HAZARDS FROM HIGH PRESSURE CARBON DIOXIDE RELEASES DURING CARBON DIOXIDE SEQUESTRATION PROCESSES[†]

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Climate change concerns have motivated several carbon dioxide capture and sequestration studies in recent years. A few of these have been implemented with other major schemes planned globally. Current work by the UK Health and Safety Executive has identified some gaps in knowledge on behaviour of CO_2 releases from supercritical pressures. This is particularly relevant at the high pressures and large volumes envisaged for transport of and storage within depleted reservoirs in the North Sea. The combination of high pressures and large quantities have major accident hazard implications for large scale CO_2 processing Three primary areas of concern are discussed: source terms for dispersion modelling, strong cooling effect from pressure reduction and erosive effect of two phase solid/gas flows.

To manage risks to persons involved with large quantities of supercritical it is necessary to be able to predict accurately its properties, both in containment and also during releases to atmosphere; both intended and accidental. At the high pressures being considered, CO_2 is above its supercritical pressure and in certain parts of the process will also be above its critical temperature. In the supercritical state CO_2 exhibits properties that need to be fully understood for accurate dispersion modelling. Some dispersion modelling of supercritical carbon dioxide releases has been carried out, but these have involved assumptions about the source terms and material properties at the point of release that are not considered reliable with present data. None of the available models account for the thermodynamics of solid formation and subsequent sublimation; the thermodynamic path followed during release is uncertain. As the release source terms largely define the subsequent dispersion characteristics, they are critical factors in modelling accurately carbon dioxide release behaviour.

Carbon dioxide has a high Joule-Thomson effect that implies severe cooling effects in the immediate region of any pressure reduction event. In view of the large quantities to be handled, this will have significant cooling envelope on the surrounding plant. This applies to piping throttle downs, operational blowdown events and accidental releases. High cooling rates may lead to local solid carbon dioxide formation and/or low temperature enbrittlement of process plant or structural members.

Supercritical CO_2 is used commercially for erosion jet cleaning and cutting, and it is also used to enhance drilling penetration rates. Accidental releases of supercritical CO_2, e.g. from flange failures, might lead to serious effects on adjacent piping, plant or structures. However, as with the other areas of concern, experimental evaluation of its release characteristics will be necessary to enable plant to be designed to a minimum risk configuration.

Results of preliminary small-scale experimental tests are also presented to help quantify the above issues.

KEYWORDS: hazard, risk, carbon dioxide, sequestration, supercritical, offshore

INTRODUCTION

The proposed sequestration of supercritical carbon dioxide ($SCCO_2$) into offshore hydrocarbon reservoirs, via a manned platform has major accident hazard implications for the persons on board the installation. In the UK it will require a case for safety for the $SCCO_2$ high-pressure system along with other aspects, to ensure that risks to persons are properly controlled. For economic and technical reasons, CO_2 will be handled when above its critical pressure of 73.3 bar (sometime known as 'dense phase') and in its supercritical state, namely above both 73.3 bar and 31.1°C. The consequence analysis of both dense phase and supercritical ($SCCO_2$) releases will require a

sound understanding of the characteristics of $SCCO_2$ when released from high pressure. This is especially true of large mass releases at certain thermodynamic conditions. Releases of both dense phase and supercritical CO_2 have many similarities and are considered together in this paper.

BP are developing a project (Decarbonised Fuel Project 1 – DF1) that involves stripping the carbon from methane at Peterhead power station and injecting the CO_2 into the Miller reservoir in the North Sea. Various early studies of CO_2 releases carried out for this project have involved assumptions about the source terms and properties of the material at the point of release. Unfortunately, as was recognised by both BP and HSE, there is little or no

data to substantiate some assumptions, which have assumed a source term of a mass of CO_2 in its 'normal' gas state throughout. This was highlighted when a DTI study (Vendrig 2003) of CO_2 release and dispersion was subject to analysis by HSE that revealed insufficient details in the thermodynamic parameters of the release source terms for its dispersion to be modelled accurately.

CO_2 at the high pressures being considered (170–400 barg) is well above its critical pressure and its properties have rarely been considered from a safety view point. CO_2 is an asphyxiant and $SCCO_2$ is a powerful solvent giving possible toxic contamination problems. It has zero surface tension, near zero viscosity that may cause sealing difficulties, and forms an acid solution in the aqueous phase leading to corrosion issues. Its release may lead to low temperatures in plant, structures and instrumentation all of which may cause problems if outside the design temperature. As the release source terms largely define the subsequent dispersion characteristics, and hence major hazard scenarios, they are a critical factor in modelling accurately CO_2 release behaviour.

TECHNICAL ISSUES WITH MAJOR ACCIDENT HAZARD (MAH) IMPLICATIONS

MAH presented by handling high pressure CO_2 on an offshore installation need to be considered in the context of about 10,000 years cumulative operating experience in the managing of hazards associated with hydrocarbon processing. This is based on about 250 installations in operation in the UK North Sea since $\sim$1965. In comparison there is probably less than 100 operating years for handling CO_2 and significantly less in dealing with supercritical CO_2. The Sleipner CO_2 disposal project in the Norwegian sector of the North Sea (Chadwick 2004) has been operational since about 1996. Globally, there is some other operating experience notably through enhanced oil recovery in North America. However, many of the other large scale carbon dioxide operations are either operating below super-critical pressures and/or are in remote on-shore locations that present significantly less safety issues than the proposed Miller field sequestration.

Lack of substantial operational experience in a novel process or technology generally leads to significant difficulties in identifying accurately the hazards associated with that process/technology. There are very few risk-based reference points in handling high pressure CO_2 in large (1000 tonne quantities) against which estimated risks to persons can be compared to establish if a robust case for safety has been made. Consequently, poorly defined major hazard implications require that we fully define the characteristics of the process and particularly the release behaviour of $SCCO_2$. MAH associated with $SCCO_2$ are clearly relevant to onshore industrial sites as well as offshore e.g. around compressors, considering topography and co-location of carbon dioxide and flammables pipelines.

The highest risks on offshore installations are associated with fires and explosions (Connolly 2006), resulting from loss of containment (LOC) events. Predicting the dispersion and accumulation of flammable mixtures is a fundamental requirement in managing fire and explosion risks to persons. For example, the flammability envelope of hydrocarbon clouds will be reduced by the presence of CO_2, but the cooling effect of CO_2 on release may cause embrittlement of structural steelwork reducing its integrity. The presence of CO_2 in the hydrocarbon streams will change the hazard profile of the process. Design for mitigation and detection of heavier-than-air CO_2 instead of lighter-than-air methane is clearly quite different.

In order to assign reasonable confidence to the predicted hazard ranges of gaseous releases, dispersion models are normally validated against actual or experimental data. To achieve results with reasonable confidence it is essential that the "source terms" (initial inputs to the dispersion models) describe accurately the release conditions of the hazardous agent. Input parameters include such values as temperature, velocity, release rate and physical form and source dimensions.

The thermodynamic equilibrium properties of CO_2 are reasonably well known and can be compared successfully to experimental data (Cusco 1995). There is a detailed multi-parameter equation of state for CO_2 (Span 1996) and also a more accessible route to the fluid thermophysical properties of CO_2 on-line (NIST 2005). However, the thermodynamic path of a release also has to be understood, so that we describe sufficiently phase changes, temperature changes etc in consequence modelling. A temperature-entropy plot with lines of constant enthalpy is useful for visualising the possible phase changes on release (Perry 1973). Where a release occurs with phase transition (e.g. from dense phase through vapour-liquid to gas-solid to gas) then the transition between states must be determined to enable a reasonable estimate of the "effective source(s)" to be input into the dispersion models.

ENGINEERING CONSIDERATIONS

Consideration of the engineering aspects of handling high pressure CO_2 in large quantities in a LOC incident, have highlighted several issues with major accident implications:

i. Scale of thermal cooling envelope from a $SCCO_2$ release
ii. $SCCO_2$ containment issues
iii. Fire and explosion hazard profile changes
iv. Toxic contamination effects on $SCCO_2$ release
v. Dry ice 'grit blasting effects'
vi. CO_2 detection
vii. Emergency response & temporary refuge integrity issues

The resolution of these issues is being actively pursued by BP through their Decarbonised Fuels projects, and also independently by HSE in its Offshore Division (OSD) and our laboratories (HSL) at Buxton. Engineers and scientists from BP, OSD and HSL meet regularly to compare findings and also to 'peer review developments'. Further details of the MAH issues are outlined below.

CONSEQUENCES OF SCCO$_2$ THERMAL COOLING – INTERNAL AND TO THE ENVIRONMENT

A gas below its inversion temperature will cool upon expansion. This is described thermodynamically as the Joule-Thomson effect: $(\neq T/ \neq p)_H$. Carbon dioxide has a particularly large Joule-Thomson effect and therefore causes a large cooling effect on pressure release. In general the expansion of CO$_2$ on release is isenthalpic. However, any shock behaviour during in the release could be isentropic. There are difficulties with predicting the thermodynamic path with accuracy during representative release scenarios, e.g. in predicting the scale of the cooling effect in an industrial environment. Depending on the starting conditions of temperature, pressure and composition, initial pressure drops would be to a 2-phase release of vapour and liquid until its triple point pressure of 5.18 bar. Further reduction in pressure below 5 bar would most likely generate solid CO$_2$ as well as the gas and a transient liquid state. Liquid CO$_2$ cannot exist at ambient pressures as CO$_2$ sublimes.

It is important to be able to estimate accurately the scale of the cooling effect on the surroundings (including any pipes, structures etc) as SCCO$_2$ will absorb large quantities of heat on release. There will be thousands of tonnes of SCCO$_2$ per day flowing through the large-scale sequestration projects that have been suggested, such as on the Miller platform. If a release occurred, the near field effects could include a rapid cooling of the surrounding topsides process equipment and the platforms structure. The emergency response to that large cooling effect, in combination with dealing with an asphixiant cloud, needs to be carefully evaluated for effective management of the situation.

Carbon steel (structure) is subject to brittle fracture (ductile-brittle transition) at around 0°C. The extent of the cooling envelope surrounding a release must therefore be estimated accurately in order to evaluate the major hazard implications on the platforms' structural integrity and subsequently its personnel. In the Miller reservoir there is about 20% CO$_2$ occurring naturally. The platforms hydrocarbon process plant was built to handle CO$_2$ rich streams with duplex stainless steels that have a useable temperature limit of -40°C. This has fortuitously given materials of construction, not generally installed, that are particularly well suited for CO$_2$ sequestration. It is believed therefore that the process plant on Miller should not be affected by a SCCO$_2$ release, but this issue will need to be confirmed by BP and OSD's specialist structural inspectors.

Although it is believed that the processing plant on Miller will be largely unaffected structurally by the CO$_2$ releases, the cooling effect is very likely to have a detrimental effect on the blowdown system with the possibility of the Emergency Blowdown Valves freezing (Eggeman 2004; Ouderkirk 2003). There may also be slugs of solid CO$_2$ formed within piping. Hydrocarbon process blowdown systems cannot be guaranteed to operate successfully if the CO$_2$ component is included in the flow stream and its cooling effect is added to that of the hydrocarbon stream.

It is known that unreliable freezing point predictions are made by several process simulators and that most of the thermodynamic data of solid CO$_2$ formation was collected in the 1950–70's. The issue of unknown source terms adds another layer of complexity to handling of SCCO$_2$ within hydrocarbon streams.

SCCO$_2$ CONTAINMENT AND INTEGRITY ISSUES

In its highly compressed state CO$_2$ has zero surface tension and very low viscosity. It has the tendency to creep or wet surfaces and valves rely to a certain extent on the surface tension of a liquid to prevent it from 'seeping' through small gaps in the sealing surfaces within the valve structure. Water will absorb its own volume of CO$_2$ at STP with CO$_2$ dissolution increasing with increasing pressure. It forms a weak acid, carbonic acid, with a small equilibrium constant of 1.7×10^{-3}, and as such only about 1% of the acid is formed when the gas dissolves in water. However, over time the corrosive effects of the, albeit weak, acid will have detrimental effects on the process plant particularly those parts not built of stainless steel.

SCCO$_2$ behaves as a liquid in that it has a solubility capability but also acts as a gas in having extremely low surface tension. Standard assumptions about the sealing capability of valves used to contain hydrocarbon liquids and gases will have to be demonstrated as being effective with SCCO$_2$. It is known that seals and sealing compounds can be rapidly degraded by the introduction of contaminants. The literature lists CO$_2$ among the contaminants such as H$_2$S etc, in hydrocarbon processing. The Miller project will see its process going from hydrocarbons with $\sim$20% CO$_2$ to $\sim$100% CO$_2$.

Phenomena known as explosive decompressions can occur when elastomer seals have absorbed gas at high pressure following sudden pressure drops. Equipment Failure Datasets (OREDA) and other sources of failure rate data are all based on 'normal' fluid behaviour. SCCO$_2$ as a supercritical fluid has characteristics for which there is little known failure data for the equipment associated with handling the material. A risk assessment based on assumptions that will be difficult to substantiate will produce a fragile case for safety for persons onboard the installation and in the onshore plant.

Wells have a natural pressure and temperature that is related to their depth. Typically the hydrostatic pressure within a well at 700 m or more is greater than 74 barg and the temperature is in excess of 31°C (CO$_2$ critical temperature). CO$_2$ is therefore in its supercritical state in wells.

The density and phase of CO$_2$ is dependent on its pressure/temperature envelope. If containment integrity is lost, pressure can fall rapidly and the SCCO$_2$ in a dense phase will expand significantly in volume with potential for internal pressurisation of both well and topsides process components (Skinner 2003). Within the wells themselves, integrity is maintained via hydrostatic balances of the well fluids to control 'downhole' pressures and flows. Rapid changes in hydrostatic heads in a well due to

$SCCO_2$ dense phase expansion can cause the reservoir fluids to flow into the well tubes (influx) with severe consequences. An influx can occur following loss of well containment integrity very rapidly, such that control valves cannot be closed fast enough to avoid loss of pressure control.

Rapid $SCCO_2$ expansion and associated cooling may also allow the formation of solid CO_2 (dry ice) and hydrates within the well fluids. The potential for loss of well control will hence be exacerbated by the presence of solids within the flowing well fluids, i.e. tube blockages, physical impact damage, erosion and corrosion.

It is known that drilling with $SCCO_2$ as a drill fluid (instead of the usual 'mud') has benefits for drilling rates. $SCCO_2$ low viscosity and surface tension enhance mechanical drilling of granite and shale's high-pressure jet erosion rates (Kolle 2000). Drilling is in essence the engineered wear of rock formations by mechanical (or erosion) means. Conversely, machine bearings are designed to minimise wear between surfaces by the inclusion of lubricating fluids, usually oil. $SCCO_2$ is used for enhanced oil recovery (EOR) because it is soluble in oil, reducing its viscosity, hence making it easier to recover. Viscosity is one of oil's critical properties as lubricant, and the presence of CO_2 within rotating or reciprocating equipment has the potential to migrate into lubricating oil. Reduction in the oil's viscosity will therefore reduce its lubricating property leading to accelerated wear in the associated bearings or contact surfaces. Loss of well control leading to blowouts appears to be increasing in CO_2 containing wells (Skinner 2003). Corrosion-related problems appear to be the cause of integrity degradation leading to containment loss.

FIRE AND EXPLOSION HAZARD PROFILE CHANGES

The flammable limits of methane in air are between about 5 and 15% v/v, with a stoichiometric concentration of about 9.8% v/v. Methane – air mixtures are quoted here for illustrative purposes only; clearly there are other flammable mixes to be considered. CO_2 is a known fire extinguishant and its presence in a methane-air mix will reduce the mixture's flammable limits. In a LOC event, the effect of the presence of CO_2 in a flammable mixture will therefore need to be established with some confidence if credit is given for its extinguishant properties. If a hydrocarbon stream containing CO_2 is accidentally released, the threat of fire and/or an explosion must be evaluated, with additional conservatism if necessary.

TOXIC CONTAMINATION EFFECTS ON RELEASE

$SCCO_2$ is a highly efficient solvent. It is used to decaffeinate coffee, extract herb and spice essences and is used in some complex chemical reactions. CO_2 is sometimes referred to as a 'super solvent' as a supercritical fluid, and this property can lead to complications in the analysis of MAH. When $SCCO_2$ undergoes significant pressure reduction it moves from its supercritical state (super solvent) to a gaseous state with very low solvent capability. Any solute held in 'solution' will therefore 'precipitate' out.

Reduction of pH in reservoir fluid will enhance dissolution of scales, toxics, heavy metals, radioactive elements etc and return them to the surface via gas or oil streams. Response to such LOC incidents becomes complicated, particularly with presence of scale. Eggeman (2004) indicated that a significant loss of containment issue appears to be the reaction of 'O' ring and other elastomer/rubber seals to CO_2. It is known that elastomer seals swell and harden in the presence of $SCCO_2$, and explosive decompression of the seals has been observed. Teflon appears to be one of the few sealing materials apparently unaffected by CO_2.

DRY ICE 'GRIT BLASTING EFFECTS'

$SCCO_2$ is used commercially (Coldjet 2006) for cleaning to provide low contamination surfaces in medical sterilization and integrated circuit manufacture. At temperatures below $-78°C$, dry ice forms and when entrained in high-pressure air streams is used to remove contamination from surfaces. Dry ice erosion effects are proportional to the kinetic energy and hardness of the particles, when a pure dry ice stream is considered. However, if a LOC event is considered, a gaseous release of CO_2 is likely to be contaminated by other solid particles such as reservoir-derived sand and other solid debris. Erosion effects will be enhanced if the dry ice formed on depressurisation carries sand and other solids with it.

To evaluate the potential for escalation effects via loss of containment the high kinetic energy of dry ice at 170-400 bar release pressure will need to be evaluated. Discharged particles could erode process pipework and vessels adjacent to leaks with subsequent escalation potential.

CO_2 DETECTION

There is a wide range of CO_2 detectors available. One common issue of concern is that the electronics upon which they depend for functionality may be affected by low temperatures of major CO_2 release. There is no significant initial human response to CO_2 that could be useful as a detection mechanism, whereas there is a very sensitive human response to H_2S and to SO_2 by smell at very low (ppm) concentrations. CO_2 is present with an atmospheric concentration of about 370 ppm (0.037%) which may cause some problems with instrumented detection.

There are two separate issues to be considered here; the detection of flammable hydrocarbon clouds with CO_2 in the gas – air mix, and human vulnerability to the asphixiant hazard from the CO_2, possibly compounded by the hydrocarbon vapour. The density of CO_2 at STP is 1.98 Kg/m^3 about 1.55 times that of air and 3 times that of methane. The scenario of concern associated with this high CO_2/air density difference, is the accumulation of CO_2-rich asphixiant atmospheres in depressions and modules on the platform following a hydrocarbon

and CO_2 LOC event. The presence of CO_2 in differing concentrations will also affect the accuracy of fire or explosion hazard assessments.

It is important, therefore, that effective instrumented CO_2 detection systems are installed to provide a high detection capability. In CO_2 well injection facilities in the USA, oil field workers wear personal CO_2 detectors, rather like radioactive film badges worn by nuclear industry workers. Clearly the presence of undetected CO_2-rich clouds has the potential to seriously inhibit the actions of platform workers in dealing with platform emergencies.

EMERGENCY RESPONSE & TEMPORARY REFUGE INTEGRITY ISSUES

Human vulnerability to CO_2 is well documented and only a brief outline of its hazard ranges is given here. A moderate concentration of $\sim 5\%$ causes breathing difficulties, an increase in heart rate and possible headaches. Decision-making impairment may also occur at low concentration. At 7% CO_2 anxiety is caused by breathing difficulty. Effects become severe after 6 minutes exposure. At 10% CO_2 the threshold of unconsciousness occurs in 30 minutes. At 15% the exposure limit is 1 minute and at 20% unconsciousness occurs in <1 minute. At Lake Nyos, Cameroon there were 1,800 reported fatalities when a CO_2 bubble erupted from the lake. At Mount Mammoth, USA, Skiers have been asphyxiated. Because of its relatively high density relative to air, in large quantities CO_2 can present significant major hazard issues if workers are unaware of its presence.

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