CO_2 PIPELINES MATERIAL AND SAFETY CONSIDERATIONS

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This paper presents an overview of some of the most important factors and areas of uncertainty affecting integrity and accurate hazard assessment of CO_2 pipelines employed as part of the Carbon Capture and Sequestration (CCS) chain. These include corrosion, hydrate formation, hydrogen embrittlement and propensity to fast running ductile and brittle factures. Special consideration is given to the impact of impurities within the CO_2 feed from the various capture technologies on these possible hazards. Knowledge gaps in the modelling of outflow and subsequent dispersion of CO_2 following the accidental rupture of pressurised CO_2 pipelines, central to their safety assessment, are also presented.

INTRODUCTION

Pressurised pipelines are widely considered to be the most practical, and in the case of fossil fuel power generation plant, the only option for transporting captured CO_2 for subsequent sequestration. Typically, such pipelines may be several hundred kilometres long, transporting enormous amounts of CO_2 under supercritical conditions.

CO_2 is hazardous as defined by the UK Health & Safety Executive (http://www.hse.gov.uk/hid/haztox.htm). At concentrations greater than 7% v/v the gas is likely to be instantly fatal (Kruse and Tekiela, 1996). Given this and the large quantities of CO_2 involved (typical several thousand tonnes), understanding of the factors that may undermine the mechanical integrity of such pipelines is central to the successful risk management of CCS and its implementation as an effective means for combating the effects of global warming.

It is widely acknowledged (see for example CRS Report, 2007) that existing experience with the use of pressurised CO_2 pipelines is simply too limited to draw any meaningful conclusions. Additionally, the widely different hazard profile of CO_2 as compared to hydrocarbons means that there is some lack of confidence that the existing experience with operating hydrocarbon pipelines can be wholly extended to CO_2 pipelines. Furthermore, this may result in a significant under estimation of the hazards and risks from such pipelines and such may be dangerously misplaced (Mahgerefteh et al., 2008).

This paper presents an overview of some of the most important areas of uncertainty affecting CO_2 pipeline safe operation and integrity that require further investigation. These include consideration from the molecular level, such as the impact of impurities on thermodynamics and phase behaviour of CO_2, corrosion resistance and hydrate formation to macroscopic considerations such as fast running ductile or brittle fracture propagation.

It is important to note that although many tools currently available in support of design and safety assessment can and are being applied to assess the pipeline transportation hazards, there is in general no firm scientific basis for such application in the case of CO_2 pipelines. Basic research and development work is now required in order to provide the underpinning knowledge that will form the basis of the design tools needed to ensure the success of CCS.

RESULTS AND DISCUSSION

CO_2 IMPURITIES

CO_2 transported through pipelines will contain impurities. The type and the concentration of these impurities will depend on the power production method, capture technologies employed and possible purification of the feed stream.

Table 1 shows typical data for the three main methods of power production including post-combustion (CO_2 captured from flue gas), pre-combustion (CO_2 captured before combustion) and oxyfuel combustion (almost pure O_2 used in combustion). It should be noted that these data are based on the assumption of prior drying of the CO_2 stream at the inlet. In practice, water concentrations may reach as much as 5% v/v giving rise to significant design and operational difficulties. These issues will be dealt with separately below. For now, returning to Table 1, it is clear that post-combustion capture, being the most popular of the three carbon capture technologies, presents the biggest challenge due to the largest number of impurities present in the CO_2 stream.

By far the most important effect of impurities on CO_2 pipeline transportation is the modification of the CO_2 thermo-physical and phase equilibrium behaviour. Such data for pure CO_2 spanning the triple point to supercritical conditions are extensively available and dedicated equations of state have been developed (see, for example, Span and Wagner, 1996). However, in the case of mixtures, all of the reported studies are either confined to cases in which CO_2 is present as an impurity (Weber, 1995) or for binary CO_2 mixtures (Perakis et al., 2006). There is no validated equation of state for CO_2 in the presence of multi-component impurities that would be typically encountered during CO_2 pipeline transportation. The same applies to the pertinent thermo-physical properties such as thermal

Table 1. CO_2 composition for different CCS technologies (Oosterkamp and Ramsen, 2008)

	Post-combustion	Pre-combustion	Oxyfuel
CO_2	>99 vol%	>95.6 vol%	>90 vol%
CH_4	<100 ppmv	<350 ppmv	
N_2	<0.17 vol%	<0.6 vol%	<7 vol%
H_2S	Trace	3.4 vol%	Trace
C_2+	<100 ppmv	<0.01 vol%	–
CO	<10 ppmv	<0.4 vol%	Trace
O_2	<0.01 vol%	Trace	<3 vol%
NO_x	<50 ppmv	–	<0.25 vol%
SO_x	<10 ppmv	–	<2.5 vol%
Ar	Trace	<0.05 vol%	<5 vol%

diffusivity, viscosity and flow and phase dependent frictional properties. Knowledge of such data will have a direct impact on the following CO_2 pipeline operational and design requirements.

COMPRESSOR REQUIREMENTS

Impurities may result in two-phase flow at the compressor inlet giving rise to significant operational difficulties such as cavitation. The limited experience available for binary CO_2 mixtures such as CO_2/H_2S reveals an increase in the dew point temperature (Stouffer et al., 2001). This means that a higher degree of cooling will be required at the compressor inlet to ensure liquid compression for the CO_2/impurities mixtures as compared to pure CO_2. Additionally, the increase in the dew point temperature will require higher operating pressures within the pipeline in order to maintain the liquid phase during pipeline transportation. This will mean thicker pipe walls or the use of more exotic materials to ensure pipeline integrity and hence increased costs.

A change in the bulk fluid density or viscosity on the other hand will impact the compressor power requirement with the former affecting the overall effective capacity of the pipeline in transporting CO_2.

Investigations using the REFPROP program from NIST (Heggum, 2005) for a number of relevant CO_2 binary mixtures including CO_2/C_4, CO_2/N_2 and CO_2/O_2 generally reveal a reduction in the CO_2 viscosity as compared to that for pure CO_2. Clearly, the higher molecular weight impurities will increase the bulk density.

PIPELINE INTEGRITY

Impurities may also affect pipeline integrity through hydrogen embrittlement, corrosion damage, and fast running brittle or ductile fracture mechanics. These issues are considered further below.

HYDROGEN EMBRITTLEMENT

Molecular hydrogen in the pipeline may diffuse into the pipeline material resulting in a local internal pressure which in turn reduces its ductility and tensile strength thus promoting brittle fractures. This topic has been extensively studied for hydrocarbon conveying pipelines (Irzhov et al., 1982). Hydrogen embrittlement can be overcome to a large extent through appropriate pipeline material selection such as low sulphur content steels, but at increased cost. Mikhailovski (2000) has developed a sensor technology for monitoring hydrogen embrittlement in carbon steel hydrocarbon conveying pipelines.

If hydrogen is present as an impurity in CO_2 then the hydrogen may add to the problem of brittle fracture as it exhibits a different failure mechanism associated with lattice penetration (considered later).

CORROSION

As mentioned above, the presence of water in the CO_2 pipeline will be inevitable. The post-combustion capture technology presents the biggest challenge due to the largest potential concentration of water in the inlet stream as compared to the oxyfuel or pre-combustion routes.

The solubility of water in CO_2 is a function of temperature and pressure. The problem occurs when the solubility of water in CO_2 is exceeded and free water is formed. This can then give rise to corrosion and/or hydrate formation issues.

Corrosion can occur when free water directly attacks the pipeline material by acting as an electrolyte. Alternatively, free water can react with CO_2 resulting in carbonic acid corrosion. Both types of corrosion mechanisms have been extensively studied and corrosion rate data are readily available. For carbon steel pipeline, corrosion is a serious issue and numerous studies involving hydrocarbons with relatively small amounts of CO_2 have been reported (see, for example, Kermani, and Morshed, 2003).

However, no comparative investigations involving CO_2 in the presence of impurities are available. O_2, H_2S, SO_2 and NOx are all expected to increase corrosion rates. In addition, even for CO_2-water corrosion, no data in the supercritical region are available. The fact that supercritical CO_2 is an extremely efficient solvent (IPCC, 2004) poses serious uncertainties in extrapolating the current understanding of CO_2-water corrosion behaviour to pipelines transporting supercritical CO_2.

Apart from direct and costly mitigation steps such as the use of corrosion inhibitors, pre-drying or improved pipeline material selection, the ultimate aim should be determining the conditions for which the formation of free water will be unlikely. This will require a fundamental approach involving the understanding of the thermodynamics of the CO_2/impurties corrosion mechanism in conjunction with careful experimentation.

HYDRATE FORMATION

Gas hydrates are another potential hazard associated with CO_2 pipelines. Gas hydrates are formed as a result of the combination of water and gas molecules at suitable temperature and pressure conditions. Many gases, including methane and CO_2, can form gas hydrates. Probably the first evidence for the existence of CO_2 hydrates dates back to the year 1882, when Wróblewski (Wroblewski, 1882) reported clathrate formation while studying carbonic acid. He noted that the gas hydrate was a white material resembling snow and could be formed by raising the pressure above certain limits in his H_2O-CO_2 system. Hydrates can cause the blockage of the pipeline thus giving rise to serious operational and safety issues.

Figure 1 shows CO_2/water phase diagram. The dark grey region (V-I-H) represents the conditions at which CO_2 hydrate is stable together with gaseous CO_2 and water ice (below 273.15 K). Based on the diagram, it is clear that CO_2 hydrates may be formed at temperatures below 280 K, typical for many offshore pipelines.

Even for pipelines operating above this temperature, hydrate formation can still be a serious issue during emergency blowdown due to significant localised temperature drops associated with rapid depressurisation. Once again, no comparative studies investigating the impact of typical CCS impurities on CO_2 hydrate formation have been reported.

FRACTURE PROPAGATION

Pipeline failure due to fracture propagation is a serious issue in the hydrocarbon industry (see, for example, Picard and Bishnoi, 1988). Mitigation has involved measures such as the use of fracture arrestors placed at regular intervals along the pipeline length, the selection of appropriate pipeline materials, or operating conditions which are less likely to give rise to such types of failure. The correct choice of all of these approaches requires a fundamental understanding of the fracture failure mechanism and the consequences of such failures on hazard source term and likelihood estimation to enable the establishment of appropriate material and operational standards.

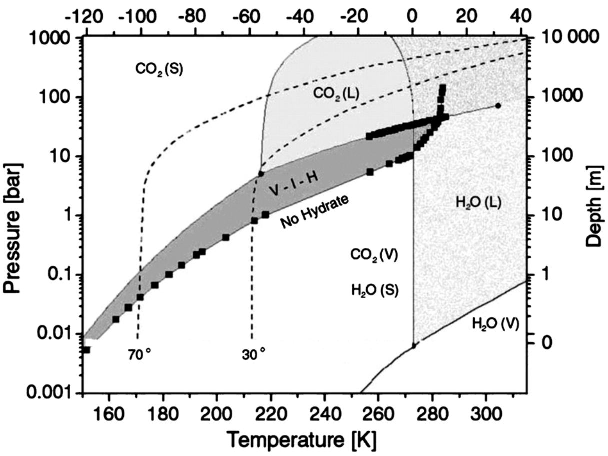


Figure 1. CO_2 hydrate phase diagram. The black squares show experimental data (Sloan, 1998). The lines of the CO_2 phase boundaries are calculated according to the Intern. Thermodyn. Tables (1976). The abbreviations are as follows: L – liquid, V – vapour, S – solid, I – water ice, H – hydrate

Little is known about the spontaneity of CO_2 pipelines to such types of failure. As will be shown later, this is important since the thermodynamic properties of the pressurised inventory play a central role in governing fracture propagation.

Pipelines can fail through either ductile and/or brittle factures. Figure 2 shows a schematic representation of both failure modes.

Ductile fractures involve significant pipeline deformation. The more insidious brittle fractures on the other hand involve little deformation during fracture growth and hence may be left unnoticed until they become unstable by which time catastrophic pipeline failure has occurred. The study of pipeline ductile fractures has received a great deal of attention (see, for example, Takeuchi et al., 2006).

Ductile fractures may start due to an external force such as loss of material (corrosion or external third party action), ground movement or impact damage and grow when the pressure stresses within the pipeline exceed the pipeline mechanical properties such as yield stress or fracture toughness.

As failure will involve a continuous drop in the line pressure due to loss of fluid, the fracture will come to rest when the corresponding fluid decompression velocity within the pipeline exceeds the fracture propagation speed or the crack is arrested. Such fractures are modelled using the rather simplistic Batelle Two Curve Methodology (Makino et al., 2001) which expresses this balance in terms of the fracture velocity and decompression velocity curve. Figure 3 shows a typical diagram for a gas decompression curve.

Much the same as ductile failures, brittle fractures are also initiated as a result of a through wall defect. However, the failure mechanism is more complex with both pressure and thermal stresses playing a major role. A comprehensive analysis of the important processes leading to catastrophic brittle failure is presented in a publication by Mahgerefteh and Olufemi (2006).

In essence, the rapid depressurisation of the inventory at the point of failure following pipeline puncture may result in a large drop in its temperature and that of the pipe wall in contact with it. If the pipe wall temperature falls to below its ductile/brittle transition temperature (DBTT), a significant drop in its fracture toughness (ca. 100% for carbon steel) will occur. Figure 4 shows a schematic representation of this phenomenon. Catastrophic failure is characterised by a fast running fracture and massive escape of inventory will occur if the transient localised pressure and thermal stresses at the defect plane exceed the *critical* pipeline fracture toughness.

The critical fracture toughness at which a crack length becomes unstable is given by (Irwin, 1957)

$$K_C = Y\sigma\sqrt{\pi a}$$

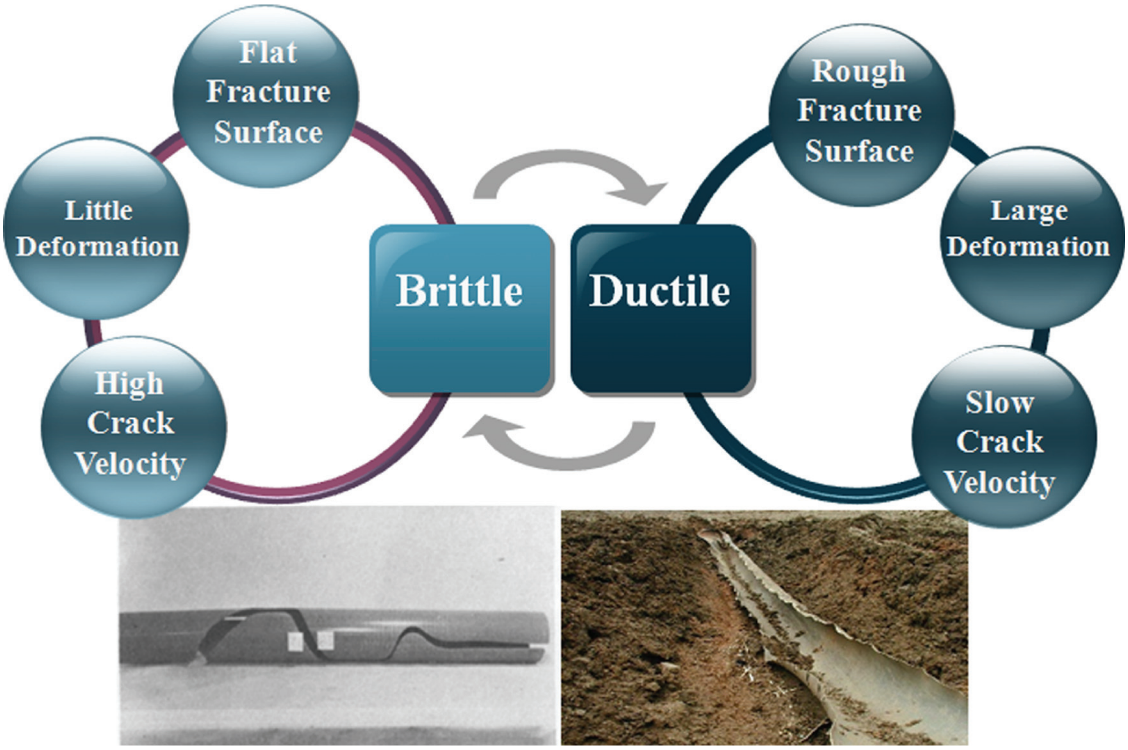


Figure 2. Schematic representations of pipeline failure through brittle and ductile fractures

where Y and a, are, respectively, the crack geometry shape factor and half length. σ, is the sum of the transient thermal and pressure stresses in the defect plane.

Figure 5 shows a schematic representation of the pertinent fluid/structure interactions leading to brittle fracture propagation in a pressurised pipeline.

As shown above, the pressurised fluid decompression velocity (manifested in the localised transient pressures stresses) and heat transfer characteristics (manifested in the localised thermal stresses) play important roles in governing fracture propagation. Table 2 gives a representation of the main features of brittle and ductile fast running fractures.

CO_2 pipelines are more susceptible to fast running fractures as compared to hydrocarbon pipelines for the following reasons:

i) CO_2 exhibits a prolonged phase transition during depressurisation. This means that the pressurise stresses driving the fracture remain relatively unchanged during failure despite loss of material from the pipeline;
ii) CO_2 undergoes marked Joule-Thomson expansion cooling during rapid depressurisation with temperatures reaching as low as 203 K. The inevitable drop

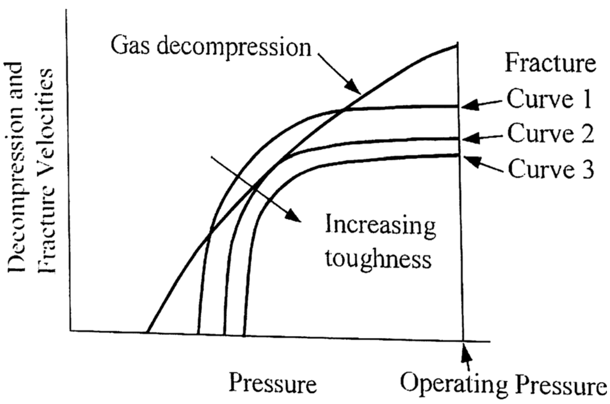


Figure 3. Schematic – Gas decompression curve and fracture velocity curve; Curves 1,2,3 correspond to different pipe toughness values (Rothwell, 2000)

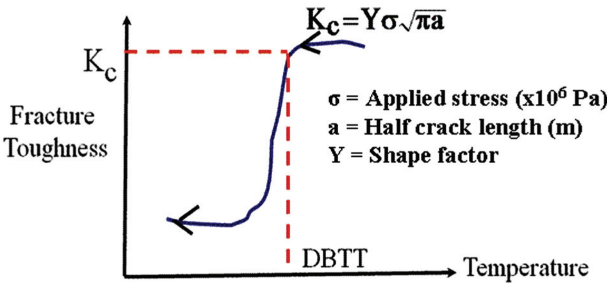


Figure 4. Schematic representation of fracture toughness as a function of temperature

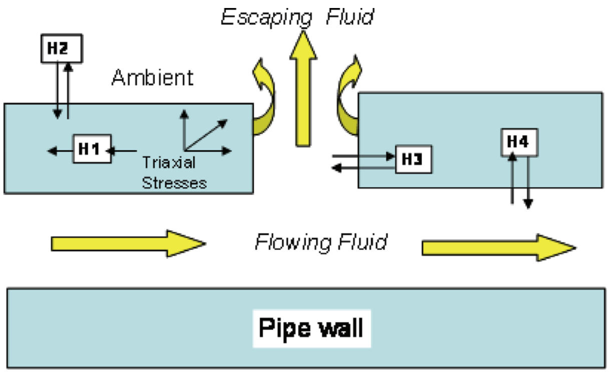


Figure 5. Schematic representation of the pertinent fluid/structure interactions leading to brittle fracture; H1: heat transfer within the pipe wall (conduction); H2: heat transfer between ambient and the pipe wall (natural convection); H3: heat transfer between the escaping fluid and defect neck (forced and natural convection); H4: heat transfer between flowing fluid and inner pipe wall (forced convection)

in the pipe wall temperature in contact with the escaping CO_2 and the corresponding likely significant drop in fracture toughness will lead to significant localised thermal stresses in the defect plane thus promoting fracture propagation.

As such the study of CO_2 pipeline ductile and brittle factures must entail detailed consideration of fluid/structure interactions involving a robust equation of state capable of correctly predicting the depressurisation thermodynamic trajectory of CO_2, especially in the presence of impurities.

OUTFLOW AND DISPERSION MODELLING

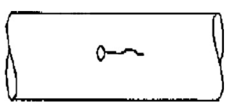
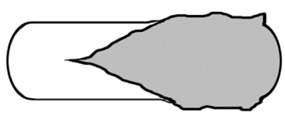
The accurate prediction of the fluid phase, discharge rate and subsequent atmospheric dispersion during accidental releases from pressurised CO_2 are pivotal to quantifying all the hazard consequences associated with CO_2 pipeline failure. Such data form the basis for emergency response planning and determining minimum safe distances to populated areas. So far, all the discharge modelling work has been either based on very simplistic and wholly unrealistic assumptions treating the ruptured pipeline as a vessel discharging through an orifice (see for example, Cruse and Tekiela, 1996), or the much more advanced CFD numerical simulations based on the homogeneous equilibrium model (HEM) in which the constituent phases are assumed to be at thermal equilibrium, travelling at the same velocity (Mahgerefteh et al., 2008). HEM has been shown (see, for example, Chen et al., 1993; Mahgerefteh et al., 2006; Mahgerefteh and Oke, 2006) to produce reasonably good, conservative predictions of discharge and decompression rates following pipeline rupture when compared to actual data. However, given that the constituent phases are assumed to be fully dispersed, HEM is incapable of correctly predicting the discharge fluid physical state in the presence of phase slip. This may be especially the case for CO_2 given the very different densities of solid, liquid and vapour.

CO_2 has very different hazard profiles in the gas or solid states directly influencing many of its features including dispersion behaviour, solubility or erosion impact of the high velocity escaping fluid.

Likewise, the near-field behaviour of releases of supercritical CO_2 is not understood. Depending on the precise time during any release, supercritical CO_2, a gas-liquid droplet mixture or gas alone will be released to atmosphere and disperse over large distances. This may also be followed by gas-solid discharge during the latter stages of depressurisation due to the cooling taking place. The detailed modelling of the near-field characteristics of these complex releases is required since predictions of major hazards used in safety and risk assessments are generally (Connolly and Cusco, 2008) based on the use of near-field source terms to provide input to far-field dispersion models.

Addressing the above limitations through the developments of robust mathematical models backed by small and large scale validations is the subject of a major multinational study by the present authors (MF and HM).

Table 2. A representation of the main features of brittle and ductile fast running fractures

	Fracture mode	
Main features	Brittle	Ductile
Driving mechanism	Heat transfer Fracture toughness	Fracture toughness
Crack propagation	Slow, followed by catastrophe	Rapid
Crack arrest length	Unlimited	Limited
Energy dissipation	Instantaneous	Slow
Fracture shape		

CONCLUSIONS

1. Presently there is insufficient knowledge to enable the correct predictions for the depressurisation thermodynamic trajectory of supercritical or dense phase CO_2 in the presence of impurities particularly those likely to be present from carbon capture resulting from power generation using fossil fuels. Our preliminary investigations show significant changes in the presence of N_2 at concentrations greater than 1%. This is followed by hydrogen and methane.
2. The study of CO_2 pipeline ductile and brittle failures must entail the development and application of appropriate equations of state and the detailed consideration of the interactions between the transported fluid and the materials of containment.
3. Development of a means for accurate thermodynamic depressurisation trajectory and multiphase outflow modelling are necessary to enable adequate determination of the mass, momentum, energy and state of CO_2 released as a result of a pipeline failure.
4. Utilising the factors determined in 3 above should enable hazard source term definition sufficiently to select and apply the appropriate transmission (dispersion) models used to estimate distance to a specified level of harm for a receiving target.
5. Establishment of the conditions for, and consequences of, ductile or brittle failure is also necessary to define the physical attributes of a release source and subsequent hazard analysis.
6. Comparison of the factors resulting in CO_2 pipeline brittle or ductile failures against established models used for such predictions of other hazardous fluids (particularly natural gas) will enable confidence in the application of available pipeline damage and failure data for the estimation of supercritical or dense phase CO_2 pipeline failure probability.
7. Satisfaction of points 1–6 coupled with appropriate vulnerability criteria should enable adequate and appropriate estimation of the risks associated with CO_2 pipelines.
8. Satisfaction of all of the above should enable the development of appropriate standards for relevant matters of material selection and maintenance activities associated with the purification and transportation of supercritical and dense phase CO_2.

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