PRECIS of “Hazards from high pressure carbon dioxide releases during carbon dioxide sequestration processes”

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Introduction

The proposed sequestration of CO_2 including its capture, transport, and (underground) storage has major accident hazard implications for both the workforce and public. For economic and technical reasons CO_2 will be handled in a ‘Dense Phase’ at high pressures and low temperatures, or when it is in its supercritical state, above 73.3 bar and 31.1^{o}C. In order to understand the consequences of a leak of CO_2, on the workforce and public, a sound understanding will be required, of the characteristics of CO_2 when released from high pressure. This is called the release ‘Source Terms’.

General Properties

It is known that CO_2 at the high pressures being considered (170 – 400 bar) is a supercritical fluid, the behaviour of which is not well understood. Supercritical CO_2 ($SCCO_2$) is a strong solvent giving possible toxic contamination problems for people following a leak. It has zero surface tension and near zero viscosity that may cause sealing difficulties in process plant. CO_2 forms an acid solution in water leading to corrosion issues. It is a known asphyxiant and it may be difficult to detect at low temperatures, because instruments do not operate well at very low temperatures. Modelling gas dispersion from a leak requires detailed knowledge of the substance at the actual point of release. When fluids are released in large quantities, which will be true of most CO_2 sequestration processes these Release Parameters or ‘Source Terms’ can be different from small-scale releases.

Technical Issues with Major Accident Hazard (MAH) Implications

There is relatively little experience worldwide in managing the risks associated with CO_2, compared with oil and gas. MAH presented by handling high pressure CO_2 offshore or onshore need to be considered in the context of about 10,000 years’ operating experience in managing hazards associated with hydrocarbon processing offshore alone, and probably much more if onshore processes are included. This is based on about 250 Installations operating in the UK North Sea since ~1965. In comparison there are probably less than 100 operating years for handling CO_2 and significantly less in dealing with supercritical CO_2. The Sliepner (Ref1) CO_2 disposal project has been operational since about 1996 while in the USA, CO_2 injection into wells has only been carried out over the last ~40 years.

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 (1000tonne quantities) against which estimated risks to persons can be compared to establish if a robust case for safety has been made. To establish that a robust case for safety has been made therefore requires that we fully define the characteristics of the carbon sequestration process and particularly the thermodynamic properties (Source Terms) of $SCCO_2$ when it leaks.

The highest risks on offshore installations (Connolly, 2006 Ref 2) are associated with fires and explosions, resulting from leaks. Predicting the dispersion and accumulation of flammable mixtures is a fundamental requirement in managing fire and explosion risks to persons. For example, the flammability of methane /air mixes will be affected by the presence of CO2. The cooling effect of CO2 on release may make structural steelwork become brittle and hence weakened. Hence the presence of CO2 in the hydrocarbon streams will change the hazard profile of the process by altering the properties of the flammable fluids and the physical characteristics of the process equipment.

Safety cases normally contain theoretical models of possible accidents that are based on data from actual incidents. To achieve results with reasonable confidence it is essential that the “source terms” i.e. the release characteristics of a leak, describe accurately the release conditions of the hazardous agent. Data that is input to the model include such values as temperature, velocity, release rate and physical form and source dimensions.

Where a release occurs in several states (gas, liquid and/or solid) 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. At present this information for CO_2 does not exist. It will be needed to assess the risks from CO_2 sequestration particularly for leaks of large quantities of the substance.

Engineering Considerations

Consideration of the engineering aspects of handling high pressure CO2 in large quantities have highlighted several possible events which could lead to a major accident:-,

i. Scale of Thermal Cooling Envelope from a SCCO2 Release
ii. SCCO2 Containment Issues i.e. leaks
iii. Fire and Explosion Hazard profile changes
iv. Toxic Contamination Effects on SCCO2 Release
v. Dry Ice ‘grit blasting effects’
vi. CO2 detection
vii. Emergency Response & effectiveness of Temporary Refuges

i. Consequences of SCCO2 Thermal Cooling – internal and to the environment.

When gases like CO_2 or are released under pressure they cool down. This phenomena is known as the Joule – Thompson (Cooling) Effect and has been utilised in Refrigeration systems for many years. The larger the quantity of gas released or the higher the pressure of release, the greater is the cooling effect. However to estimate the scale of the cooling 'envelope' of large scale (1000's tonnes) $SCCO_2$ release requires detailed knowledge of the 'Source Terms' at the release point. Carbon steel (structure) is subject to brittle fracture (ductile-brittle transition) at around 0^oC, and hence it is essential that the scale of a cooling effect on the surrounding plant equipment needs to be understood.

A major hydrocarbon process safety feature is the Blowdown System. This is a safety system designed to remove flammable substances from the process in the event of an accident. This safety system cannot be guaranteed to operate successfully if the CO_2 component is included in the flowstream because its cooling effect when added to that of the hydrocarbon stream may cause the systems components, valves etc, to malfunction.

ii. $SCCO_2$ Containment and Integrity Issues

$SCCO_2$ in its highly compressed state has zero surface tension and very low viscosity, and hence it has the tendency to creep on wet surfaces. Valves for example 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.

CO_2 dissolves in water and forms a weak acid, Carbonic acid. 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.

It is known that (polymer - rubber) seals and sealing compounds can be rapidly degraded by the introduction of contaminants.

A phenomenon known as explosive decompression can occur when elastomer seals have absorbed gas at high pressure following sudden pressure drops. CO_2 as a supercritical fluid has characteristics for which there is little known failure data for the equipment associated with handling the material.

The density and phase of CO_2 is also highly dependant on its pressure/temperature envelope. If containment integrity is lost through a leak, pressure can fall rapidly and the $SCCO_2$ in a dense phase will expand significantly in volume with potential for internal pressurisation of any sequestration Well. (worldoil.com 2003 ref 3).

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 (onshore or offshore) will hence be exacerbated by the presence of solids within the flowing well fluids. I.e. tube blockages, physical impact damage, erosion and corrosion.

iii. Fire and Explosion Hazard profile changes

The flammable limits of Methane in air are between about 5 and 15%. Some sequestration projects involve mixing CO_2 and hydrocarbon fluids, such as methane. CO_2 is a known fire extinguishant and its presence in a methane-air mix will reduce the mixtures' flammable limits and make it less likely to catch fire or explode. This may be viewed as a benefit in mixing CO_2 with flammable hydrocarbon fluids but the extent of its effects on flammability properties needs to be defined accurately in order to fully understand the fire and explosion hazards of the gas mixes.

iv. Toxic Contamination Effects on Release

$SCCO_2$ is a highly efficient solvent in its supercritical state. It is used to decaffeinate coffee, extract herb and spice essences and is used in complex chemical reactions. It is sometimes referred to as a 'super solvent' as a supercritical fluid, and it is this property that can lead to complications in the analysis of MAH. When $SCCO_2$ undergoes significant pressure reduction it moves from its supercritical state with super solvent properties, to a gaseous state with virtually no solvent capability. In a Well the CO2, which is also acid, will tend to dissolve various solid elements that may be toxic, possibly Lead, Cadmium etc. Any toxic substance (the solute) held in 'solution' will therefore 'precipitate' out, if a leak occurred, and we would therefore have a 'toxic' contamination effect on the area onto which the material was spilt.

v. Dry Ice 'grit blasting effects'

$SCCO_2$ is used commercially for cleaning to provide low contamination surfaces in medical sterilization and IC manufacture`. However if a there was a leak a gaseous release of CO_2 may 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. Discharged particles could erode process pipework & vessels adjacent to the leak which could lead to further damage to the equipment and hence and risk to people.

vi. CO2 Detection

There is no significant inherent human response to CO_2 that could be useful as a detection mechanism, in contrast to other harmful gases. Human response to Hydrogen Sulphide by smell occurs at very low (ppm) concentrations, similarly with ammonia and sulphur dioxide. CO_2 is present in the air we breath 0.037% and this may cause problems with instrumented detection because the 'background CO_2' levels are so high. Secondly the cooling effects of a CO_2 leak may have an adverse effect on the accuracy and operability of CO_2 gas detection systems.

In CO_2 Well injection facilities in the USA oil field workers wear personal CO_2 detectors, rather like radioactive film badges worn by workers in the Nuclear Industry .

vii. Emergency Response & Temporary Refuge Integrity Issues

Human vulnerability to CO_2 is very well documented so only a brief outline of its hazard ranges is given. A moderate concentration ~5% causes breathing difficulties, an increase in heart rate and possible headaches. At 20% loss of concentration, and then unconsciousness will occur in less than a minute.

Hence the presence of undetected CO_{2} - rich clouds, at concentrations below the lethal limit, have the potential to seriously inhibit the actions of workers in dealing with emergencies at oil wells or other CCS installations. The design of Emergency Response Procedures in the event of a CO_2 leak, will need to be developed to take account of the insidious nature of CO_2
and the fact that there is no ‘adverse’ and easily recognisable human reaction to the gas.

References

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