

16. A refrigeration repairman was overcome by dangerous levels of carbon dioxide from the evaporation of blocks of dry ice. The carbon dioxide released from the dry ice accumulated in a walk in freezer in a restaurant. (OSHA Region I News Release, 12.17.1999) [(6)]

17. OSHA News Release (July 31, 1996), the objective of this release was to present dangers of oxygen displacement by CO_2 in decorative waterfalls and mountains. The

operator carrying out maintenance lost consciousness in this case. So did his partner in a rescue attempt. A security guard and a passer-by tried rescue but had to give up when they too became dizzy. Adequate rescue was however provided by the fire department [6].

18. Canada, two men were asphyxiated when working in a water well 3 metres deep. A worker was trying to descale the screen at the well bottom using strong acid, which reacted with the carbonate deposits to release CO_2. The second man died while attempting to rescue the first [6].

19. Canada, a man entered a covered well that had not been used for 10 years. He became unconscious from lack of oxygen after descending 2 meters (7 feet). Fortunately, he was rescued and recovered fully [6]. (*This could be due to CO_2, H2S or any gas.*)

20. Another fatal accident was at a Department of Energy experimental test reactor in Idaho on 28th July 1998. This involved an accidental release of carbon dioxide during routine maintenance that caused the one fatality and exposure to fifteen other workers. The incident occurred when de-energising electrical circuits for routine maintenance. As the last circuit breaker was opened, a sudden discharge from the CO_2 fire suppressant system occurred without a warning alarm for evacuation. Within seconds workers found themselves struggling in a lethal atmosphere with zero visibility. The investigation committee had concluded that the safety measures and procedures were not implemented and the incident could have been avoided had they been in place [6]. (http://www.id.doe.gov/foia/ineelaiintro.pdf)

21. A cross-country skier was found dead inside a large, mostly covered snow cave, one day after he was reported missing. The autopsy report suggested symptoms consistent with asphyxiation; carbon dioxide measurements inside the hole in which he was found reached 70 %. This area is known for having a high carbon dioxide flux attributed to degassing of a large body of magma (molten rock) 10 to 20 km beneath the ski area [7].

Some More Examples Of Volcanic Origin CO_2 Discharges

22. *Nyiragongo, DR Congo,* erupted in 2002 and measured concentrations of CO_2 in some locations ranged from 20%-30% to 90 % above lethal concentrations and pockets of gas reached heights up to 40 metres. In years prior to the eruption, ground emissions of CO_2 in Goma and Lake Kivu were probably responsible for a number of fatalities[8].

Table A.2 below summarises USA experience.

Table A.2: Industrial experience in USA: 3100 km CO_2 pipelines (for enhanced oil recovery) with capacity of 45 Mt/yr[9]

Pipelines	Natural Gas Transmission (1986-2001	Hazardous Liquids (1986-2001)	CO_2 (1990-2001)
No. of incidents	1287	3035	10
No. of fatalities	58	36	0
No of injuries	217	249	0
Property damage M$	285	764	0.469
Incidents/1000km/yr	0.17	0.82	0.32
Property damage/1000km/yr $	37,000	205,400	15200
Average Length of pipeline (back calculated)	505,000	240,000	2,800

References for Appendix A

(1). Potential Carbon Dioxide Asphyxiation Hazard When Filling Stationary Low Pressure CO_2 Supply Systems. (OSHA hazard info bulletin, June 5, 1996), http://www.osha.gov/dts/hib/hib_data/hib19960605.html

(2). http://www.cdc.gov/niosh/face/stateface/ma/94ma019.html

(3). Hungarian News Agency (MTI) (WHNA); 14 November 1998. Source: World Reporter (Trade Mark).

(4). IEA greenhouse Gas R&D Programme http://www.ieagreen.org.uk/glossies/naturalreleases.pdf

(5). Carbon Dioxide as a Fire Suppressant: examining the Risks, US EPA EPA430-R-00-002, Feb 2000. http://www.epa.gov/ozone/snap/fire/co2/co2report.pdf

(6). Case histories of carbon dioxide incidents. http://members.aol.com/hydratwo/co2.htm

(7). Hill, P.M., “Possible Asphyxiation From Carbon Dioxide Of A Cross-Country Skier In Eastern California: A Deadly Volcanic Hazard”, Wilderness And Environmental Medicine: Vol. 11, No. 3, Pp. 192–195

(8). Baxter, P.J. and Ancia, A., 2002. Human health and vulnerability in the Nyiragongo volcano crisis Democratic Republic of Congo 2002: Final Report to the World Health Organisation, World Health Organisation

(9). Race, J., “designing safe CO_2 transport structure for UK”, presentation at Newcastle University school of marine science and technology, viewed at http://www.energyinst.org.uk/content/files/newcastleresearch.pdf on 21st Apr 2007

11.2 APPENDIX B: SAMPLE MATERIAL SAFETY DATASHEET FOR METHYL ETHYL AMINE (MEA)[8]

Toxicity Data[8] :
Oral:
LD50: 620 mg/kg (gpg)
LD50: 700 mg/kg (mus)
LD50: 1720 mg/kg (rat)
LD50: 1000 mg/kg (rbt)
LDLo: 1400 mg/kg (mam)
Dermal:
LD50: 1 mL/kg (rbt)
Inhalative:
LC: >2420 mg/m3/2H (cat)
LC: >2420 mg/m3/2H (mus)
Irritation of skin:
moderate: 505 mg (rbt)

Primary irritant effect:
on the skin: Irritant to skin and mucous membranes
on the eye: Irritating effect.
Sensitisation: No sensitising effects known.
Other information (about experimental toxicology):
Reproductive effects have been observed on tests with laboratory animals
Mutagenic effects have been observed on tests with human lymphocytes

Subacute to chronic toxicity:
The Registry of Toxic Effects of Chemical Substances (RTECS) reports the following effects in laboratory animals:
Behavioural - somnolence (general depressed activity)
Behavioural - muscle contraction or spasticity
Lungs, Thorax, or Respiration - dyspnea
Lungs, Thorax, or Respiration - respiratory depression
Liver - changes in liver weight
Liver - liver function tests impaired
Nutritional and Gross Metabolic - weight loss or decreased weight gain
Skin and Appendages - dermatitis, other (after systemic exposure)
Kidney, Ureter, Bladder - changes in bladder weight
Kidney, Ureter, Bladder - proteinuria
Kidney, Ureter, Bladder - other changes in urine composition
Reproductive - Effects on Embryo or Foetus - foetotoxicity (except death, e.g., stunted foetus)
Reproductive - Effects on Embryo or Foetus - foetal death
Related to Chronic Data - death
Reproductive - Specific Developmental Abnormalities - musculoskeletal system
Reproductive - Specific Developmental Abnormalities - urogenital system
Reproductive - Maternal Effects - other effects

Subacute to chronic toxicity:
Corrosive materials are acutely destructive to the respiratory tract, eyes, skin and digestive tract. Eye contact may result in permanent damage and complete vision loss. Inhalation may result in respiratory effects such as inflammation, oedema, and chemical pneumonitis. May cause coughing, wheezing, laryngitis, shortness of breath, headache, nausea and vomiting. Ingestion may cause damage to the mouth, throat and oesophagus. May cause skin burns or irritation depending on the severity of the exposure.
Additional toxicological information:
To the best of our knowledge the acute and chronic toxicity of this substance is not fully known.
No classification data on carcinogenic properties of this material is available from the EPA, IARC, NTP, OSHA or ACGIH.
Melting point/Melting range: 10 ° C
Boiling point/Boiling range: 170 ° C
Flash point: 93 ° C

Dangerous products of decomposition: Carbon monoxide and Carbon dioxide, Nitrogen oxides.
Suitable extinguishing agents
Use carbon dioxide, extinguishing powder or foam. Water may be ineffective but may be used for cooling exposed containers

Product does not present an explosion hazard

11.3 APPENDIX C: TOP-DOWN HAZID TABLES

Top- down HAZID Record Sheet: Injection			
Keywords	Causes	Hazards/consequences/incidents	Comments
Fire	Topside compression, turbine drivers, any prime mover	Compressor fires	Not in the case of sub-sea completions
Fire	Stream of oil, natural gas, CO_2 and water if CO_2 used for EOR Topside gas separation operations	Hydrocarbon fire	Over time CO_2 will break-through and the CO_2 to Natural gas ratio will in a short time be predominately CO_2 Produced oil stream composition will not change significantly, apart from increasing CO_2 content
Fire	Diesel to supply compression	Diesel fires	If no EOR but just injection then may be power supply is from gas turbine, diesel or electric cable from shore or other platform This may already be on the rig, so existing precautions will be in place The hazard for diesel fires would go away if diesel were no longer required for power turbine once oil production ceased

Top- down HAZID Record Sheet: Injection			
Keywords	Causes	Hazards/consequences/incidents	Comments
Explosion	CO_2 in an enclosed vessel (such as pipeline) can increase in pressure if exposed to extended periods of heat from external sources (e.g. sun warming exposed pipe). An explosion can occur if pressures increase beyond the design pressure of the vessel	Pressure burst explosion Escalation from CO_2 release or BLEVE can cause hydrocarbon release if hydrocarbon line is impacted	Air Products have rules for locked-in volumes. Others might also have. Sunlight is much less of an issue for buried or sub-sea pipelines as the exposed sections are very small compared to the rest
Explosion	Rapid CO_2 pressure reduction, e.g. through catastrophic vessel failure	CO_2 BLEVE can be prevented by choice of operating conditions	Although not flammable CO_2 can exhibit Boiling Liquid Expanding Vapour cloud Explosion behaviour if a pressure vessel fails.
Explosion	Escalation to hydrocarbon containment	Hydrocarbon fire or explosion	Existing hydrocarbon explosion hazard reduced by CO_2
Explosion	CO_2 BLEVE	Missiles/projectiles from CO_2 containment	CO_2 storage tanks unlikely to be involved in CO_2 injection and should be avoided Ensure pipes and vessels have low enough DBTT (X80 is –30 ºC)

Top- down HAZID Record Sheet: Injection			
Keywords	Causes	Hazards/consequences/incidents	Comments
Explosion	Corrosion of piping Undersea: additional external corrosion rates. Any free water in CO_2 causes rapid corrosion North Sea worse due to cold. CO_2 therefore needs to be very dry	Pressure Burst Explosion	Pipeline corroded by exterior forces. Would be monitored by periodic pigging and flyover inspections, possibly annually A system shutdown to occur as pressure reduction would trigger SCADA safety procedures Dryness limits not fully understood under very high pressure conditions
Explosion	Hydrate formation at low temperature Plugging, corrosion due to free water formation	Pressure Burst Explosion	CO_2 needs to be very dry, <50ppm or <10ppm. Some literature claims no hydrate formation below 50ppm while some claim the threshold to be <10 ppm. (Tests are being carried out to provide inputs to models)
Explosion	Oxygen in CO_2 From oxy-combustion process (oxygen may not be adequately removed) Issues may arise if there is a grid network and some sources have traces of H_2	• Possible Explosion issues • Water might be produced: corrosion • Bacterial growth problems can also arise, and present problems for storage sites • Water might be produced: corrosion	Specification must keep concentrations low enough. CO_2 will inert Oxygen must be removed as part of fluid specification limitation
Toxicity	CO_2 not classified as toxic but has more physiological properties than just being asphyxiant	Asphyxiation/toxic effects on people	Avoid enclosed spaces

Top- down HAZID Record Sheet: Injection			
Keywords	Causes	Hazards/consequences/incidents	Comments
Toxicity	Increased scale of Amines for stripping if EOR -- with increase in scale of EOR, the quantity of amines at the capture sites will increase and amines can have hazards of their own	Toxicity of amines	Many are non-toxic This should be a choice factor The amines may already be in use for EOR and their effects must be well known. However, it would be expected that the toxic effects of particular amines would have been assessed and documented
Toxicity	Solubility of heavy metals in dense phase CO_2. These could be brought to surface by EOR and released more so than in crude oil	Possibility of heavy metal toxicity if loss of containment of CO_2	Not specified as a problem in injection in Texas. But note that natural CO_2 (i.e. Limited amount of dissolved HMs) is being used
Toxicity	Trace metals (e.g. in oxy co-combustion) Contamination of CO_2 in pipeline e.g. mercury from oxy-combustion	Toxicity of mercury Toxicity, safe disposal of wastes e.g. from pigging or drainage of lines	Bigger problem from corrosive nature of mercury compounds is for food and drink industry For oxy-combustion the mercury content of fuel should be taken into design considerations
Electrical	When electrical conductivity of < 50 micro ohm then electrostatic hazard possible Electrostatic charge may generate in flowing CO_2 Electrostatic hazard for dry CO_2 CO_2 for purging vessels can give ice crystals (95-98 % pure) at nozzle and generates electrostatic	Ignition hazard Shock hazard	This can be addressed by standards for pipeline construction, design and operation It should be ensured that CO_2 flows are low enough to avoid static build-up. Appropriate earthing of pipes etc should be ensured

Top- down HAZID Record Sheet: Injection			
Keywords	Causes	Hazards/consequences/incidents	Comments
Electrical	Big electrical power requirements for compression	Electrical explosion/fire	No different from existing hazards e.g. at power stations
Mechanical	More lifting, e.g. during retrofit construction	Hydrocarbon release if incident during lifting over live equipment	No different to any offshore construction/retrofit Minimised if all compression done onshore
Mechanical	CO_2 will add pressure to well	Overpressure	Integrity issue for wells Depleted field capped based on existing pressure Prudent operator will also be able to validate parting pressure down-hole and design injection plan accordingly Pressure gradients, maximums will be part of any EOR or storage program Will require re-qualification and retesting of some injection equipment for higher pressure and also re-qualification of wells suitable for storage
Mechanical	Longitudinal failure of CO_2 pipelines	Catastrophic CO_2 release	Control using pipe metallurgy, wall thickness or possibly crack arrestors Fracture control requires both low DBTT steels and steels with a sufficiently high toughness (i.e. the steel must be ductile and it must be tough enough).

Top- down HAZID Record Sheet: Injection			
Keywords	Causes	Hazards/consequences/incidents	Comments
Other Issues	Visibility, CO_2 release	Poor visibility due to CO_2 ice cloud and fog formation due to moisture in air	Needs to be taken into account in emergency response plans

Top- down HAZID Record Sheet: Pipeline			
Keywords	Causes	Hazards/consequences/incidents	Comments
Fire	In pre-combustion captures small % of H_2 present, hence reducing atmosphere. also H_2S is present, thus chance of pyrophoric iron deposits. These could be brought out during pigging operation	Possible fire on opening pig launcher/catcher e.g. for maintenance	Hydrogen will be dissolved in CO_2 well below LEL H_2S can be benefit to EOR but produces hard to remove scale For CO_2 pipelines, the hard scales produced by H_2S, prevent softer CO_2 scale from forming if CO_2 is not dry, thus preventing potential holing (holing as in leaks) Much experience in USA, no problems. Offshore has not been done, would need procedures
Fire	Energy required to compress CO_2	Compressor or pump fire	Not a new hazard
Fire		Booster station fire	Pump/compressor may be driven by oil/gas,(unlikely if land-based, more probably electrical)

Top- down HAZID Record Sheet: Pipeline			
Keywords	Causes	Hazards/consequences/incidents	Comments
Fire		Gas turbine fires	If lube oil fire then it can be a commercial decision whether to shut down, no different for CO_2
Explosion	Catastrophic failure - pressure energy release causing longitudinal ripping Third party intervention Land slip can cause shear, can be catastrophic No different than for any pipeline type	Catastrophic failure – pressurised release	CO_2 pipelines buried at appropriate depth and/or of suitable wall thickness and/or of right material (PD8010), crack arrestors are used in US. Metallurgy solutions are being looked into as well Designs and control systems to shut pipeline off
Explosion	Catastrophic release	CO_2 BLEVE (discussed in injection)	Can be prevented by choice of operating conditions May not occur for pipeline (rather than vessel)
Explosion	Exploding pigs Unsuitability of pig for CO_2 e.g. CO_2 dissolving in plastic components	Explosion of pig	This hazard will be addressed by operational/safety design. No pigs will be inserted that can blow up. If technology does not exist, there are (and have been) other ways to ensure integrity of pipeline either on or offshore. There is a hazard that a pig may explode if safety and design procedures are not followed Pigs for CO_2 pipelines is still in infancy, development programme in hand in USA

Top- down HAZID Record Sheet: Pipeline			
Keywords	Causes	Hazards/consequences/incidents	Comments
Explosion	CO_2 dissolving in plastic seals	Explosive decompression of valve sealing Materials, leading to leaks and failure to shut off	Requires suitable design and choice of seal material This is a design requirement and one that is known and is not an issue in CO_2 pipelines. It is well mitigated and part of the safety integrity system of CO_2 companies. Such dissolving is mentioned only because it is not prevalent in other media and must be designed for and safety standards set to ensure against it.
Toxic	Injection stops. Back-up and line pack. How much can be line packed?	Release of CO_2 if not designed for this situation	Requires venting/safety valves/design consideration. Emit CO_2 at source, if possible Pipe venting system need to be designed to prevent asphyxiation hazard Potential non-compliance if CO_2 will be released
Toxic	Venting of CO_2 is different from emitting at source as concentration would be high	Asphyxiation/toxic hazard when venting pipeline if venting of $CO_2$is in large quantities under atmospheric conditions in geographical locations that might cause CO_2 to pool for long periods	Design of vent pipes for air entrainment or other suitable route for air entrainment: dispersion modelling will need to be carried out
Toxic	Digger causing rupture of pipeline Toxic hazard from major release	Asphyxiation/toxic hazard	Concrete mattress, pipeline markers above buried pipeline in urban areas? Can stenching agent be used? E.g. very low concentration of H_2S left in CO_2.

Top- down HAZID Record Sheet: Pipeline			
Keywords	Causes	Hazards/consequences/incidents	Comments
			H_2S is detectable by smell at 0.1 ppm. H_2S is not toxic at this level, and easily detectable in the initial phases Staff on rigs and refineries are trained to be sensitive to this, and personal detection equipment is available to alarm at very low levels. They will also alarm at very low levels of CO_2 (and are in regular use by the UK nuclear power industry)
Toxic	Welding operations on CO_2 pipelines; Hot tapping, different procedures	Loss of containment of CO_2	Procedures needed for welding/hot tapping CO_2 pipelines, no different than any other pipeline. One procedure might be to isolate hot tap joint with block valves, perform hot tap, and ensure no water encroaches into pipeline before allowing hot tap to become operational
Toxic	Longitudinal ripping of CO_2 pipelines	Asphyxiation/toxic hazard	Careful choice of steel specs, crack arrestors. Crack arrestors will work sub-sea as well Depends on area. Urban areas must be more safely designed. Perhaps lower pressure or increased valving or even very high CO2 release valve poles in urban areas that would take pressure away before explosion could occur, to allow SCADA system to shut in line?

Top- down HAZID Record Sheet: Pipeline			
Keywords	Causes	Hazards/consequences/incidents	Comments
Toxic	Retrofitting existing pipelines for CO_2	Asphyxiation/toxic hazard	Make sure all valves etc are suitable for same service range All ancillary parts should be made fit for the purpose
Toxic	Corrosion in CO_2 pipelines, drying very important, lot of trace elements, carbonyls etc may be corrosive, anything can be formed	Asphyxiation/toxic hazard	Ensure water content is low
Electrical	If very remote region, and no other source of power for booster stations	Electrical fire	No different than any other service Build booster stations where there is an adequate source of power at a convenient distance away
Electrical	Interaction between pipeline and HT line	Capacitive pickup of electrical charge	It is not considered good practise to route steel pipes parallel to HV electrical cables
Electrical	Electrostatic	Ignition source Shock hazard	See discussion under 'injection'. Pipelines are designed to shed electrical charges to earth.

Top- down HAZID Record Sheet: Pipeline			
Keywords	Causes	Hazards/consequences/incidents	Comments
Mechanical	Corrosion	Asphyxiant/toxic hazard of CO_2	Must ensure CO_2 adequately dry Cold climates for North sea, hence CO_2 needs to be adequately dry (<50ppm or <10ppm. Some literature claims no hydrate formation below 50ppm while some claim the threshold to be <10 ppm., tests are being carried out to provide inputs to models)) and pure to prevent free water or hydrate formation An adequate standard is needed Might need glycol. Pre-combustion capture may well already have come from a glycol wash (e.g. Selexol, DMEPEG), but this only delivers about 350ppmv of water, and additional drying stages are needed to go to <50ppmv or <10ppmv). Will be captured in final CO_2 specifications
Mechanical	Expansion loop systems	Possible above ground failure	Requires adequate design Much experience of supercritical ethylene pipelines
Mechanical	Slopes in pipeline		Speeds up CO_2 flow. May require baffles to slow it down
Mechanical	CO_2 compressors going to carbon steel from stainless steel	Stress Corrosion cracking (SCC)	Design issue – not a problem if designers are aware of the potential

Top- down HAZID Record Sheet: Oxy Combustion			
Keywords	Causes	Hazards/consequences/incidents	Comments
Fire	Oxygen handling ASU configuration Intrusion of HC into ASU Particulates intruding into ASU in case of oxy coal	Fuel/oxygen fire (or explosion)	Layout issue; well-understood HC getting into re-boilers of oxygen columns can cause 'mini explosions' If HC levels not adequately controlled explosions, and damage can occur
Fire	Flame stability, issues with flare-out	Fire due to loss of flame and build up of flammables	IR flame detection not applicable (CO_2 prevents hydrogen detection)
Fire	Oxygen storage can be thousands of tonnes		7000 t/d is Air Products standard. 10,000 t/d is approximately required for 1000 MW
Fire	CO_2 in ASU:	ASU will stop working, ice flakes in ASU. No fire hazard	There are monitors. No other problems as long as no other Hydrocarbons; but would want to shutdown on high CO_2
Fire	Starting an oxy-fired unit, purging	No hazard identified	Its first operated with air-fired case and then switching to oxy-fired at part- load
Explosion	Boiler/furnace High pressure equipment	Explosions in oxy-boiler/furnace Explosive depressurisation	In early years explosions have occurred in test furnaces Layout Issues: Keep ASU and O_2 away Design issues: Wrong controls; control is the main safety feature Explosion panels on fire box likely to be too big so prevent explosion. Not new technology, oxy-fuel burners well understood

Top- down HAZID Record Sheet: Oxy Combustion			
Keywords	Causes	Hazards/consequences/incidents	Comments
Explosion	Mercury embrittlement, 30-80 bars in separation system.	Explosive depressurisation	
Explosion	Coal dust explosions.	Coal dust explosions	Will depend on fuel type and milling design
Toxics	Ammonia (used for refrigeration).	Release of Ammonia	
Toxics	SO_2 (produced during combustion).	Sulphur dioxide release	Levels higher due to concentration of SO_2 caused by the flue gas recycle
Toxics	NOx	NOx Release	NO and NOx is mechanism for explosion in ASU. Low as recycle lowers it
Toxics	SO2 and NOx causing corrosion.	Equipment Failure	Depends on how NOx and SO_2 handled. They exist in liquid phase rather than high conc in vapour phase Flue gas could have 30 % water: highly corrosive. This can give material issue for compressors; Duplex steel can be an option. It would be preferred to de-sulphurise after compression. If SCR is used then FGD not a problem.
Toxics	Effluents; Lot of acid soup, will contain mercury	Occupational toxicity Environmental toxicity	
Electrical	Similar considerations as for an existing power plant	Electrical explosion shock	Not too much change is required

Top- down HAZID Record Sheet: Oxy Combustion

Keywords	Causes	Hazards/consequences/incidents	Comments
Mechanical	Mechanical Design of system including ASU	Equipment failure Loss of containment	ASU designs are well proven Need for educating the operators on handling the chemicals/chemical plants More reliance on chemical engineers than mechanical
Mechanical	Boiler design: SO_2/SO_3, higher possibility of deposition, coal dependent Coal issues: tube fouling, ash	Operational problems	
Mechanical	Reaction of NO and SO_2 in purification system to give SO_3. SO_3 mist in compressor will be fatal to compressor Other Issues: Critical quality issues	Compressor failure	

Top- down HAZID Record Sheet: Pre-Combustion Process

Keywords	Causes	Hazards/consequences/incidents	Comments
Fire	Carbon monoxide; critical concentration of CO can cause fire. (NB. Requires oxygen to be present, which there is not in a reducing atmosphere!). A very rich CO stream after gasifier expected.	CO fire	As CO is shifted the risk is lower than not taking CO out (as in-existing/traditional power generation processes)
Fire	Hydrogen	Hydrogen fire	Compared with no shift reactor the hydrogen concentration is higher (>40 % typical). Not a new hazard compared to oil refineries, ammonia plants etc

Top- down HAZID Record Sheet: Pre-Combustion Process			
Keywords	Causes	Hazards/consequences/incidents	Comments
Fire	ASU	Fires due to enhanced oxygen	Large size of ASU (quarter the size as for oxy but still large) Not a new hazard compared to oil refineries, steel plants etc
Fire	Burner control	Operational	Use nitrogen, gives bulk for mass flow in gas turbine. Also gives NOx suppression and blanketing
Fire	Rectisol	Rectisol fires	Selexol eliminates flammability issues associated with methanol (used in Rectisol process). No different to limestone/gypsum flue gas de-sulphurisation. Minimise amount of AGR process above the flash point of DMEPEG
Fire	Gas turbine enclosures (different to natural gas)	Hydrogen and CO fire	H_2 and CO detection Hydrogen rises to the top. Monitoring needed at different places Fire rating of the enclosure and of installed electrical equipment
Fire	Concentrated H_2S (inlet to Claus)	Corrosion of equipment Loss of containment leads to fire.	Not a new hazard compared to oil refineries etc
Explosion	Operating pressure	Loss of containment leading to explosion	More possibility upstream of shift rather than in the shift (482 C)?

Top- down HAZID Record Sheet: Pre-Combustion Process			
Keywords	Causes	Hazards/consequences/incidents	Comments
Explosion	Hydrogen embrittlement		Layout/congestion Parameters not really different but difference in modelling Hydrogen has more buoyancy and dilutes readily Material issues can be dealt with by intelligent design aspects as residence time, wall thickness etc. The issue is well known. Not a new hazard compared to oil refineries, ammonia plants etc
Explosion	Hydrogen compared to HC has very high propensity to detonate	Detonation	Avoid leaks, design with ventilation in mind, not a new hazard compared to oil refineries, ammonia plants etc.
Explosion	Gas turbine enclosures different for hydrogen and CO rich syngas. Hydrogen detection cross-sensitive to CO	Syngas explosion	Have to monitor for H_2 at top
Toxic	CO	Potential for CO release less than in standard system A pipe fracture would emit large amounts of CO	Not a new hazard compared to oil refineries, ammonia plants etc
Toxic	CO_2 stream going out of specification	Reduction in downstream safety case.	Venting of CO_2 would need design to prevent ground level asphyxiation/toxic hazards If outside of design limits, vent rather than capture the CO_2. Issue may be adequate real-time gas analysis? Plot trends and set 'alarm' levels for appropriate contaminants

Top- down HAZID Record Sheet: Pre-Combustion Process			
Keywords	Causes	Hazards/consequences/incidents	Comments
Toxic	COS/carbonyls	Toxic particulates	Well understood Not a new hazard compared to oil refineries, ammonia plants etc
Toxic	Heavy metals in ash	Toxic particulates	All heavy metals apart from volatiles (mercury and Arsenic for example) are frozen within the frit or removed in the quench water treatment plant. Volatile HMs are captured in the GAC filters
Toxic	Highly concentrated H_2S stream is produced	H_2S toxic release.	Not a new hazard compared to oil refineries etc
Electrical	As before		
Mechanical	Hydrogen embrittlement	Loss of containment of syngas leading to explosion	Design/material issues Maintenance procedures established to minimise potential for explosive or toxic gas release situations to occur
Mechanical	Coal conveyers Gasifiers	Particulates	Not a complex issue Some use coal/water slurry Others use dense phase in nitrogen or screw conveyers

Top- down HAZID Record Sheet: Post Combustion			
Keywords	Causes	Hazards/consequences/incidents	Comments
Fire	Flammability of amines	Amine fire	Flashpoints of amines are quite high (200 C) Need to assess if pure amine feed-stocks are flammable Amine processes: mostly proprietary
Fire	Amines susceptible to Sulphur, oxygen and NOx	Operational problems	
Explosion	Ammonia and CO_2 form solids, carbonates, which condense in cool parts of the system. Accumulates under the relief valves Ammonium sulphate is very sticky	Overpressure explosion	
Explosion	Flooding of big columns, can cause back-pressurising but not pressure release	Overpressure	Low pressure system; just above atmospheric
Toxics	Ammonia	Toxic release	Already present at most power stations
Toxics	Amines	Possible toxicity depending upon amine chosen	Constituents of flue gas may contaminate amines; O_2, SOx, NOx
Toxics	Fly-ash Mercury	Operability Aluminium components downstream-packing in absorber beds; may get corroded	In normal coal fired plants about 85-90 % captured More of operability, rather than safety issue
Electrical	Large compressors; lots of power needed to compress gas from atmospheric and therefore larger power requirements.	Electrical explosions Electrical shocks	
Electrical	Can loss of power initiate problems?	CO_2 release	Would shut down and vent to atmosphere

Top- down HAZID Record Sheet: Post Combustion			
Keywords	Causes	Hazards/consequences/incidents	Comments
Electrical	Start-up will require significant electrical capacity		
Electrical	Steam recovery system	Dry steam can give electrostatic charge build up	
Mechanical	Compression requirements will be huge. Several compressors might be used in parallel	Equipment design issues	

11.4 APPENDIX D: CHANGE HAZID TABLES

NB This brainstorm was on underlying issues rather than direct causes of hazards

Change HAZID Record Sheet: Post combustion capture

Keywords	Issues	Hazards/consequences/incidents	Comments
LAYOUT	Difficult to fit in Need 30 % more space than an existing power plant	Construction issues Lifting over live equipment Constraints on layout/separation	Typical 9 m diameter pipes, 20 m diameter column Older power plant standards led to relatively poor separation in power stations (New facilities are based on newer guidance and require more separation for HAZOP reasons) There may be large sunken areas around coalfields but most probably they would be unusable because of stability issues High voltage switch-houses cannot be easily moved as they are not owned by the power stations but by National Grid, along with the land they are on
LAYOUT	Unproven Technology	This scale of plant does not exist anywhere in the world, so the risks associated with scale-up are essentially unknown	The largest operational unit in Europe at the moment is probably the 24t CO_2/day at Esjberg power plant as part of the CASTOR project

Change HAZID Record Sheet: Post combustion capture

Keywords	Issues	Hazards/consequences/incidents	Comments
		Minimum increase in size over largest built is factor of six to ten	
LAYOUT	Anhydrous ammonia	Offices and Construction yard in close proximity to toxic chemicals	Space is going to be a constraint Amine and/or SCR can be an option but expensive
LAYOUT	Sulphur	Produced by some FGD processes Hazards from fire	No different from conventional FGD For amine units to properly work, FGD must be taken farther than sulphur rules by themselves dictate, as amines are destroyed by sulphur compounds (same for NOx)
LAYOUT	Power station design	Asphyxiation/toxic effects of CO_2 release in confined space	Power stations have extensive tunnels under turbine hall for cabling etc People may be present and there would be inadequate ventilation to cope with CO_2 ingress, which could concentrate there Escape would be difficult

Change HAZID Record Sheet: Post combustion capture			
Keywords	**Issues**	**Hazards/consequences/incidents**	**Comments**
LAYOUT	Railways adjacent to power station, can be hazardous if CO_2 line is laid too close to a railway line	Derailment can be a cause of escalation to process Risk of CO_2 blowing on to main line areas and affecting passengers on the trains	Coal delivery trains go very slowly HAZOP studies will be required
LAYOUT	Coal	Coal dust can contaminate ASUs and cause fire/explosion (but not an issue for Post-combustion capture)	Layout important and well-understood Space may be an issue
LAYOUT	Natural gas pipelines	Possible interaction/escalation potential of a Natural Gas explosion leading to CO_2 release	This won't be any different than at a current CCGT plant
LAYOUT	Size of amine towers for capture of CO_2	Can such large towers be specified to give adequate corrosion resistance and prevent LOC?	Concrete towers for amines, on same lines as cooling towers, can be rubber-lined or stainless steel and should be possible
LAYOUT	Hydrogen cooled alternators in power station	Potential for H_2 explosion and possible escalation	No different from the present situation
LAYOUT	Water treatment plants (NaOH)	None identified	No different from the present situation

Change HAZID Record Sheet: Post combustion capture

Keywords	Issues	Hazards/consequences/incidents	Comments
LAYOUT	Dosing (chlorine) of water systems	Escalation potential	No different from the present situation
LAYOUT	Finding suitable time point(s) on power plant for commissioning; in terms of redirecting duct flow-chimney and redirecting back	Operability	Retrofitting of CCS plant will be required to be contained to within normal plant maintenance outages
LAYOUT	Fabrication of new equipment at live plant	Cause of LOC e.g. dropped load Ignition sources	Welding, lifting etc at heights It might be possible that because of space constraints, fabrication of new equipments might be in congested areas
INTERFACES	Bypass dampers to emit CO_2- instead of storage. This option will be driven by commercial decisions e.g. depending upon price the CO_2 may be emitted and more energy put to electricity generation	Release of CO_2 to atmosphere (environmental hazard)	It might have big louvers to close the plant off In case pipeline is idle and CO2 must be diverted, then diversion would most likely be to stack, which is what happens today, and not be captured, which would mean NO hazard

Change HAZID Record Sheet: Post combustion capture

Keywords	Issues	Hazards/consequences/incidents	Comments
INTERFACES	Isolation requirements for maintenance How to isolate very big ducts containing CO_2	Asphyxiation hazard to maintenance workers	Duct may be square with steel flaps/dampers/spade Flaps/dampers will leak to some extent, so no good for isolation for maintenance; use of bolt-in spade can be an option
INTERFACES	An amine-based system will need a purge to purge the salts	Hazardous waste might be produced	Specialist treatment needed: some 'special waste' will be produced
INTERFACES	Could be issues with vacuum and pressure	Over/under pressure	Design issues Would normally operate boiler under slight vacuum Preferable to put fan before the absorber so that absorber does not have to be designed for partial vacuum. This may be particularly difficult for large diameter vessels.
INTERFACES	Power supply	Electrical hazards	Power station has existing heavy electrical infrastructure. If this is already at, or close to capacity, additional substation may be needed

Change HAZID Record Sheet: Post combustion capture

Keywords	Issues	Hazards/consequences/incidents	Comments
INTERFACES	Extra steam requirements from the boilers for regeneration	Operability issues e.g. control of the LP turbine	Redesigning would be needed to some extent The operating regime at power station may change Reluctance to shut-down/start-up
INTERFACES	Cooling water/ drainage	Will classification of drainage change?	Amine drainage or bunds may be needed
INTERFACES	Control systems may be of older technology on older power plant Some new systems based on different operating systems etc might be needed Adding different systems is human factors problem	A mix of old and new control systems not ideal Integrating old with new and SIL rating it. There will be issues about how will two systems interact? There will be a mix of interfaces/alarm systems and issues with SIL rating interfaces Human factors issues for control room operators. Issues will be with fitting new control equipment to already congested control rooms Some existing control systems built around obsolete computer operating systems with minimal current support	Refineries may be better acquainted than power stations with these systems An existing power station might be too old for this to be worthwhile! CCS might be feasible if boiler is replaced but this means 2-3 years outage

Change HAZID Record Sheet: Post combustion capture

Keywords	Issues	Hazards/consequences/incidents	Comments
ORGANISATIONAL FACTORS	New technology	Competence	Getting old staff to sit with new recruits Retention will be an issue- keeping in mind the current shortage of qualified engineers
ORGANISATIONAL FACTORS	Training needs	Competency issues	Availability of engineers Retention issues, trained personnel will be vulnerable to be recruited elsewhere
ORGANISATIONAL FACTORS	Knowledge issues	Universities to introduce suitable modules. Integrated CCS processes should be mentioned on Chem. Eng courses in the context of important chemical processes Interaction of chemical process with power generation needs to be covered. Ongoing professional training: needs to be appropriate courses available Should demo projects be offering 1 week placements? Short and sharp. At operator/foreman level? There may be an issue of who, with experience, will be able to provide meaningful tuition?	In most industry settings, specific training is taken on job and safety and other training is function of ongoing work

Change HAZID Record Sheet: Post combustion capture

Keywords	Issues	Hazards/consequences/incidents	Comments
ORGANISATIONAL FACTORS	New feedstocks	Competency issues	New feedstock will be vetted before they can be used in everyday situations and should be part of any training procedures IF they require special considerations/handlings
ORGANISATIONAL FACTORS	Language issues e.g. construction workers	Human factors/communication issue	An example was quoted of non-English speaking construction crew as being excellent. Language not big issue as the supervisor knew both the languages
ORGANISATIONAL FACTORS	Lack of existing experience; no one operates at this scale	Competency issues	Joint ventures so that new capture process operated/managed by organisation with chemicals experience?
ORGANISATIONAL FACTORS	Control of contractors		Already dealt with in industry. Just have to teach current incumbent staff that now its new chemicals and related procedures onsite. It would be good if staff could be trained at pre-construction/construction/ commissioning stage

Change HAZID Record Sheet: Post combustion capture			
Keywords	**Issues**	**Hazards/consequences/incidents**	**Comments**
ORGANISATIONAL FACTORS	Organisational interaction between personnel at carbon capture plant, pipeline and plant	Conflicting priorities of different parts of plant Possible non-compliance if CCS system is turned off and CO_2 is vented through stack	Grid system; how flexible does it need to be? Will CCS be turned off if not economic and will pipeline operation be flexible – e.g. line-packing (similar system for natural gas – but have more storage in system than for the NG) Regulation e.g. deep political questions Trade offs. Continuity of power supply or of CCS- could eventually be pressure to shut down non-CCS facilities

Change HAZID Record Sheet: PRE-COMBUSTION CAPTURE

Keywords	Issues	Hazards/consequences/incidents	Comments
Some of the issues mentioned for post-combustion can also be applicable for pre combustion-these should be read in conjunction. Only the issues specific to pre-combustion are presented here			
LAYOUT	ASU has to be kept away from any combustibles, layout issue with power station	Explosion	Could build ASU next door to existing IGCC and then retrofit. If built next to existing power station then would have boundary fence between them
LAYOUT	Hydrogen production	Explosion following LOC Desire to minimise congestion	Gasifier can be operated remotely and hydrogen can be supplied through a pipe
LAYOUT	Hydrogen pipelines	Explosion following LOC	Standard practice Minimum congestion to stop detonating Hydrogen distribution network to sell hydrogen. Hydrogen emerges at pressure above 25 bar (no need for compression) If provided as ‘green’ fuel 85% hydrogen acceptable, but for purity levels required by a refinery, PSA may be used Outside of the scope of the present exercise

Change HAZID Record Sheet: PRE-COMBUSTION CAPTURE

Keywords	Issues	Hazards/consequences/incidents	Comments
INTERFACES	Nitrogen pipes	Huge flow rates – asphyxiant	N_2 line would be new. Big leak could be a hazard; in emergency could be vented back to atmosphere but would require suitable design. This is not very different from other installations where there is bulk nitrogen present (e.g. ammonia) Oxygen 20 %, 80 % will be nitrogen
INTERFACES	Interface with ASU	Enhanced combustion in presence of oxygen	Layout requirements are well understood
INTERFACES	Forced ventilation in gas turbine buildings, in case of hydrogen major release	Flammables Asphyxiation	Gas turbines themselves are in a hood, GT burning CO and H_2 mix has instrumentation in roof and floor to detect leaks. For H_2 only, the instrumentation is in roof only
INTERFACES	Vibrations in gas turbine	Noise	Vibration on GT is very low Sound levels: planning permission will deal with sensitive receptors distant from the site; no areas will have local levels above 80-85 dbA at 1 m
INTERFACES	Selexol or any other physical solvents		Mist guards

Change HAZID Record Sheet: PRE-COMBUSTION CAPTURE

Keywords	Issues	Hazards/consequences/incidents	Comments
INTERFACES	Bypass dampers to emit CO_2 – instead of storage. Commercial option. What does this mean…commercial option? This option will be driven by commercial decisions e.g. depending upon price the CO_2 may be emitted and more energy put to electricity generation		Covered under post-combustion capture
INTERFACES	Isolation requirements for maintenance. How to isolate very big ducts? Not sure context here – in context of very big ducts containing CO_2. Could be issues with vacuum and pressure		Covered under post-combustion capture
INTERFACES	Power supply		Covered under post-combustion capture
INTERFACES	Extra steam requirements for the boilers		Covered under post-combustion capture
INTERFACES	Cooling water/drainage		Covered under post-combustion capture
INTERFACES	Control systems, old ones run on CEGB system How does this apply for hazard? Some new systems based on different operating systems etc might be needed. Adding different systems is human factors problem		Covered under post-combustion capture

Change HAZID Record Sheet: PRE-COMBUSTION CAPTURE

Keywords	Issues	Hazards/consequences/incidents	Comments
ORGANISATIONAL FACTORS	Availability	Operability	Can be addressed by choosing different equipment. Getting better, up to 80 % these days
ORGANISATIONAL FACTORS	New skill sets will be needed with requirements of new training	Competence issues	The risks are more from the chemical processing side
ORGANISATIONAL FACTORS	Competence issues	Competence issues	Skill shortage in design People who can understand design for checking/peer review Oil/gas industry standards (use independent competent persons who can carry out design review)
ORGANISATIONAL FACTORS	Contractors	Competence/interface issues	Try to transfer skills and experience from last job to new job/technology; it might not necessarily be what is required
ORGANISATIONAL FACTORS	Scale shift in the CO_2 removal part of IGCC e.g.1475 t/day IGCC is different to standard power plant.	Competence issues	Large scale IGCCs are different to ordinary power plant Similar competence issues for operation and maintenance as for design will be there Multi-disciplinary team needed initially but with regular review as

Change HAZID Record Sheet: PRE-COMBUSTION CAPTURE

Keywords	Issues	Hazards/consequences/incidents	Comments
			this may be scaled down later as experience gained
ORGANISATIONAL FACTORS	Maintenance and spares	Issues with cross contamination e.g. sweet/sour	Spares should be readily available. Care not to mix those for sweet/sour service Process critical operations can be highlighted in the design

Change HAZID Record Sheet: OXY COMBUSTION

Keywords	Issues	Hazards/consequences/incidents	Comments
Some of the issues mentioned for post-combustion can also be applicable for Oxy-combustion-these should be read in conjunction. Only the issues specific to Oxy-combustion are presented here			
LAYOUT	Pulverised fuel/coal	If high surface area available it can explode in excess oxygen atmosphere (ASU)	Layout issues well understood Coal mill is integrated with boiler
LAYOUT	Remote ASU	LOC from O_2 pipeline Enhanced combustion in O_2 enriched atmosphere	There would be space constraints for this size of ASU required (approx 46,000 metres square needed for 1.5 GW)

Change HAZID Record Sheet: OXY COMBUSTION

Keywords	Issues	Hazards/consequences/incidents	Comments
		Remote ASU requires cross-country pipeline	Space requirement can be up to the size of power station itself Established technology for buried pipelines. PD8010.1 applies
LAYOUT	Oxygen pipeline failure Cryogenic storage failure	Enhanced combustion in O_2 enriched atmosphere	The issue here is not only storage of liquid oxygen, but also the sheer volumes that would need to be stored in order to make any difference to a 500 MW unit, which will consume about 435 tonnes/hour[1]
LAYOUT	Boiler issues	Asphyxiation of operators due to high CO and CO_2	Small boilers will be required to operate under slight pressure, not suction Not safety-practical to operate boilers for greater than 800-1000 MW to operate at positive pressure. Results awaited from Callide and Lacq projects Air ingress in boilers is a fact of life and 5-7% is usually allowed. This will be tolerable but by no means

[1] "Oxy-Combustion Processes for CO_2 Capture From Advanced Supercritical pf and NGCC Power Plant", D J Dillon, R S Panesar, R A Wall, R J Allam , V White, J Gibbins & M R Haines

Change HAZID Record Sheet: OXY COMBUSTION

Keywords	Issues	Hazards/consequences/incidents	Comments
			ideal, since this could be handled by CO_2 processing unit Boiler shut-down will require purging (with air) and sensors for CO/CO_2
LAYOUT	CO_2 clean up, where should it be done?	Corrosive nature of flue-gas stream	If liquefy CO_2 to dry, it might best be done at ASU which may be remote. However, it would be very impractical to clean up CO_2 in this fashion. Cleanup must be in location where compression exists. If so, the 7-10 bar or so flue gas could be in plastic (due to corrosion issues) lines up to 5-10 km May need multiple parallel pipelines –to limit diameter OR 1st stage separation/drying at power station so that can use carbon steel pipe Design issues - all can be very safely done in today's environment
LAYOUT	Venting of CO_2	Asphyxiation/toxic hazard	If have to vent CO_2 up stack (in case of say non-availability of pipeline), heavy cold cloud will tend to slump. Velocity of pure CO2 will be low

Change HAZID Record Sheet: OXY COMBUSTION

Keywords	Issues	Hazards/consequences/incidents	Comments
			compared with starting up on air. Multiple flue ducts might mitigate this (use less for CO2 venting). Pressure will be near ambient and CO_2 will be very moist after FGD. In one power plant (Drax), stack is lined with titanium Further analysis/interface with local environment will be needed Acid gas incompatible with refractory-lined stack If retrofit, need to look at stack dispersion again
LAYOUT	Start up		Have to start on air firing ∴ need stack for full volume. (Need to build up recycle.)
LAYOUT	Implication of large vessel and duct sizes	Difficulty in designing to be leak tight Asphyxiation/toxic hazard	Large size of flue gas recycle duct and vessels in FGD plant. Has to be started air fired and thus the stack has to be of the size to take the full volume. Further analysis on stack dispersion needed

Change HAZID Record Sheet: OXY COMBUSTION

Keywords	Issues	Hazards/consequences/incidents	Comments
ORGANISATIONAL FACTORS	Contract for supplying O_2	LOC of O_2 storage	Contract may require uninterruptible supply with big cost penalty. If so, would need more buffer storage and more trains for redundancy Would also want must-take contract for O_2. May be electricity-supply linked
ORGANISATIONAL FACTORS	O_2 pipeline and power line	Operability	May not be in same trench because of tendency to want to keep going if a problem due to cost penalties
INTERFACES	CO_2 is very moist when it comes out of FGD Needs to be given buoyancy and is very corrosive	Asphyxiation/toxic hazard Corrosion/escalation	Though CO_2 itself will be contained for majority of cases in closed loop from combustion through to turbine then on to separation (from steam) to cleanup (H_2O removal) and then to compression, there will be need to lookout during design and later stages for where upset may occur

Change HAZID Record Sheet: PIPELINE

Keywords	Issues	Hazards/consequences/incidents	Comments
LAYOUT	Above ground/below ground	LOC of CO_2 Asphyxiation/toxic hazard	Above ground – several problems - Liquid expansion and need to vent - Terrorism - 3rd party damage (helicopters have to overfly route every 2 weeks to look for 3rd party damage. Higher freq in USA) Buried - Uniform temperature but can't have same visual inspection. Interior pipe inspection via pigs is coming of age at this moment Otherwise no different than any other pipeline consideration. Hazard same
LAYOUT	Pressure build-up	Overpressure	Might need relief points on dense phase line. Worldwide temperature can be a major issue. Relief design will need to reflect local temperature and temperature variations
LAYOUT	Roads/physical features	Asphyxiation/toxic hazard	Can use fibre optics but can't run them through tunnels etc under roads with pipe so integrity of fibre optics compromised

Change HAZID Record Sheet: PIPELINE

Keywords	Issues	Hazards/consequences/incidents	Comments
			Standards take into account road and rail crossings etc. Valleys should be avoided, should go through river plains at 90°- standard practice for pipelines. Avoid hollows that can be easily avoided
LAYOUT	Cracks/Wear and Tear No difference from any other type of metal pipeline built with similar pipe.	Asphyxiation/toxic hazard	CO_2 pipelines can rupture from excessive pressure and nature of CO_2 molecule may create longitudinal fractures Crack arrestors can mitigate and do so in CO_2 pipelines which are in service today. Metallurgy/pipe wall thickness solutions may be preferable to crack arrestors.
LAYOUT	Access to and maintenance of valves	Asphyxiation/toxic hazard	Block valves are easy to put above ground but will most probably only be at booster stations. If placed in a pit/structure below ground there will be risk of filling it with CO_2 - then it might be hazardous area for service personnel. Also even for a small leak in a pit, the risk of accumulation would be greater, CO_2 being heavier than air.

Change HAZID Record Sheet: PIPELINE

Keywords	Issues	Hazards/consequences/incidents	Comments
			Put valves, booster stations in fence. Places in areas with minimum population. It should be ensured that CO_2 not exposed to increase in heat/pressure. If line idle then in areas with concern, it should be ensured that release valves or other pressure reduction safety measures are installed
LAYOUT	CO_2 capture networks of pipelines - network of pipelines in CO_2 capture and transport service Several pipes join: need separate pigging stations at size changes/joints in pipes Every so often depending upon pipe size, booster station might be needed	Construction safety issues for new pipelines (next to live pipeline) Not an issue of CO_2 pipeline safety - issue of ALL pipelines	Build sequentially This is not a CO_2 issue. Under construction there will be no CO_2 present. Therefore, this is a standard safety issue that applies to all lines. In operation, it is the same because safety procedures must ensure all lines identified before digging begins This should be taken care of in standards and design manuals and shouldn't be any different from any other network of pipelines Need adequate separation to avoid digging up 1st pipeline when laying 2nd

Change HAZID Record Sheet: PIPELINE

Keywords	Issues	Hazards/consequences/incidents	Comments
LAYOUT	Hazard distances	Asphyxiation/toxic hazard	Awaiting dispersion information to decide on layout, distance for people etc
LAYOUT	Pigging	LOC of CO_2 Operational issues	Pigs get stuck. Properly designed purpose-built pigs must be used for CO_2 service Arrangements to prevent depressurisation and development of successful design for CO_2 service will be required
INTERFACES	Authorities that would be involved		Local authorities Landowners Other service providers Construction companies Rail companies Regulators
INTERFACES	Interfaces	Operability problems which could lead to loss of control	Network control will be needed. Best model is one organisation completely in control of pipeline Current CO_2 pipeline operations systems are exactly the same as for all other types of complex pipeline system and use state of art SCADA

Change HAZID Record Sheet: PIPELINE

Keywords	Issues	Hazards/consequences/incidents	Comments
			systems. This is not unique to CO_2. However leak detection may not be as accurate in view of the properties of supercritical CO2. Need to know what tolerance level is. Density varies a lot with pressure so simulation to calculate inventory may not be so easy.
INTERFACES	Network control interfaces: smaller suppliers of CO_2	Operability problems which could lead to loss of control	All suppliers of CO_2 need compression and clean-up. Some may share with larger facilities The difference from any multiple injection point pipeline in use today will be that in this case product composition can be very varied-owing to different capture options Pipeline quality specifications must be designed and adhered to for all issues Issue on ensuring consistent quality of CO_2 – contaminant minimisation
INTERFACES	Interface with injection facilities	Operability problems which could lead to loss of control	Couplings etc and emergency response should be designed for CO_2

Change HAZID Record Sheet: PIPELINE

Keywords	Issues	Hazards/consequences/incidents	Comments
ORGANISATIONAL FACTORS	Management	Operability problems which could lead to loss of control	Dedicated pipeline managing teams/companies can be an option (probably also for offshore injection?)
ORGANISATIONAL FACTORS	Competence	Lack of competence leading to loss of control	Some enterprises might be interested in owning offshore injection platforms with little prior experience
ORGANISATIONAL FACTORS	Competence	Operability	EOR potential of different wells varies considerably EOR would be applied on a field wide or specific area, group of wells or single well operation within control of one entity which would have expertise to do so

Change HAZID Record Sheet: INJECTION

Keywords	Issues	Hazards/consequences/incidents	Comments
LAYOUT	Retrofit into existing offshore facility: existing jacket/separate jacket	Escalation from/to existing platform operations, hydrocarbon hazards etc	Ideal would be to put on separate jacket. Maybe use Normally Unattended Installation, NUI as standalone facility When existing in-service platform goes obsolete for drilling oil but is still needed for sequestration, then entire platform will have to be kept maintained for as long as it is used for sequestration
LAYOUT	Availability of space	Congestion, which could increase existing hydrocarbon hazards	May have to do much of compression onshore. Explosion due to hydrocarbons may get worse due to added equipments at already congested offshore platforms Some platforms could have CO_2 removal/compression on them Structure/equipment needs to be designed for sublimation temp of CO_2
LAYOUT	Possible use of Floating Production Storage and Offloading Vessels (FPSOs)	Contained volume that could fill with CO_2 Asphyxiation/toxic hazard	FPSOs also weather vane so that toxic hazards tend to remain on board

Change HAZID Record Sheet: INJECTION

Keywords	Issues	Hazards/consequences/incidents	Comments
			FPSOs would have to be redesigned to incorporate CO_2 in the way that field development would dictate Storage area at present is more toxic because of OIL than would occur with CO_2 and anyone in that area would already be wearing protective breathing apparatus
LAYOUT	Injection pressure	Overpressure	High injection pressure may be required to overcome reservoir pressure and start flow. Needs to be accounted for in design
LAYOUT	Utilities	Hazards including electrical, fuel fires	Umbilical may come from another platform for power Limitation to how far power line can be run
LAYOUT	Contingency planning	Operability	EOR may not be available
		Venting CO_2 (environmental hazard or regulatory non-compliance) if injection not available	Buffer with saline reservoir or depleted gas reservoir?
INTERFACES	Pipeline operators	Operability problems which could lead to loss of control	Lots of operators of different fields. Each will have particular CO_2/EOR regime Main pipeline will be isolated. No different from operation

Change HAZID Record Sheet: INJECTION

Keywords	Issues	Hazards/consequences/incidents	Comments
			of natural gas system
INTERFACES	Pressure difference issues	Operability Overpressure	Reservoir pressure can be low to start and will build Need pressure control at well head and clear understanding of pressure limitations of equipment For EOR, pressures are different as oil is at different depths and porosity of rocks differ
INTERFACES	Injection methods	Operability Overpressure	Different injection methods for EOR – some may not be compatible with requirement for constant flow of CO_2 Some reservoirs could collapse if get well pressure wrong and it flashes underground Some reservoirs will have to be throttled
INTERFACES	Back reverse flow; from reservoir to pipeline	Unwanted flow from the reservoir. Dense phase CO_2 being super-solvent, anything coming into it can be undesirable/possible toxic hazard	Will need overpressure and backflow protection More or less standard for gas wells anyway. Needs to be appropriate for CO_2

Change HAZID Record Sheet: INJECTION

Keywords	Issues	Hazards/consequences/incidents	Comments
INTERFACES	Contingency planning	Venting CO_2 (environmental hazard) if injection not available	If too much CO_2 for EOR, need back-up options. Many interfaces would be needed. Need somewhere else to store as a buffer, e.g. saline aquifer. CO_2 could be returned from saline aquifer for use for EOR Any project for EOR only will use ONLY enough CO_2 for EOR and oil production. All other CO_2 will be sent elsewhere. Recycled CO_2 after breakthrough will be part of project design Project should be designed, whether CO_2 EOR, EOR with storage, pure storage, to anticipate or allow for overflow/alternate storage location in event of lack of flow space Ultimate backup and contingency plan is to vent enough CO_2 into atmosphere to ensure no damage to equipment Venting can be accomplished with air injection nozzle to ensure CO_2 mixing with air

Change HAZID Record Sheet: INJECTION

Keywords	Issues	Hazards/consequences/incidents	Comments
ORGANISATIONAL FACTORS	Regulations	Lack of regulation leading to lack of control	Offshore storage could be more complicated than onshore Injection is likely to be heavily regulated In USA, CO_2 pipelines are governed under the US Department of Transportation hazardous liquid pipeline regulations as well as State regulatory bodies
ORGANISATIONAL FACTORS	Maintenance of H&S standards, Safety Management System	Loss of containment Structural failure	Problems of ageing installations without benefit of oil revenues to pay for maintenance etc When existing in-service platform goes obsolete for drilling oil but is still needed for sequestration, then entire platform will have to be kept maintained for as long as it is used for sequestration
ORGANISATIONAL FACTORS	Long term life of project	Need to achieve long-term management, maintenance etc	Consideration will be needed for 'What to do after oil is finished and no scope for EOR'? There could be a small module attached to the main module and all it is doing is just compression while requiring the main platform to be painted

Change HAZID Record Sheet: INJECTION

Keywords	Issues	Hazards/consequences/incidents	Comments
			inspected and maintained Need separate considerations for onshore versus offshore. Also for EOR versus pure storage. Guidelines and regulations would be written beforehand to ensure that prudent operator performs in workmanlike manner and obeys regulations Would need fundamental look at lifetime of EOR projects and beyond EOR. Possibility of decommissioning of parts of the existing platform functions as they become no longer required Regulations would also apply to subsurface abandonment and site closure as well as handover to long-term storage regulatory agency After EOR life, if field has been operated as both EOR and storage facility, then operator would modify storage locations to maximize CO_2 storage. If CO_2 used for EOR only, CO_2 storage would be minimised (that is oil company would use as little CO_2 as possible to produce as

Change HAZID Record Sheet: INJECTION

Keywords	Issues	Hazards/consequences/incidents	Comments
			much oil as possible), and when project ended, field and wells would be plugged and abandoned with CO_2 in place, subject to governmental regulations as is now the case. MMV would be part of that equation. Applies to both onshore/offshore operations

11.5 APPENDIX E: BOW-TIE DIAGRAMS

Bow-tie diagrams provide a systematic and structured way of analysing risk control measures to ensure that protection is available for all initiating events. The risk control measures may be termed 'barriers', 'lines of defence' or 'layers of protection'. The reason for initiating a Risk Assessment (RA) will often be the loss of degradation of one or more barriers, the introduction of a new hazard, or a change to the exposure of personnel.

Bow-tie diagrams can be presented in different ways. An outline example is shown in Figure 12. The diagram shows the development of an incident (usually a loss of containment event), from various possible initiators to various possible outcomes. Barriers to the development of the incident are shown on the diagram. The left-hand side can be seen as a simplified fault tree and the right-hand side as a simplified event tree.

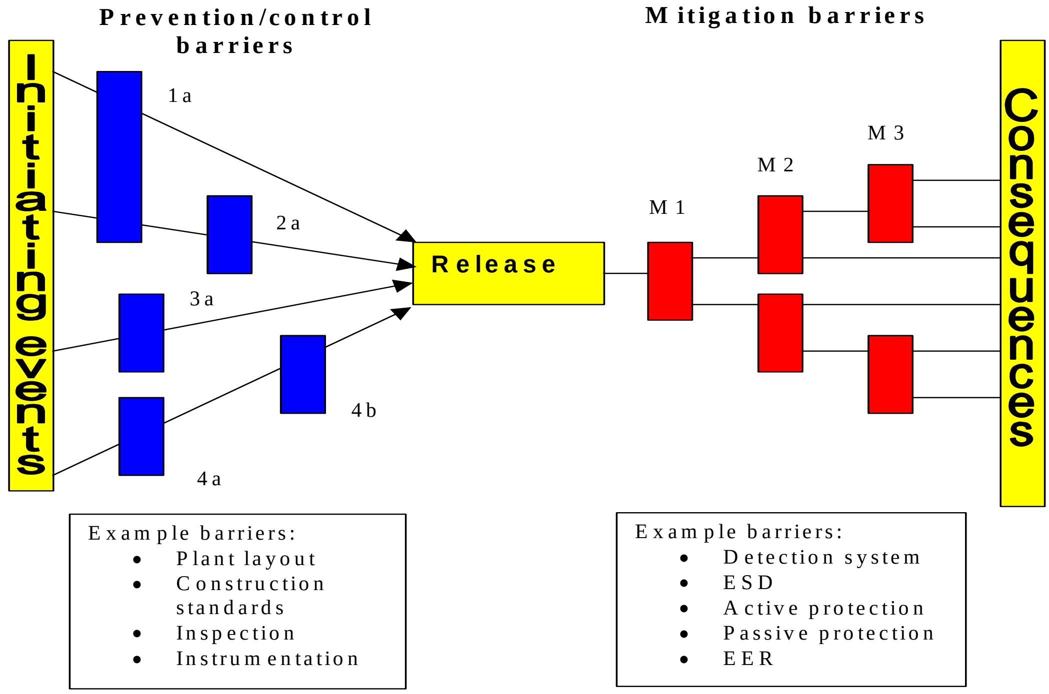

Figure 12 Example bow-tie diagram

The construction of a bow-tie diagram entails the following stages:

1. Definition of the event for which the bow-tie diagram is to be constructed. This will depend on the reason for carrying out the ORA. This will usually be loss of containment of a particular inventory. This event forms the centre (knot) of the bow-tie.

2. Brainstorming and identification of initiating events (or threats) for the loss of containment event. The usefulness of the analysis will depend on the completeness of this identification of initiators. Such initiators may include (but may not be limited to) those in the table below. Initiators are not necessarily root causes. They are events, which could initiate an accident.

3. For each initiating event, identifying and brainstorming barriers. For example:
   - Barriers to overfilling could include a basic control system, high-level trips, operating procedures etc.
   - Barriers to corrosion failure could include quality assurance of specification, inspection regime, sacrificial anode system etc.

4. These barriers may be shown on the bow-tie diagram between the initiating event and the loss of containment event. In some cases the same barrier will be common to several initiators.

5. Brainstorm all the possible outcomes of the loss of containment event, i.e. the event tree. Possible outcomes may include fires, explosion, toxic clouds etc.

6. Brainstorm the mitigation barriers, which mitigate the different outcomes. For example:
   - Fire might be mitigated by gas detection/emergency shut down valves which limit the quantity released, exclusion of ignition sources, fire detection, deluge systems, passive fire protection to prevent further escalation etc.
   - Explosion might be mitigated by gas detection/emergency shut down valves which limit the quantity released, exclusion of ignition sources, design to minimise confinement and congestion, blast walls to prevent escalation.

7. The initiators, loss of containment event, outcomes and barriers can then be assembled into a bow-tie diagram. Various software is available which can assist with this.

The bow-tie diagram provides a summary of all the barriers in place to prevent and mitigate the event being analysed. It facilitates the identification of initiators with no or few prevention barriers and outcomes with no or little mitigation. This allows consideration of further risk reduction to focus in places where it will be of most benefit. It also promotes a systems approach in which all initiators are considered.

11.6 APPENDIX F: PRECURSOR TABLES FOR THE DEVELOPMENT OF BOW-TIE DIAGRAMS

11.6.1 Loss of containment of CO_2

	Causes	Barriers	Consequences	Mitigation Barriers
1	Undersea: additional corrosion rates	Prevent free water		
2				
3	Catastrophic failure of pipelines - Pressure energy release causing longitudinal ripping	CO_2 pipelines buried deeper Crack arrestors Metallurgy solutions		
4	Land slip can cause shear, can be catastrophic	Designs and control systems to shut pipeline off		
5	Third party intervention	Control systems to shut pipeline off		
6	Explosive decompression of valves			
7	Injection stops	Back-up and line pack Venting/safety valves/design consideration Emit back at source	For underground injection, temperatures would be around 28 deg C, if stopped then temperature and pressure go down Environmental issues with pipe venting Sudden concentration of CO_2 in an area	
8	Venting of CO_2	Vent tip design to entrain air, sprays 20 times air at source; can be an option	Different from emitting as concentration would be high If have to vent CO_2 up, stack (in case of say non-availability of pipeline) will slump Pressure will be near ambient and	In one power plant stack is lined with titanium Further analysis/interface with local environment will be needed Cannot put acid gas up refractory-line stack

	Causes	Barriers	Consequences	Mitigation Barriers
			CO_2 will be very moist after FGD	If retrofit, need to look at stack dispersion again
9	Corrosion	Prevent free water		
10	Digger causing rupture of pipeline	It might go straight up in air		
11	Longitudinal ripping	- Modifications to steel - Crack arrestors (will work sub-sea as well) - Steel bends with concrete		
12	Retrofitting existing pipelines	All equipments and ancillary parts suitable for the service range		
13				
14	Other issues: Drying: For oxy possible reaction: NO + SO2 → SO3.	Cold climates - for North Sea, hence CO_2 needs to be superdry and very pure to prevent free water or hydrate formation	Might need glycol Will be captured in final CO_2 specifications	
15	Welding operations on CO_2 pipelines	Procedures		
16	Escalation from explosion			
17	Fire in Condenser			
18	Interaction between pipeline and HT line			
19	Expansion loop system (pipelines)	Design. Similar pipelines exist for supercritical ethylene, problems known	Expansion loop might get very hot or cold. It does not like temperature changes	Mitigations should be stressed in report Bellows cannot be an option at 100 bars
20	Combustion explosion or pressurised CO_2 release	Existing hydrocarbon explosion reduced by CO_2	If it explodes there is lot of head pressure, it does not dissipate like LNG Escalation from CO_2 explosion, can cause HC fire, which may lead to fire + explosion	Air products have rules for locked-in volumes
21	CO_2 BLEVE,	Choice of operating		

	Causes	Barriers	Consequences	Mitigation Barriers
	resulting in projectiles	conditions		
22	Exploding pigs: CO_2 can permeate plastic etc, when taken out it can explode	-Improvement in technology -Pressure relief at pig receiver		
23	Catastrophic failure of pipelines - pressure energy release causing longitudinal ripping	-CO_2 pipelines buried deeper -Crack arrestors -Metallurgy solutions		
24	Interaction between carbon capture plant, pipeline and plant There will be issues of trade offs- Continuity of power supply or of CCS. Eventually there could be pressure to shut down existing	Grid system; how flexible it needs to be? Will CCS be turned off if not economic? Will pipeline be flexible? (Similar system for natural gas – but have more storage in system than for the NG) Regulation e.g. deep political questions 60 months to get new turbine & $50m deposit		
25	-Boiler issues Boiler - must now (in Oxy) operate under slight pressure not suction -Airtight boiler shells would be needed to avoid asphyxiation to operator as boiler's atmosphere is more of CO_2	Leak tightness of boiler Boiler shut-down will require purging (with air) and sensors for CO_2	Leak tightness of boiler Boiler shut-down will require purging (with air) and sensors for CO_2	

11.6.2 Loss of containment of oxygen

	Causes	Barriers	Consequences	Mitigation Barriers
1	Oxygen storage can be	Covered by		

	thousands of tonnes.10,000 t/d is approximately required for 1000 MW	COMAH regulations Makes little sense to store O_2 (capital costs, safety issues) 7000 t/d is air pdts standard		
2	Detonation: will take aluminium with it and most of the unit as plants are made of aluminium	ASU configuration		
3	Enhanced combustion in ASU: 40% and above CO_2 causes problems. Also velocity limitations			
4	Coal dust explosions			
5	Oxygen pipeline failure			
6	Contract for supplying O2 may require Uninterruptible supply with big cost penalty			Would need more buffer storage and more trains for redundancy
7	Cryogenic storage failure			
8	Unfamiliar technology			

11.6.3 Fire

	Causes	Barriers	Consequences	Mitigation Barriers
1	Injection compressor fire			
2	External power supply to injection compressor			
3	Pig launcher could bring out/come out of something that is flammable			
4	Hot tapping, different procedures			
5	Booster station fire: In some parts booster station will be driven by oil/gas	Regulators might limit possibility to have dense phase CO_2 in urban areas		
6	Gas turbine fires			In case of lube

	Causes	Barriers	Consequences	Mitigation Barriers
				oil fires in existing power plants it is commercial decision whether to shut down; will be no different for CO_2
7	Hydrocarbon fire			
8	Flame stability, issues with flare-out No safety data sheet on CO_2 - O_2 mixture			
9	Intrusions of HC in ASU or say pure O_2; particulates intruding ASU in case of oxy coal	Layout		
10	IR flame detection not applicable (CO_2 prevents hydrogen detection)	Honeywell IR band		
11	Fire in condensor (oxy-combustion)	Problem well understood		
12	Carbon monoxide; critical concentration of CO can cause fire A very rich CO stream after gasifier expected (pre-combustion)	The risk should be lower than not taking CO out		
13	Hydrogen in pre-combustion			
14	Selexol/Rectisol	Both are physical solvents. Selexol is non-flammable		
15	H_2 and CO detection CO sinks to bottom and hydrogen moves to top Gas turbine enclosures will be different	Monitoring needed at different places Fire rating of the enclosure		
16	Concentrated H2S (inlet to Claus)			
17	Flammability of amines	Flashpoints quite high (200 C) Need to access if pure amine feedstock are flammable		

	Causes	Barriers	Consequences	Mitigation Barriers
18	Amine processes (mostly proprietary).			
19	Electrostatic ignition -When electrical conductivity < 50 μohm then electrostatic hazard possible	Standards of construction and design		
19a	-If CO_2 is a non-static liquid then electric charge may generate -Electrostatic hazard also exists for dry CO_2 -CO_2 for purging vessels can give ice crystals (95-98 % pure) at nozzle and generates electrostatic Steam recovery system: dry steam can give electrostatic			
20	Huge electrical power requirements e.g. compression, (MW machines)	Would not be any different from existing power stations		
21				
22	Interaction between pipeline and HT line			

11.6.4 Explosion scenarios

	Causes	Barriers	Consequences	Mitigation Barriers
1	Hydrocarbon intrusion in ASU	ASU configuration		
2	Coal dust explosions	Would not be any different, will depend on fuel type and milling design		
3				
4	Increase in volume due to heat/expansion	In a pipe CO_2 has to be liquid, it would not be in vapour phase However, at point of injection consideration should be given to this		
5	If lot of sunlight it will expand	It should be kept moving		
6	Combustion explosion or	Existing	If it explodes there	Air products

	Causes	**Barriers**	**Consequences**	**Mitigation Barriers**
	pressurised CO_2 release	hydrocarbon explosion reduced by CO_2	is lot of head pressure, it does not dissipate like LNG Escalation from CO_2 explosion, can cause HC fire Fire + explosion	have rules for locked-in volumes
7	CO_2 BLEVE, resulting in projectiles	Material like carbon steel for containing CO_2 There will be no tanks involved in CO_2 process; this should be highlighted in design process		
8	Oxygen in CO_2: for oxy-combustion process oxygen may not be removed	Limited by reservoir conditions, also less		
9	Issues may arise if there is a grid network and some sources have traces of H2			
10	Catastrophic failure of pipelines - pressure energy release causing longitudinal ripping	CO_2 pipelines buried deeper Crack arrestors Metallurgy solutions		
11	Exploding pigs: CO_2 can permeate plastic etc; when taken out it can explode	Improvement in technology Pressure relief at pig receiver		
12	Third party intervention	Control systems to shut pipeline off		
13	Land slip can cause shear, can be catastrophic	Designs and control systems to shut pipeline off		
14	Explosive decompression of valves			
15	Boiler/furnace explosions	Keep boiler away from open flames		

	Causes	Barriers	Consequences	Mitigation Barriers
		Keep ASU and O2 away Design and control Oxyfuel burners well understood		
16	Explosion in steam lines	Already well understood		
17	High pressure equipment	Relief panels- but prevent, else too big equipment		
18	Mercury embrittlement, 30-80 bars in separation system			
19	NH3/Propane explosion (oxy-combustion)	Depends on what type of cryogenic system used		
20	Nox: NO and NOx is mechanism for explosion in ASU	Concentration of NOx will be low as recycle lowers it		
21	Hydrogen embrittlement	More possibility upstream of shift rather than in the shift (482 C)? Might be close as 550 C		
22	Hydrogen detonation: compared to hydrocarbons, hydrogen has very high propensity to detonate	Layout/avoid congestion Hydrogen has more buoyancy and dilutes readily Mostly safer with good design		
23				
24	Ammonia and CO_2 do not go very well, they form solids, carbonates which condensates in cooling parts of the system Accumulates under the relief valves			
25	Ammonium sulphate is very sticky			
26	Flooding of big columns	Low pressure system; just above atmospheric	Can cause back-pressurising but not pressure release	

	Causes	Barriers	Consequences	Mitigation Barriers
27	More lifting involved	Well understood; no more than putting extra module on offshore station		
28	Well integrity: CO_2 will add pressure	Depleted field capped to pressurise a field Re-qualification and retesting for higher pressures will be done		
29	Expansion loop system (pipelines)	Easy to design Similar pipelines exist for supercritical ethylene, problems known	Expansion loop might get very hot or cold. It doesn't like temperature changes	Mitigations should be stressed in report Bellows can't be an option at 100 bar
30	Shut down	Controls and procedures can be very different		

11.6.5 Toxic release

	Causes	Barriers	Consequences	Mitigation Barriers
1	H2S: can be brought out by pigging CO_2 captured from pre-combustion process will have around 5 % hydrogen and pyrophyric (iron sulphide) hazard will also exist			
2	Concentrated H2S at inlet to Claus (pre-combustion)	Same issues as usual FGD.		
3	SO3: Reaction of NO and SO2 in purification system to give SO3. (For oxy possible reaction: NO + SO2 → SO3) SO3 mist in compressor will be fatal to			

	Causes	Barriers	Consequences	Mitigation Barriers
	compressor			
4	SO2		Fairly high, recycle back to flue gas -SO2 can be readily separated	
5	Sulphur: (Lime slurry, wet Line FGD)			
6	CO	Less than in standard system Venting/flare stack design Designing for low ground level Venting may be designed to vent CO? Flare stack	In pre-combustion capture process e.g. pipe fracture between quench of gasifier and shift would emit large amounts of CO	
7	H2 and CO detection CO sinks to bottom and hydrogen on the top Gas turbine enclosures will be different	Monitoring needed at different places Fire rating of the enclosure	Hydrogen detection cross-sensitive to CO	
8	Major release of CO2. (For North Sea cannot put corrosion inhibitors or stenching agents into CO2)	Leave very low concentration of H2S in CO2 as stenching agent		
9	Sub-spec drying: lot of trace elements, carbonyls etc can be formed		.	
10	COS/carbonyls	Well understood		
11	Ammonia	Already present at most power stations: well understood		
12	NOx	Low concentrations as recycle (e.g in oxy-combustion) will lower it		
13	Effluents: lot of acid soup, will contain mercury (e.g. in oxy-combustion)	Will depend on how NOx and SOx are handled -They exist in liquid phase rather than high concentration in vapour		

	Causes	Barriers	Consequences	Mitigation Barriers
		phase		
14	Amines	Concrete towers for amines, on lines of cooling towers, can be rubber-lined or stainless steel and should be do-able		Steel spade damper.
15	NaOH (Various amines for dosing and water dosing)			
16	Chlorine (For water dosing)			
17	Heavy metals in ash		All heavy metals apart from volatiles (e.g. Hg and Arsenic taken care by GAC filters) end up in frit	
18	Fly-ash			
19	Mercury	In normal coal fired plants about 85-90 % captured (More of operability, rather than safety issue)	Aluminium components downstream- packing in absorber beds; may get disintegrated	

12 REFERENCES

1. Terry F. Wall, Combustion processes for carbon capture, Proceedings of the Combustion Institute (2007),doi:10.1016/j.proci.2006.08.123 http://www.combustioninstitute.org/documents/Wall.pdf
2. Personal communication with Dr Bruce Ewan, Sheffield University, UK
3. Review of the Feasibility of carbon Dioxide capture and Storage in the UK', DTI Report DTI/Pub URN 03/1261, September 2003(26)
4. 'Risk Analysis of the Geological Sequestration of CO_2', Report to DTI CFT Programme, DNV Consulting, May 2003 (27)
5. Figueroa, J.D., Fout, T., Sean Plasynski, S., McIlvried, H. and Srivastava, R.D., Advances in CO_2 capture technology—The U.S. Department of Energy's Carbon Sequestration Program. International Journal of Green House Gas Control, *Volume 2, Issue 1, January 2008, Pages 9-20*
6. Connolly, S. and Cusco, L,2007, "Hazards From High Pressure Carbon Dioxide Releases During Carbon Dioxide Sequestration Processes", IChemE Symposium series No 153
7. IEA report on oxyfuel
8. http://www.labseeker.com/ChemicalBiotech/msds%5CAlfa%5C41000%5C41398.pdf viewed on 27/02/2008.
9. Bøe,R., Zweigel, P., Polak, S. & Lindeberg, E., "Potential risks associated with CO_2 storage, Case Study Mid-Norway, CO2STORE project", 30th June 2005. Viewed at http://www.co2store.org/TEK/FOT/SVG03178.nsf/Attachments/NGUReport2005Risks.pdf/$FILE/NGUReport2005Risks.pdf
10. http://www.berr.gov.uk/energy/sources/renewables/publications/page20736.html viewed on 29.02.2008
11. Weeks.D., Driscoll,J., "Processing Considerations For Carbon Capture & Storage". Kellog Paper No 2059. viewed on 12/2007 at http://www.kbr.com/publications/technical_papers/Processing_Considerations_for_Carbon_Capture_and_Storage.pdf
12. Seevam,P.N., Downie, M.J., "Theme A6: CO_2 Transport Infrastructure Newcastle University presentation
13. Race, J.M., Newcastle University, School of Marine Science & Technology, "Designing a Safe Carbon Dioxide Transport Infrastructure for the UK", Presentation to CCSA – 24th July 2006
14. Improvement In Power Generation With Post-combustion Capture of CO2, report prepared for Executive committee of the Programme-IEA GHG, Report No PH4/33, November 2004
15. Oxy-combustion Processes for CO2 Capture from Power Plants, report prepared for Executive committee of the Programmae-IEA GHG, Report No 2005/9, July 2005.
16. Catelin, M. "Global Role of Coal" Presented at Four Ways to Capture CO2: An IChemE Seminar on the Future for Coal London 11 June 2008
17. "Australian carbon storage legislation released2, Carbon Capture Journal Sep 18 2008. viewed on 24/09/2008 at http://www.carboncapturejournal.com/displaynews.php?NewsID=272?PHPSESSID=3c6905829d1c051b86ad1c8d39bfef4b
18. Barrie, J., Brown, K., Hatcher, P.R. & Schellhase, H.U. 2005. Carbon Dioxide Pipelines: A preliminary review of Design and Risks. Proceedings of the 7th International Conference on Greenhouse Gas Control Technologies, 5-9 September 2004, Vancouver, Canada

19. Topham, C., “Pre-combustion capture”, talk delivered in “Four Ways to Capture CO2” , IchemE, London, June 2008

20. HSE: “Interim guidance on conveying CO_2 in pipelines in connection with carbon capture, storage and sequestration projects” viewed at http://www.hse.gov.uk/pipelines/co2conveying.htm on 25/09/2008

21. Haroun Mahgerefteh, Garfield Denton, and Yuri Rykov, (2008), Pressurised CO2 pipeline rupture, IChemE Symposium Series No 154

22. Dixon C & Hasson M, (2007) 'Calculating the release and dispersion of gaseous, liquid and supercritical CO2', IMechE Seminar on Pressure Release, Fire and Explosion, 2 October 2007

23. Haroun Mahgerefteh and Olufemi Atti, (2006), Modeling Low-Temperature–Induced Failure of Pressurized Pipelines, AIChE Journal, March 2006 Vol. 52, No. 3, 1248-1256

24. CCPS, (2007), Guidelines for risk based process safety, AIChE, New York, 2007

25. CCPS, (2008), Guidelines for hazard evaluation procedures, AIChE, New York, 2008

26. Crawley F, Preston M & Tyler B, (2000), HAZOP: Guide to best practice, IChemE, Rugby, 2000

27. Crawley F & Tyler B, (2003), Hazard identification methods, IChemE, Rugby, 2003

28. Energy Institute, (2008), CCS Workshop, 3 November 2008 (various relevant presentations) http://www.energyinst.org.uk/index.cfm?PageID=1153

29. Oosterkamp A & Ramsen J (2008), State-of-the-art overview of CO_2 pipeline transport with relevance to offshore pipelines, Polytec Report No POL-O-2007-138-A, 8 January 2008

30. DNV, 2008, Mapping of potential HSE issues related to large-scale capture, transport and storage of CO_2, DNV report number: 2008-1993, revision 02

31. HSE, 2008, Assessment of the dangerous toxic load (DTL) for specified level of toxicity and significant likelihood of death (SLOD), HSE website