Towards a CO$_2$ Pipeline Specification: Defining Tolerance Limits for Impurities

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ABSTRACT

As more Carbon Capture and Storage (CCS) projects are proposed, it is becoming clear that the specification of the carbon dioxide (CO$_2$) in the pipeline is an under researched area. Research has been conducted into the effect of the impurities on the different aspects of pipeline hydraulic design, pipeline integrity and public safety, however, the inter-relationship of these differing, and sometimes competing, requirements has not been investigated in detail.

This paper reviews the current pipeline specifications for CO$_2$ pipelines and then discusses the effects that different impurities have on key aspects of pipeline design, operation, integrity and health and safety and the requirements that need to be considered when specifying the maximum levels of these impurities for entry into the pipeline system.

INTRODUCTION

Worldwide, it is estimated that there are over 3500km of operational, long-distance, high-pressure carbon dioxide (CO$_2$) pipelines (Table 1). The majority of these pipelines are located in the United States of America (USA) and are transporting mainly natural sources of CO$_2$ for onshore Enhanced Oil Recovery (EOR). There is only one high-pressure pipeline currently transporting CO$_2$ for storage purposes, the offshore Snøhvit pipeline operated by Statoil. None of the pipelines introduced in Table 1 transports pure CO$_2$ and, whether the source is natural or anthropogenic, the CO$_2$ stream will contain some level of other components. There is therefore a requirement to define a pipeline entry specification for the CO$_2$.

In many respects the definition of a universal specification is less complicated when the CO$_2$ is derived from naturally occurring sources, which are relatively pure and fairly consistent in composition. As a result, in the USA, and particularly for EOR applications, the quality specification is driven by the requirements of EOR as well as pipeline integrity. However, for pipeline transportation for CCS schemes, particularly from power plant capture, the purity of the CO$_2$ is affected, not only by the various types of capture technology and processes, but also by economics (*i.e.* the increased cost associated with the removal of impurities to low levels), legislative and regulatory requirements, specifications and safety considerations.

The definition of a CO_2 pipeline specification from carbon capture plants can therefore be undertaken by analysing the types and levels of impurities that could be present from each capture technology and then by specifying the levels of impurities that could be safely transported from a health, environmental and technical point of view.

This paper will review the current pipeline specifications for CO_2 pipelines and then discuss the effects that different impurities have on key aspects of pipeline design, operation, integrity and health and safety and the requirements that need to be considered when specifying the maximum levels of these impurities for entry into the pipeline system. It is accepted that this approach only considers the effect on the pipeline section of the CCS chain and it is appreciated that the requirements of the storage site will also influence the CO_2 specification.

REVIEW OF CO_2 SPECIFICATIONS FOR PIPELINE TRANSPORTATION

Before analysing proposed CO_2 specifications for CCS, it is first informative to consider the quality specifications of currently operating CO_2 pipelines in order to put the discussion into context.

Currently Operating Pipelines CO_2 Quality Specifications

As mentioned previously, for transmission pipelines in the USA, the quality requirements for the CO_2 are primarily dictated by the effects of impurities on the EOR process rather than economic, safety or hydraulic considerations. For EOR, impurities can affect the Minimum Miscibility Pressure (MMP) of CO_2 with crude oil. Impurities such as nitrogen (N_2), hydrogen (H_2) and methane (CH_4) increase the MMP and therefore are undesirable, however, hydrogen sulphide (H_2S) decreases the miscibility of CO_2 and therefore it could be considered to be a desirable impurity, ignoring all other effects of H_2S.

Table 2 provides a comparison between the required CO_2 quality specifications and the actual compositions achieved in currently operational CO_2 pipelines. Most natural sources of CO_2, which are transported by pipeline, contain impurities such as CH_4, higher hydrocarbons and N_2 as shown in the Kinder Morgan (KMCO2) CO_2 quality specification (Kinder Morgan 2006) and the Cortez pipeline specification (Marsden and Wolter 1986). Anthropogenic sources of CO_2 can also include carbon monoxide (CO), oxygen (O_2) and hydrogen sulphide (H_2S). A typical quality specification for the anthropogenic Canyon Reef Carriers (CRC) CO_2 pipeline, as defined in IPCC (2005), is also presented in Table 2.

It is interesting to note from Table 2 that the Cortez pipeline, operated by KMCO$_2$, is transporting CO_2 at concentrations well above those required by the specification and that the Weyburn pipeline is transporting significantly more H_2S than the other pipelines. As discussed previously, the presence of

H_2S is desirable for EOR applications. In addition, as CO_2 is odourless, the presence of H_2S acts as an odorant which can alert the public to the presence of a leak in the pipeline.

Projected CO_2 Purity Specifications from Different Capture Technologies

The focus for CCS projects is to capture CO_2 predominantly from power plants. The amount and type of impurities in the CO_2 stream captured from a power plant are dependent on the capture process, the capture technology, the fuel source, regulatory constraints and also, as mentioned previously, economic considerations. Studies of the levels and types of impurity that could be present in the captured CO_2 from different capture technologies and fuel sources have been published by IPCC (IPCC 2005), the EU Framework 6 ENCAP (European Enhanced Capture of CO_2) project (Anheden, et al. 2005), Oosterkamp and Ramsen (Oosterkamp and Ramsen 2008) and the International Energy Agency Greenhouse Gas R&D Programme (IEAGHG 2011; Kather and Kownatzki 2011). A review of some of these specifications, as they relate to pipeline transportation, is provided in Mohitpour *et al.* (2012) and a summary is presented in Table 3.

Comparison of Table 2 with Table 3 indicates that there are some types of impurities which are not currently being transported in operational CO_2 pipelines *e.g.* NO_x, SO_x[1], argon (Ar) and H_2. It is therefore important to understand the impact of these impurities in particular on the specification. In terms of defining a CO_2 specification, it should also be noted from Table 4 that, although some impurities are not produced by some of the capture technologies, *e.g.* H_2S is only produced in pre-combustion processes, co-mingling of CO_2 from different capture technologies in a single transportation pipeline requires a specification to be "universal" and to consider all impurities that could be present from every capture technology. Another challenge for a pipeline specification is illustrated by the difference in the levels of some impurities between different technologies *e.g.* in post combustion capture the combined levels of Ar and N_2 could be as low as 0.01vol%. However, for some types of oxyfuel capture technology the combined levels could be over 10vol%. This range of requirements for a pipeline specification makes it difficult to specify the CO_2 composition from the point of view of the capture processes and the components that could be present in the captured CO_2 stream. An alternative position has therefore been to define the composition from the point of view of the requirements of the pipeline. This is the basis of the Dynamis and Ecofys studies described in the next section.

Projected CO_2 Pipeline Specifications for CCS Transport

The Dynamis transport specification (de Visser and Hendriks 2007) presented in Table 4 is based on the ENCAP specification (Anheden, et al. 2005) for pre and post-combustion capture (Table 3). It is

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[1] Collective terms for oxides of nitrogen and sulphur respectively.

highlighted that, as other capture technologies were not considered in the analysis (*e.g.* oxyfuel), the application of the Dynamis specification to pipelines carrying CO_2 from processes other than pre and post-combustion technologies should be considered with care.

For the Dynamis specification, the ENCAP specification has been modified to take account of safety and toxicity limits, in the event of a release from the pipeline; infrastructure durability, in terms of the need to avoid free water formation to prevent hydrate formation and corrosion; and transport efficiency (de Visser and Hendriks 2007). These considerations have decreased the allowable levels of H_2S, carbon monoxide (CO), SO_x and NO_x from the ENCAP limits, using the Short Term Exposure Limits (STELs) for these compounds to set a maximum concentration in the CO_2 stream on the basis of toxicity effects. The allowable water content has also been increased from the ENCAP specification. This increase has been justified on the basis that the specified level is below the water saturation limit at the pipeline operating conditions considered, allowing for the effects of other impurities on the solubility of water in CO_2, particularly H_2S and CH_4 and the risk of hydrate formation.

The Ecofys study took a similar approach to the Dynamis project, except that the case study was based on potential impurities from coal fired power plants (Hendriks *et al* 2007). In contrast to the Dynamis specification, the Ecofys specification does not set a limit for SO_x and NO_x as these are not considered to be critical impurities if no free water is present (Table 4).

In both the Dynamis and Ecofys studies, the total amount of the non condensable components such as N_2, O_2, H_2, CH_4 and Ar is limited to <4%. This limit is primarily based on the assumption that these gases will reduce the pipelines transport capacity and therefore increase the pipeline investment and compression energy costs. Although no cost-benefit analysis is presented in either the Dynamis or Ecofys studies for this limit, (Yan, *et al.* 2008) have studied the techno-economic impact of non-condensables at different levels (13%, 4% and 1% by volume) on the transportation of CO_2 from oxyfuel capture. They conclude that the limit on non-condensable components of <4% is a reasonable purification limit in terms of the cost balance of the CCS chain. However, they indicate that, for short distances and where the storage conditions permit, the level of non-condensables could be raised to 10%vol.

EFFECT OF IMPURITIES ON PIPELINE DESIGN

Having reviewed the literature relating to CO_2 specifications and discussed the impurities that could be present in a pipeline transporting CO_2 for CCS schemes, the remainder of this paper will discuss the impact of these impurities on pipeline design, operation, integrity and health and safety aspects. Each section will discuss the effect of the CO_2 specification on hydraulic efficiency, fracture control,

material degradation (in terms of corrosion and cracking) and health and safety. In each section, the effect of the individual impurities will be discussed in isolation without reference to any other constraints, *e.g.* the effect of NO_x on hydraulics is not coupled to the effect of NO_x on health and safety. In addition, the concentrations of some impurities are relatively high in this analysis to demonstrate an effect, although it is recognised that some levels of impurity are not feasible from the capture processes discussed previously.

CO_2 Specification for Hydraulic Efficiency

In order to understand the issues relating to the hydraulic efficiency and in particular the composition of the CO_2 in the pipeline, it is first necessary to consider the phase in which the fluid is being transported. Reference to the phase diagram for pure CO_2 in Figure 1 defines a critical point in the phase diagram at 74 bar and 31°C. At pressures and temperatures above the critical point, CO_2 no longer exists in distinct gaseous and liquid phases. In this paper, two regions are defined above the critical pressure, the "supercritical phase" which lies above the critical temperature and the "dense phase" which lies below the critical temperature. In moving from the supercritical phase to the dense phase there is no distinct phase change although the density of the fluid increases with decreasing temperature. However, below the critical pressure there is an abrupt change in phase and physical properties when crossing the vapour-liquid equilibrium (VLE) curve. At any point along the VLE curve both gas and liquid phases can co-exist at the same conditions of temperature and pressure resulting in a two-phase condition.

In pipelines it is most efficient and economic to transport the CO_2 as a supercritical or dense phase fluid as under these conditions the fluid has the density of a liquid but the viscosity of a gas. It is also important to prevent the pipeline from operating near the VLE conditions and consequently all of the high pressure pipelines referred to in Table 1 are operating above the critical pressure. The outlet temperature from the compressor may be as high as 40-50°C (Farris 1983) and therefore at the start of these pipelines, the CO_2 will be in the supercritical phase. However, further along the pipeline, the temperature will drop due to heat transfer from the pipeline and although, the CO_2 in the pipeline will start in the supercritical phase, it could move into the dense phase with increasing distance along the pipeline.

Although the supercritical phase is the most efficient phase in which to transport large volumes of CO_2, gaseous phase pipelines are also being considered for CCS schemes and could be viable for short pipeline sections or for transport through more densely populated areas. In these regions, high pressure pipelines may not receive regulatory approval and it may be desirable to make use of existing infrastructure that has been designed for lower pressures (Seevam, *et al*. 2010). For example, the Lacq

pipeline operated by Total in France is transporting CO_2 in the gaseous phase from an oxyfuel capture plant through a 27km pipeline at a pressure of 30bar to an onshore storage site (Total 2007).

Impact of Impurities on Pipeline Operating Pressure

The phase behaviour of CO_2 changes when impurities are introduced into the system. This change is dictated by the type, amount and combination of impurities present, as the impurities interact both with CO_2 and each other (as in the case of water). The general effect of any impurities when added into the CO_2 stream is to raise the critical pressure and open out a two phase (liquid-gaseous) area in the phase diagram. Components having a critical temperature and pressure higher than CO_2 form a phase envelope that expands below the VLE of pure CO_2 whereas those with a lower critical temperature and pressure than CO_2 expand above the VLE for pure CO_2. The critical temperatures and pressures of the major components from power plant capture (as presented in Table 3) relative to CO_2 are illustrated in Figure 2 and the effect on the phase diagram for binary combinations of CO_2-NO_2 and CO_2-H_2 is illustrated in Figure 3.The implications of the size of the two phase area and changes in the critical pressure lie in the operating flexibility of the pipeline system.

For dense phase pipelines, a high critical pressure and large two phase area will require the pipeline to be operated at higher pressures to reduce the risk of two phase flow during upset conditions. Operating at a higher pressure will have economic implications in that, in order to comply with the maximum allowable stress in the pipeline, the wall thickness will have to be increased, or the diameter of the pipeline will have to be reduced or a higher strength steel specified for the pipeline. However, for a gaseous phase CO_2 pipeline, the formation of a large two phase area below the pure CO_2 VLE line reduces the Maximum Allowable Operating Pressure (MAOP) of the pipeline to avoid two phase flow, particularly at low ground temperatures. Reducing the operating pressure level limits the throughput and operational flexibility of the pipeline and therefore has economic implications.

Therefore, it can be concluded that, in order to increase the operational flexibility of the pipeline, the components with the highest relative critical pressures and temperatures (e.g. SO_x and NO_x) should be limited when specifying the quality of the CO_2 to be transported in the gaseous phase and the components with the lowest relative critical pressures and temperatures (e.g. H_2 and N_2) in the CO_2 mixture should be limited when specifying the quality of the CO_2 to be transported in the dense phase.

Impact of Impurities on Pipeline Sizing

One of the first stages in the design of a pipeline is to size the pipeline, in terms of internal diameter, for the anticipated flow rate. The capacity of the pipeline is dependent on the required pressure and temperature as well as on the fluid's physical properties, in particular compressibility and density. The way in which the density of CO_2 changes with pressure and temperature and the sharp discontinuity it

exhibits close to the VLE curve is significantly influenced by the level of impurity present. This behaviour, and the effect on CO_2 pipeline transportation, has been discussed in Seevam *et al.* (2007 and the relationship between density, pressure and level of impurity is illustrated in Figure 4. It is highlighted that around the discontinuity in Figure 4, small changes in pressure can have large influences on the density. The addition of impurities will move the location of the discontinuity to higher pressures (for components with lower critical temperatures and pressures than CO_2) and to lower pressures (for components with higher critical temperatures and pressures than CO_2). A further key point that was concluded by Seevam *et al.* (2007) relates to the effect of temperature on density. Reducing the temperature increases the density of the CO_2 fluid and therefore, for dense phase pipeline transportation in particular, lowering the inlet temperature will increase pipeline capacity.

In order to illustrate the effect of the specification of the pressure, temperature and level of impurities on pipeline diameter, a series of hydraulic simulations are presented for a case study pipeline transporting pure CO_2 and a mixture of CO_2-5mol%H_2. The study was conducted for a pipeline length of 100km with a 0.0002bar/m pressure drop along the pipeline. The ground temperature was specified as 5°C. The results are presented in graphical form in Figure 5. As would be expected, from the density changes described previously, the study showed that increasing the temperature and reducing the pressure results in larger diameters having to be specified for any given fluid at any given flow rate. However, Figure 5 illustrates that, for the CO_2-5%H_2 mixture, the effect of the addition of H_2 is to increase the required diameters over pure CO_2 and that the increase (in terms of additional steel requirements) is greater at higher flow rates and lower pressures. It should be noted that this relationship will not hold for all impurities and is dependent on the density of the CO_2 mixture at the inlet temperature and pressure relative to pure CO_2. For example, reference to Figure 4 indicates that, at some conditions of temperature and pressure, a CO_2-5%NO_2 mixture is denser than pure CO_2 and at some conditions it is less dense and therefore the diameter required to transport this mixture will either be greater or less than that required to transport pure CO_2 depending on the operating conditions.

For dense phase pipeline transportation, it can therefore be concluded that lower inlet temperatures, higher inlet pressures and the minimisation of low density impurities (such as H_2) will maximise the CO_2 throughput. This allows smaller diameter pipelines to be used for the same flow rate, thereby reducing the capital cost of pipeline projects. However, this cost has to be balanced against the operational costs associated with achieving these conditions.

Impact of Impurities on Pressure and Temperature Drop

As mentioned previously, for pipeline transport in the dense phase, the pressure has to be maintained above the critical pressure to keep the CO_2 in the dense phase. If, due to frictional losses or gravity

based losses, the pressure drops below the critical point, intermediate pumping stations would be required to raise the pressure back into the dense phase region. Alternatively, the diameter of the pipeline would have to be increased or the initial pressure raised to ensure that the pressure drop did not result in two phase flow within the pipeline length. All of these mitigation methods have associated economic impacts and in some cases are mutually exclusive. For example, increasing the diameter to avoid two phase flow will increase the stress in the pipeline and, if wall thickness and steel grade remain constant, would require a reduction in operating pressure to maintain the allowable operating stress of the pipeline.

The impact of impurities on pressure drop along a pipeline in the dense phase has been reported previously in Seevam, Race *et al*. (2008). This work concluded that, for binary combinations of impurities, the addition of H_2 resulted in the largest pressure and temperature drops along the pipeline for the impurities studied. However, all of the impurities with lower critical temperatures and pressures than CO_2 also showed this effect of increasing the pressure and temperature drops relative to pure CO_2. It can be concluded that the levels of H_2 in particular should be minimised for dense phase transportation. Conversely, it was observed that the addition of nitrogen dioxide (NO_2), SO_2 and H_2S resulted in a lower pressure drop than observed for pure CO_2 and therefore could be seen to be beneficial in terms of the hydraulic characteristics of dense phase pipelines.

It is recognised that, due to the high density of the CO_2 fluid, the effect of static head on the pressure drop can be significant. Therefore, in some cases, gravitational effects due to the changes in elevation can counteract any frictional losses and the effects of impurities.

For transportation in the gaseous phase, the pressure profile is not as significant as the temperature profile and in particular the ground temperature. In this case it is important that the temperature does not drop to a level such that the fluid will enter the two phase region. As mentioned previously the addition of components such as NO_x and SO_x should be limited in this respect. However, reducing the inlet pressure will have a greater effect on increasing the operating temperature range of the pipeline, but has impacts for operating efficiency.

Impact of Impurities on Compression and Pumping

In addition to the effects of impurities on the design of the pipeline in terms of inlet temperature and pressure, diameter, wall thickness and steel grade, the level of non-condensable impurities in the CO_2 stream will also affect the energy required for pumping and compression. Although there is not much data available on cost comparisons for compression, preliminary work has indicated that the compression and pumping costs increase as the level of impurities increase. In addition, as has been shown in the preceding sections, if a higher inlet pressure is required for certain stream compositions

then this will also increase the power and the number of compression stages required, escalating project and energy costs. These costs should also therefore be included in any techno-economic analysis.

CO$_2$ Specification for Fracture Control

The problem of ductile fracture propagation was recognised in the gas industry over forty years ago and fractures of in-service natural gas pipelines have propagated in this mode for distances up to 300m. Many authors have indicated that ductile fracture propagation may be an issue for CO$_2$ pipelines (King 1982a ; King 1982b ; Decker, *et al.* 1985 ; Maxey 1986 ; Marsili and Stevick 1990; Cosham and Eiber 2007) and the requirement to consider fracture propagation in CO$_2$ pipelines is included in the federal regulations in the USA (49CFR195 2008).

The concept and modelling of fracture propagation in CO$_2$ pipelines has been described in detail in Seevam *et al.* (2010b) and is reviewed here. On initiation of a fracture, the fluid starts to decompress and a decompression wave propagates in both directions from the fracture point at a velocity which is dependent on the fluid properties. Whether the fracture will propagate once initiated is dependent on whether there is sufficient driving force for propagation *i.e.* whether the initial pressure is high enough to sustain a fracture. If fracture can be sustained, then a crack will propagate along the pipeline at a velocity which is dependent on the strength and toughness of the pipe steel and also on the geometry of the pipeline (*i.e.* the diameter and wall thickness). If the crack propagation velocity is slower than the decompression velocity then there is no driving force for propagation and the crack will arrest.

Extensive world-wide research has led to the establishment of a number of models, which describe the fracture propagation behaviour for gas pipeline systems. These models have been very successful in defining toughness requirements for pipe material for natural gas and rich gas mixtures, which ensure fracture arrest. The most widely used model is the Battelle Two Curve Model (BTCM) (Maxey 1974). Although, the BTCM has not yet been validated for ductile fracture propagation in CO$_2$ pipelines, it can be used to study the effects of impurities on the decompressing fluid and therefore the likelihood of being able to arrest the crack once it has started to propagate.

An illustration of the BTCM for pure CO$_2$ is provided in Figure 6 (Cosham and Eiber 2007). The 'two curves' in the model are the fluid decompression curve (shown in brown), and the fracture velocity curve (shown in black). If the fracture velocity curve and the fluid decompression curve intersect or are tangent, then there exists a pressure at which the decompression wave and the crack are travelling at the same speed and the crack can propagate indefinitely under those conditions. In order to prevent crack propagation therefore, the toughness of the steel is increased so that the fracture velocity curve lies above the fluid decompression curve. By observation of Figure 6, it was concluded by Maxey

(1986) and Cosham and Eiber (2007) that an estimate of the toughness requirement for arresting a ductile fracture in a CO_2 pipeline could be obtained from the calculation of the arrest pressure[2] and the saturation pressure[3] *viz*, in order to arrest a ductile fracture, the arrest pressure must be greater than the saturation pressure *i.e.* either the arrest pressure must be raised or the saturation pressure must be lowered.

Maxey (1986) indicates that the saturation pressure can be lowered by lowering the operating temperature or by removing impurities with lower critical temperatures than CO_2. Figure 2 illustrates the impurities with lower critical temperatures than CO_2. The effect of initial temperature, pressure and impurity levels is currently being investigated by the authors using the BTCM decompression model (Maxey 1974). This work is ongoing but a sample calculation at the starting decompression conditions of 100 bara and 5^oC is presented in Figure 7. This preliminary work confirms the result of other researchers that H_2 in particular has the most potent effect, in terms of mol% addition, in raising the saturation pressure above pure CO_2 and therefore the largest detrimental effect on fracture propagation (King 1982a). At the pressure and temperature condition presented in Figure 7, it can however been seen the SO_2 would have a beneficial effect.

Conversely, it has been shown that the arrest pressure can be raised by increasing the wall thickness, increasing the toughness, decreasing the pipe diameter or increasing the pipe material yield strength (King 1982b). All of these measures have economic implications and must also be balanced against the hydraulic requirements mentioned previously (*i.e.* decreasing the diameter of the pipeline will increase the pressure drop and reduce the hydraulic efficiency). In addition, wall thickness, yield strength and toughness all have practical upper limits in terms of the capabilities of steel and pipe manufacturers. The balance therefore has to be made between the lowering of the saturation pressure (and the resultant costs on the CO_2 purification) and the raising of the arrest pressure (and the resultant costs on pipeline materials). However, one conclusion that can be drawn is that, for certain pipe diameters and wall thicknesses, the CO_2 may need to be specified to ensure fracture arrest as the required levels of toughness and yield strength cannot be achieved. If this specification cannot be attained then mechanical crack arrestors would need to be installed along the pipeline, as is the practice on some pipelines in the USA (Marsili and Stevick 1990 ; McCollough 1986), at additional cost of construction for the pipeline.

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[2] The arrest pressure is defined as the pressure below which a propagating ductile fracture cannot be sustained.
[3] The pressure at which the fluid crosses the two-phase boundary, *i.e.* in the case of pure CO_2 decompressing from the dense phase, the pressure at which fluid changes to the gaseous phase.

CO_2 Specification to Prevent Material Degradation

Material degradation in terms of internal corrosion or cracking mechanisms will only occur in the presence of water. Therefore, prior to a discussion on the effect of impurities on corrosion and cracking mechanisms, it is first necessary to discuss the specification of the maximum water content allowable in the CO_2 stream to avoid water formation in the pipeline.

Water Specification

The solubility of water in pure CO_2 has been studied extensively as a function of temperature and pressure and is discussed in the context of CO_2 pipeline transportation in Mohitpour *et al.* (2012). However, the effect of impurities on the solubility of water in CO_2 containing impurities is less well researched. Seiersten and Kongshaug (2005), Heggum *et al.* (2005) and Austegaard *et al.* (2006) have studied the CO_2-H_2O-CH_4 system and their experimental results and models indicate that the solubility of water in the system decreases with increasing CH_4 content *i.e.* adding CH_4 to the system will require the water content to be more stringently specified to avoid free water formation. Conversely, on the basis of calculations alone, for the CO_2-H_2O-H_2S system at 4°C and 100bar, de Visser and Hendriks (2007) found that the addition of H_2S would have the opposite effect and would increase the solubility of water, although the effect was found to be negligible at the levels of H_2S proposed in the Dynamis specification.

The specification of water content in currently operating pipelines has been reviewed by Seevam *et al.* (2010) and ranges between 640ppmv (parts per million by volume) in the KMCO2 pipelines and 20ppmv in the Weyburn pipeline. Both the Dynamis and Ecofys projects recommend a water content of 500ppmv to ensure that no free water is present in the pipeline and therefore to minimise the risk of corrosion and hydrate formation (Hendriks *et al.* 2007 ; de Visser and Hendriks 2007). It is noted, however, that the Dynamis project concluded that this water level should be reviewed if the operating temperature and pressure of the pipeline could result in operation below the solubility limit for water in CO_2 or if other impurities, not considered in the Dynamis report, were present in the CO_2 stream.

Despite the lack of data, the conclusion that can be drawn from these observations is that the drying specification for CO_2 containing impurities is dependent on the type and quantity of impurities present and that the effect of different impurities on the saturation limit needs to be understood in order to be able to ensure dry conditions in the pipeline.

Hydrate Formation

Apart from potential material degradation, another consideration in the specification of the water content in the CO_2 stream is the risk of hydrate formation. The published literature in this area becomes confusing as some authors indicate that free water is required for hydrates to form (Wallace

1986), whereas others indicate that hydrates can form with dissolved water (Hendriks *et al.* (2007) and Carroll (2008)). It has been stated that, under CO_2 pipeline operating pressures, it would be possible for hydrates to form at around 10-11°C (Fradet *et al.* 2008 ; Wallace 1986). However, it was considered by the Dynamis project that the amount of hydrate that could be formed with the levels of water required to prevent corrosion will not be sufficient to cause pipeline operational problems (de Visser and Hendriks 2007). Chapoy *et al*. (2009), from their work on hydrate formation and two-phase flow, have concluded that in pure CO_2 systems, it is unlikely that hydrate will form in the temperature range -2°C to 30°C and for pressures up to 200bara provided that the water content is less than 250ppm.

There has been little work on the effect of impurities on the CO_2-H_2O phase behaviour although work by Chapoy *et al*. (2009) on the CO_2-H_2 and CO_2-H_2-N_2-CO systems in the presence of water indicates that higher dehydration requirements might be necessary in the presence of H_2 to prevent hydrate formation.

Corrosion

Pure, dry CO_2 is not corrosive to carbon or stainless steel. However, in the presence of water, CO_2 can dissolve and form a concentrated carbonic acid (H_2CO_3) solution which is highly corrosive to carbon steel. This form of CO_2 corrosion is termed 'sweet' corrosion and is well understood in the oil and gas industry where the combination of CO_2 in the product and free water can cause internal pipeline corrosion. As a result there is an extensive volume of literature published on the mechanism, influencing parameters and prediction of sweet corrosion rates under the conditions of temperature, pressure, CO_2 concentration and flow rates relevant to the oil and gas industry. Less work has been published on 'sweet' corrosion in CO_2 pipelines, particularly in the presence of impurities. In CO_2 pipelines there are two scenarios whereby corrosion could occur; due to the presence of water in a water-rich phase and due to the presence of water dissolved in a CO_2-rich phase.

If the level of water is above the saturation limit at the operating temperature and pressure, then water can 'drop out' of solution as free water. Water could also enter the pipeline due to an upset in the dehydration equipment. Recent work on CO_2 corrosion relevant to the transportation of CO_2 for CCS schemes indicates that high rates of corrosion (up to 20mm/yr) could be observed in the water-rich phase in equilibrium with pure CO_2 at high pressure and temperature (Choi and Nesic 2010). In the CO_2-rich phase, water is dissolved in the CO_2 and the corrosion rates reported were much lower and typically around 0.2mm/year. However, work conducted by McGrail, *et al*. (2009) suggests that corrosion can occur in the CO_2-rich phase at water levels below the water solubility limit at the test temperature and pressure, suggesting that a separate water phase is not necessary for corrosion to

occur. From their work it can be concluded that, a threshold level did appear to exist for the onset of corrosion, which has implications for the specification of the water content to prevent corrosion.

There has been little experimental work conducted on the effect of impurities on corrosion rates, however, the principle impurities that might be considered to have an effect are H_2S, O_2, SO_2 and NO_2.

From work conducted for the hydrocarbons industry, the influence of small amounts of H_2S (*i.e.* <0.0035 bar partial pressure H_2S) on CO_2 corrosion is dependent on the concentration of H_2S and whether iron sulphide can precipitate as a protective surface scale. As the H_2S concentration increases, the formation of the iron sulphide surface film becomes more favourable and can reduce the rate of corrosion. McGrail *et al.* (2009) indicate that one of the effects of H_2S was to promote corrosion in the CO_2-rich phase at lower water levels than seen with pure CO_2. Another potential issue with H_2S and the formation of iron sulphide films is reported by Wong (2005) in compression equipment. If the iron sulphide film becomes dislodged it can coat the stainless steel aerial coolers resulting in a decrease in compressor efficiency.

There is limited experimental evidence to indicate that the addition of O_2, SO_2, and NO_2 in ternary combinations with CO_2 and H_2O or mixtures of O_2-SO_2-CO_2-H_2O increase the corrosion rate above those observed with pure CO_2 in the CO_2- rich phase under the same experimental conditions (Choi, Nesic and Young 2010 ; Xiang *et al*. 2011; Ayello 2009). Although none of these works indicate acceptable levels of these components from a corrosion point of view, Xiang *et al.* 2011 recommends that the specification of the water content should be reviewed when SO_2 is present. However, Ayello (2009) indicates that, in terms of corrosion, NO_2 could be more effective than SO_2 in increasing corrosion rates. Consequently, the influence of NO_2 on the water specification could also be crucial.

The levels of SO_x and NO_x in the CO_2 stream have recently been reviewed by Santos and Yan (2009) as it has been reported that, during the compression process, SO_2 and nitric oxide (NO) can react with water and O_2 to form sulphuric and nitric acid, causing corrosion problems in the compressor. Work reported by Santos and Yan (2009) indicates that this reaction could occur at very low concentrations, *i.e.* below those specified by Dynamis, however, no limits are specified.

CO$_2$ Specification to Prevent Cracking
H$_2$S (Sour) Cracking
In CO_2 environments containing partial pressures of H_2S greater than 0.003bar, as found in the oil and gas industry, the mechanism of corrosion described in the previous section changes from one of general or pitting corrosion to cracking and the product is termed sour. This limit has been defined in

the standard BS EN ISO 15156-2 (2009) to prevent sour cracking in H_2S environments for oil and gas production. The methodology outlined in that standard has been applied in the current study to CO_2 pipelines and the effect on the specification of H_2S levels at different pipeline pressures is illustrated in Figure 8. This figure indicates that the specification of H_2S is dependent on system pressure and that raising the pressure reduces the allowable levels of H_2S. This is significant when considered against the other implications discussed in this paper regarding the raising of system pressure on hydraulic efficiency and fracture propagation.

If a pipeline is going to be operated in sour service (*i.e.* above the levels in Figure 8), sour-resistant steel has to be selected to prevent rapid failure, as failure times as short as days or hours have been observed for sour corrosion mechanisms under test conditions in oil and gas environments. High strength steels are more susceptible to cracking in a sour environment, and consequently steels have to be selected to comply with maximum hardness levels to avoid cracking in both the parent and the weld material. As well as the additional costs associated with specifying sour resistant steel, there are additional requirements on welding and inspection when operating a sour pipeline which will increase pipeline construction and maintenance costs and need to be taken into consideration in the cost-benefit analysis associated with reducing levels of H_2S and/or ensuring that the CO_2 stream is completely dry.

CO Cracking

Another contaminant that may pose a threat to pipeline steels is CO in terms of cracking. This type of cracking has been identified as a potential risk in $CO-CO_2$ environments in carbon steels (Berry and Payer 1979). There is very little published research in this area and therefore the level of impurity required to cause CO_2-CO cracking under pipeline operating conditions is not yet known.

CO_2 Specification for Health and Safety

As mentioned previously, the Dynamis specification sets the levels of H_2S, CO, NO_x and SO_x using an approach based on the STELs, which defines the maximum concentrations for H_2S, CO, NO_x and SO_x in the CO_2 stream based on the maximum amount of these components to which a person can be exposed for a period of 15 minutes without adverse effects. The approach outlined by de Visser and Hendriks (2007) assumes that there is no additional toxic effect on people due to the combination of the components, which could increase the toxicity of the resultant stream and may require further investigation.

DEFINING CO_2 SPECIFICATIONS FOR PIPELINE TRANSPORTATION

Although the approach taken in this paper has been to consider each aspect relating to the pipeline specification individually, one of the principal conclusions that is drawn from this analysis is that the

specification of CO_2 must be considered as a whole as any changes to the specification to improve one aspect of pipeline design and operation will affect another aspect. For example, increasing NO_x levels to improve operational flexibility for dense phase pipelines will adversely affect corrosion in the event of water being present in the pipeline and there are also safety concerns in the event of a release.

In addition, the results presented have indicated that the pressure and temperature of the system is also important in defining a pipeline specification. For example increasing the pressure of the system to accommodate mixtures with higher critical pressures will have an impact on the cost of the pipeline system and also the compression costs. In addition, at higher system pressures, the specification of the maximum allowable levels of H_2S to prevent sour cracking would also have to be reduced, adding additional costs at the capture plant.

Therefore in defining a specification, for some impurities, the specification will be driven by a cost-benefit analysis to balance the additional costs required to attain required inlet temperature and pressure conditions and to specify larger diameter or thicker wall thickness pipe against the costs of improving the purity of the CO_2 stream. However, for other impurities, the specification will be driven by the requirement to maintain the integrity of the pipeline and prevent a release of CO_2.

This concept is illustrated in the summary in Table 5 . From this table, it is important to highlight that some of the drivers for the specification presented here (*e.g.* fracture control and sour cracking) have not been considered in previous pipeline specifications (de Visser and Hendriks 2007). However, the analysis presented here indicates that these aspects may drive the specification to lower limits than have been previously specified.

From Table 5, it is considered that the specification of impurity levels for hydraulic analysis and fracture control is primarily driven by a cost-benefit analysis. However, as highlighted in this paper, the specification for fracture control does become limited by available pipe dimensions and material properties. In this respect, H_2 and N_2 have the greatest effect on saturation pressure and should be limited in this situation.

It is also considered that the specification of the water level is critical in driving the specification of impurities such as NO_x, SO_x, H_2S, O_2 and CO. The mechanisms of corrosion and cracking discussed in this paper will only occur in the presence of water, whether that is dissolved in the CO_2 or as a separate liquid phase and therefore in normal operation it is critical to prevent corrosion and cracking by limiting the water content. In the event of an upset condition developing, where water could enter the pipeline, it is important to limit the extent of corrosion (through limiting the quantities of NO_x, SO_x and O_2) and prevent cracking by limiting the concentrations of H_2S and CO to below the cracking

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thresholds. A cautious approach to the specification of water would therefore seem prudent in the early stages of CCS transportation until further work has been conducted which would allow a relaxation of these limits.

CONCLUSION

The effect of impurities which may be present in the CO_2 stream on pipeline design, operation, integrity and health and safety has been considered in this paper. The work has demonstrated that, in order to define a pipeline specification, these requirements have to be considered as a whole. In particular, it has been shown that fracture control and cracking mechanisms will play a key role in limiting the allowable concentrations of certain components. These aspects have not been considered previously in the published literature.

The review conducted in this paper has also indicated that the majority of the work conducted to date on issues related to the CO_2 specification has only considered the effects of individual impurities. There has been little research published on the combined effects from different impurities in the CO_2 stream. In conclusion, there remain a number of uncertainties which require further investigation in order to define a CO_2 specification which maintains safety and integrity whilst ensuring cost efficient design.

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TABLES

Pipeline	Location	CO_2 Capacity (Mt/y)	Length (km)	MAOP (bar)	Source	Sink	Year
Canyon Reef Carriers	USA	5.2	225	140	Anthropogenic	EOR	1972
Bati Raman	Turkey	1.1	90	170	Natural	EOR	1983
Cortez	USA	19.3	808	186	Natural	EOR	1984
Bravo	USA	7.3	350	165	Natural	EOR	1984
Central Basin Pipeline	USA	20	278	170	Natural	EOR	1985
Bairoil	USA	8.3	180	-	Anthropogenic	EOR	1986
Val Verde	USA	2.5	130	140	Anthropogenic	EOR	1998
Weyburn	USA/Canada	5	328	186 & 204	Anthropogenic	EOR	2000
Snøhvit	Statoil	0.7	153	150	Anthropogenic	Storage	2008

Table 1: Typical operating conditions for long-distance, high-pressure CO_2 pipelines
(Source data: (Gale and Davison 2004) (Seevam, Race and Downie 2007)*)*

	KM CO_2 Specification (Kinder Morgan 2006)	CRC Pipeline		KMCO$_2$ Cortez Pipeline (Marsden and Wolter 1986)		Weyburn Pipeline
		Specification (IPCC 2005)	Actual (Marsili and Stevick 1990)	Specification	Actual	Actual (APGTF 2003)
Source		Anthropogenic		Natural		Anthropogenic
CO_2	>95%	>95%	95%	>95%	98.35%	96%
N_2	<4%	<4%	<0.5%	<4%	1.514	<300ppm
Hydrocarbons	<5%	<5%	5%	1-5%	0.136%	0.7% (CH_4) 2.3% (C_2^+)
H_2O	30 lbs/MMscf	<0.48 g/m^3	0.11g/m^3	30 lbs/MMscf	Not reported	<20ppm
O_2	<10 ppm wt	<10 ppm wt	--		--	<50ppm
H_2S	10-200 ppm	<1500 ppm wt	--	0.002%	--	0.9%
Glycol	0.3 gal/MMcf	<4x10^{-5} L/m^3				
CO	--	--	--	--	--	0.1%

Table 2: Examples of CO_2 pipeline quality specifications and compositions (all percentages are vol%)

	Comp (vol %)	CO_2	CH_4	H_2S	C2+	CO	O_2	Ar	N_2	NO_x	SO_x	H_2	HCN	COS	NH_3	CH_3OH
Post Combustion	IPCC Coal	>99.97						0.01		<0.01	<0.01					
	IPCC Gas	>99.97						0.01		<0.01	<0.01					
	ENCAP	99.8			0.003	0.001	0.003	0.021	0.021	0.002	0.001					
	Oosterkamp *et al*	>99	0.01	Trace	0.01	0.001	0.01	Trace	0.17	<0.005	<0.001	Trace				
	IEAGHG - Comp1	99.93				0.001	0.015	0.045		0.002	0.001					
	IEAGHG - Comp2	99.92				0.001	0.015	0.045		0.002	0.001				0.005	
	IEAGHG - Comp3	99.81				0.002	0.03	0.045		0.002	0.001					
Pre Combustion	IPCC Coal	>96.39	0.01	0.01-0.6		0.03-0.4		0.03-0.6				0.8-2.0				
	IPCC Gas	>95.65	2	<0.01		0.04		1.3				1				
	ENCAP - CO_2/H_2S	97.8	0.035	0.01	Unknown	0.17	Unknown	0.05	0.03	Unknown		1.7	<0.0005	<0.0005	0.003	
	ENCAP - CO_2+H_2S	95.6	0.035	2.3	Unknown	0.17	Unknown	0.049	0.03	Unknown		1.7	<0.0005	<0.0005	0.003	
	Oosterkamp *et al*	>95.6	<0.035	<3.4	<0.01	<0.4	Trace	<0.05	<0.6			<0.05		Unknown		
	IEAGHG - Selexol	97.95	0.01	0.01		0.04		0.03	0.9			1		With H_2S		
	IEAGHG - Rectisol	99.7	0.01	0.01		0.04		0.15	0.21			0.002		With H_2S		0.02
Oxyfuel	IPCC Coal	>95.79						3.7		0.01	0.5					
	IPCC Gas	>95.88						4.1		<0.01	<0.01					
	ENCAP - CO_2/SO_2	91				Unknown	1.6	5.7	0.61	0.25	0.076			Trace	Trace	
	ENCAP - CO_2+SO_2	90				Unknown	1.6	5.6	0.6	0.24	1.5			Trace	Trace	
	Oosterkamp *et al*	>90		Trace		Trace	<3	<5	<7	<0.25	<2.5	Trace				
	IEAGHG - Comp1	85					4.7	4.47	5.8	0.01	0.007					
	IEAGHG - Comp2	98					0.67	0.59	0.71	0.01	0.007					
	IEAGHG - Comp3	99.94					0.01	0.01	0.01	0.01	0.007					

Table 3: Comparison of published CO_2 compositions from different capture technologies (all percentages are vol%)

	DYNAMIS		ECOFYS
	Storage	**EOR**	
CO_2	>95%	>95%	>95%
H_2O	<500 ppm	<500 ppm	<500ppm
SOx	<100 ppm	<100 ppm	Not critical
NOx	<100 ppm	<100 ppm	Not critical
H_2S	<200 ppm	<200 ppm	<200ppm
CO	<2000 ppm	<2000 ppm	<2000ppm
H_2	Total non-condensable gases <4%vol	Total non-condensable gases <4%vol	Total non-condensable gases <4%vol
Ar			
N_2			
O_2		<100ppm	
CH_4		<100ppm	

Table 4 : Pipeline specifications proposed by the Dynamis and Ecofys project
(de Visser and Hendriks 2007)(Hendriks, Hagedoorn and Warmenhoven 2007)

	Hydraulics (dense phase)	Hydraulics (gas phase)	Fracture Control	Water solubility	Corrosion	Cracking	Hydrate Formation	Health & Safety
H_2O	Not studied				• Promotes corrosion	• Promotes cracking	• Promotes hydrate formation	
SO_x	• Increases critical pressure	• Reduces operating pressure	• Reduces saturation pressure	• Decreases water solubility	• Promotes corrosion	• Effect unknown	• Effect unknown	• Toxic in event of release
NO_x			• Effect unknown					
H_2S			• Effect unknown	• Increases water solubility	• Effect unknown	• Promotes cracking		
CO	• Increases critical pressure • Reduces pipeline capacity • Increases pressure drop • Increases power requirements	• Increases operating pressure	• Increases saturation pressure	• Effect unknown	• Not studied	• Promotes cracking	• Effect unknown	• Effect unknown
H_2						• Effect unknown	• Promotes hydrate formation	
Ar						• Not studied	• Effect unknown	
N_2							• Promotes hydrate formation	
O_2					• Promotes corrosion		• Effect unknown	
CH_4				• Decreases water solubility	• Not studied			

Table 5 : Summary of effects of different impurities

FIGURES
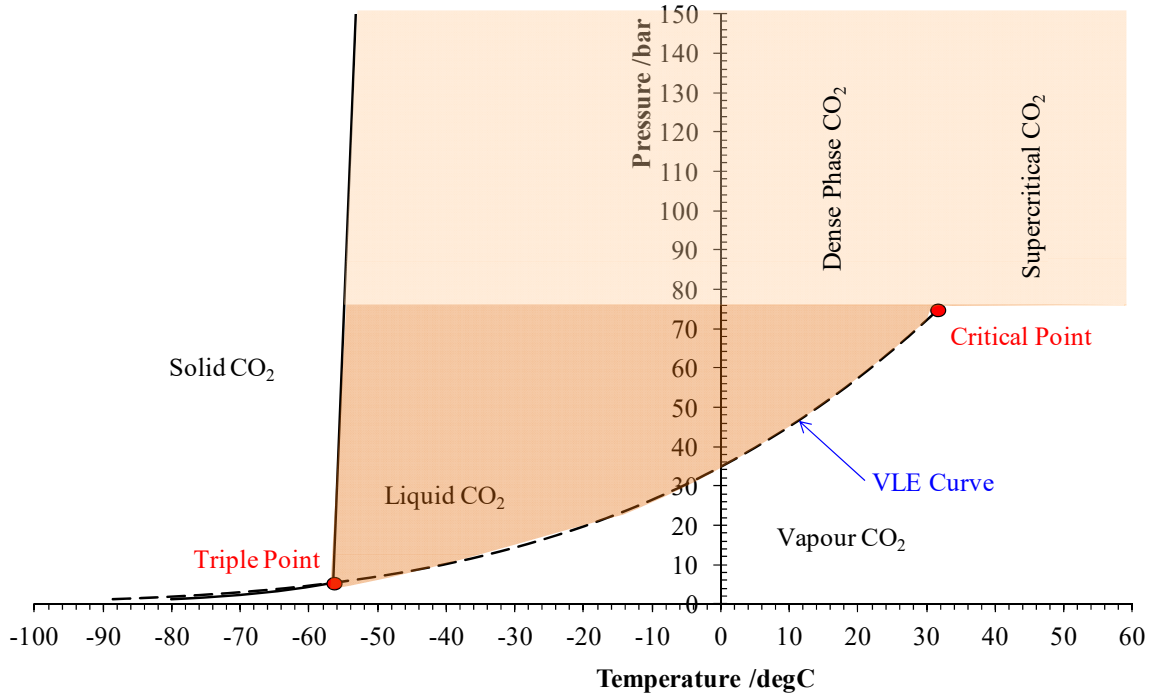
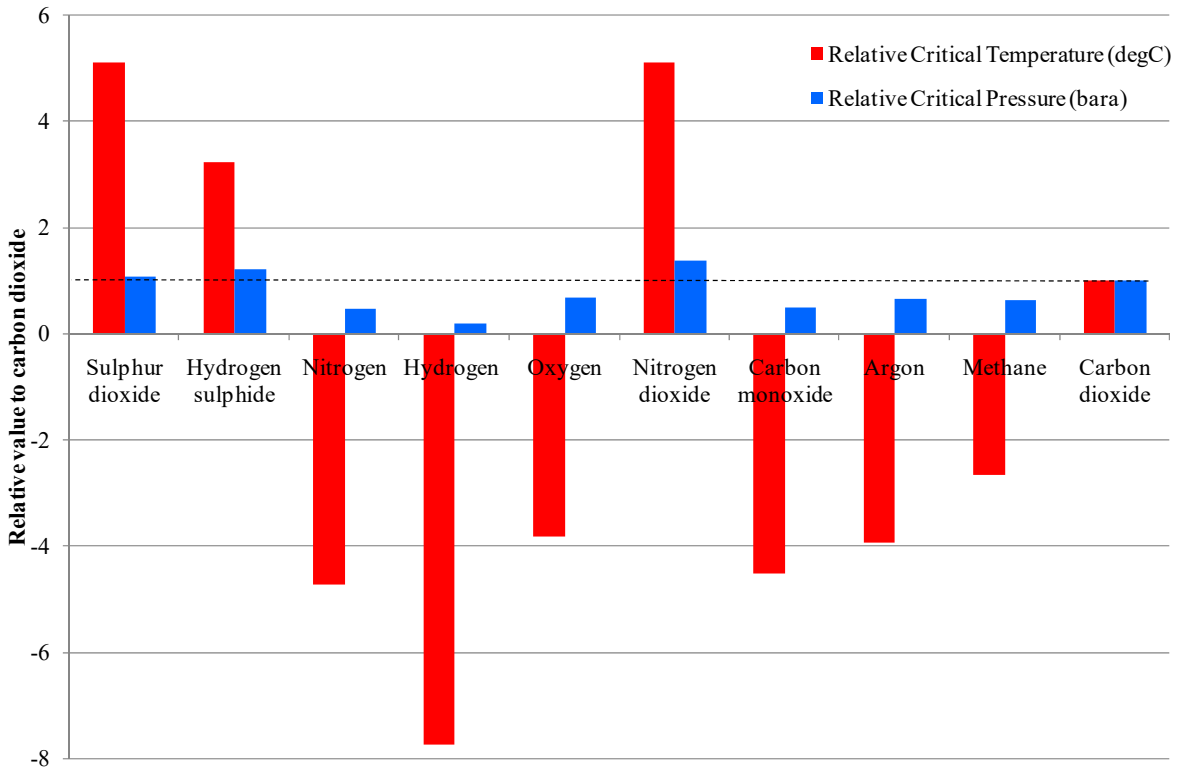*Figure 1 : Phase diagram for pure CO₂*

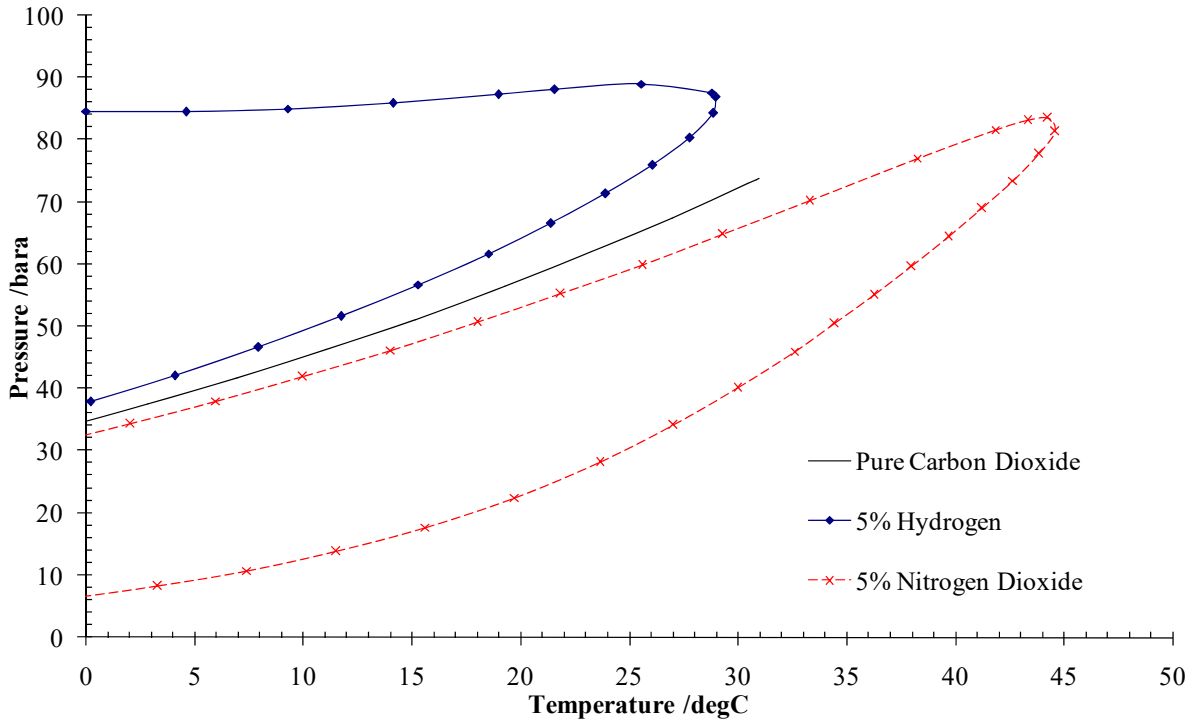*Figure 2 : Relative critical pressures and temperatures*

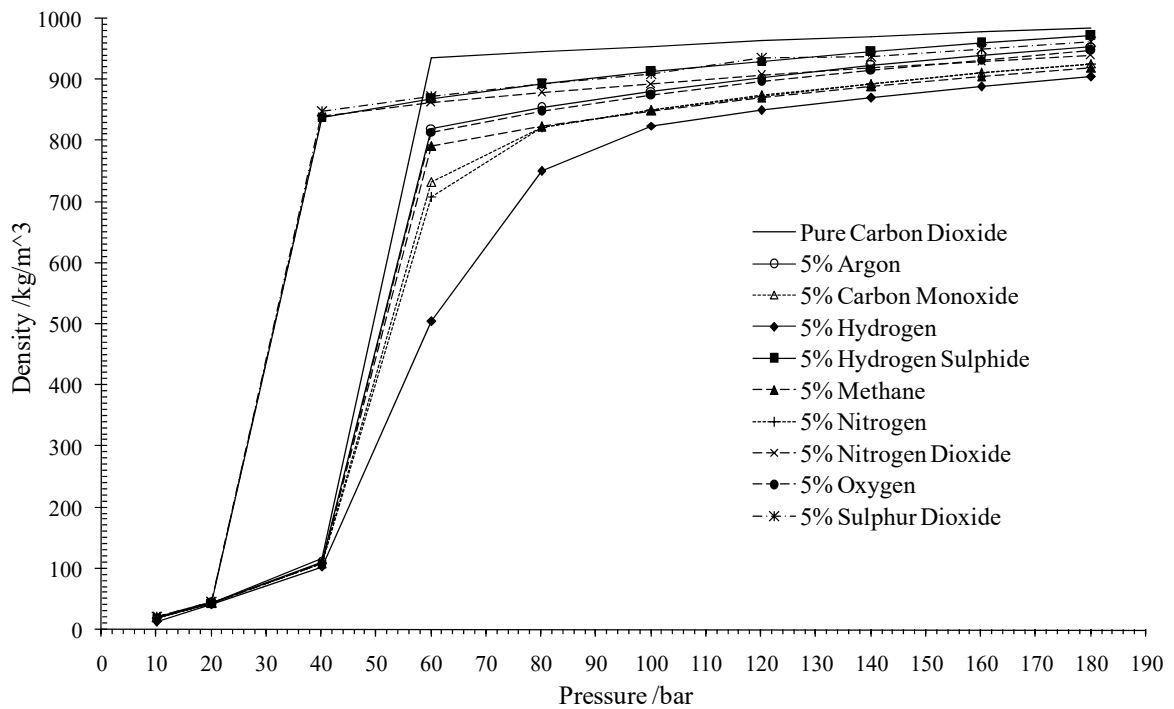*Figure 3 : Pressure-temperature diagram for pure CO_2, CO_2-5mol%H_2 and CO_2-5mol%NO_2*

Figure 4 : Variation of density with pressure and temperature for pure CO_2, and CO_2 with 5mol%impurity
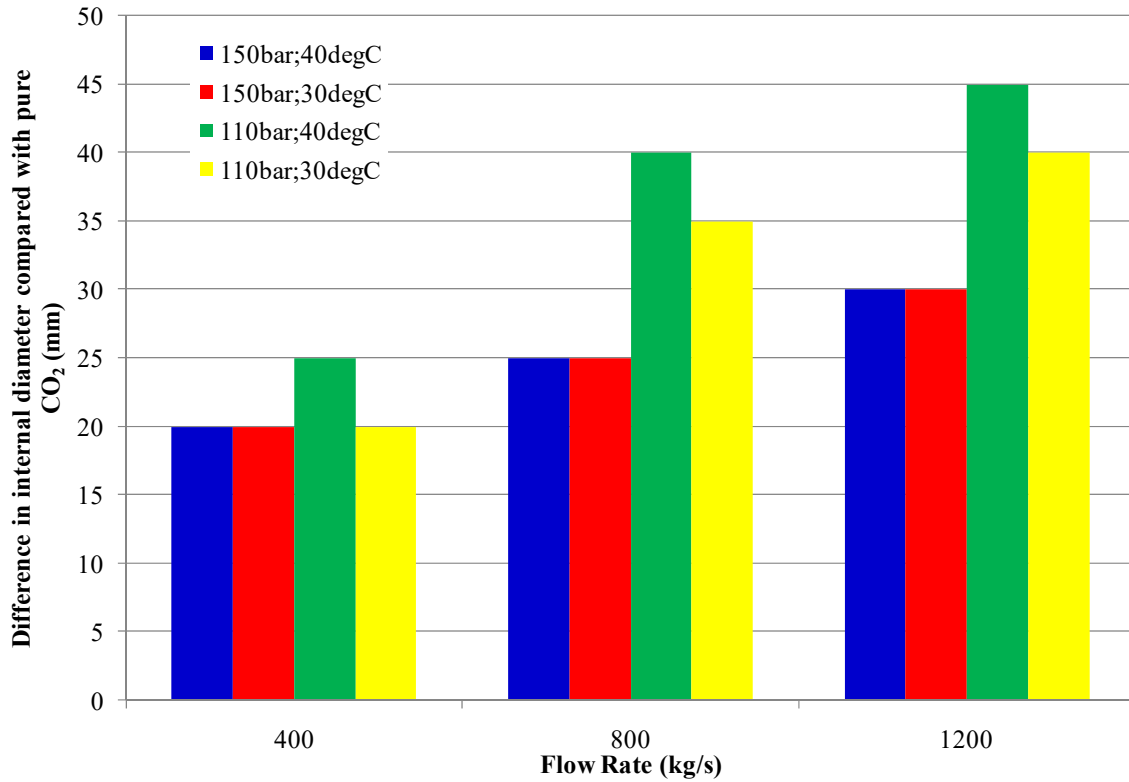
Figure 5 : Difference in diameter between pure CO_2 and a CO_2-5mol%H_2 mixture with changing temperature and pressure
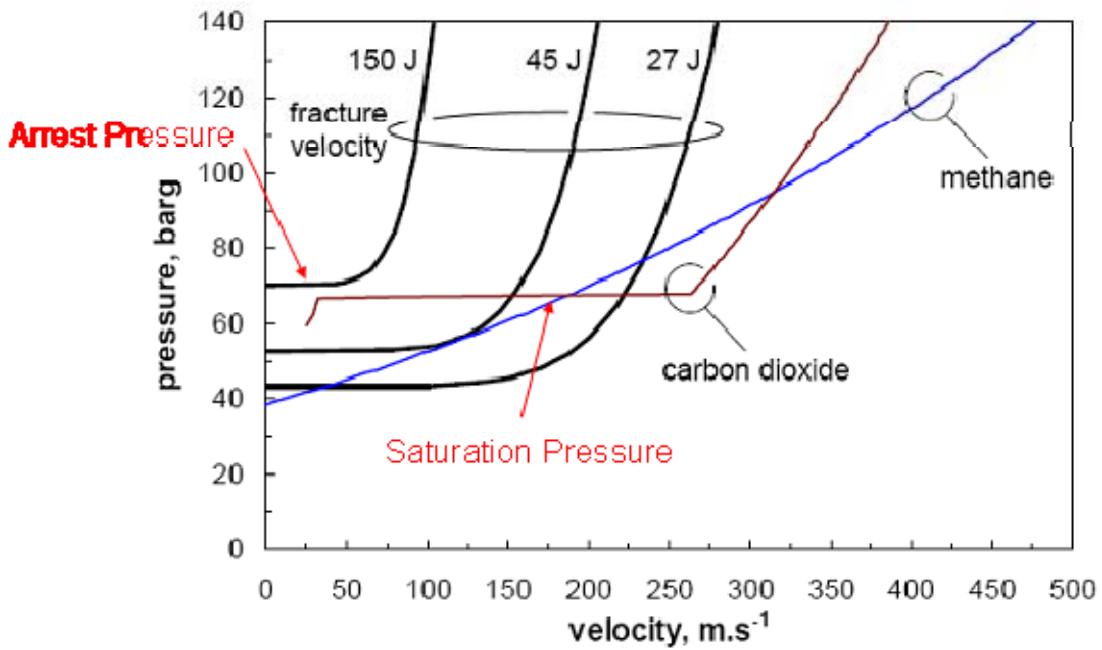

Figure 6 : Battelle TCM for CO_2 illustrating the decompression characteristics
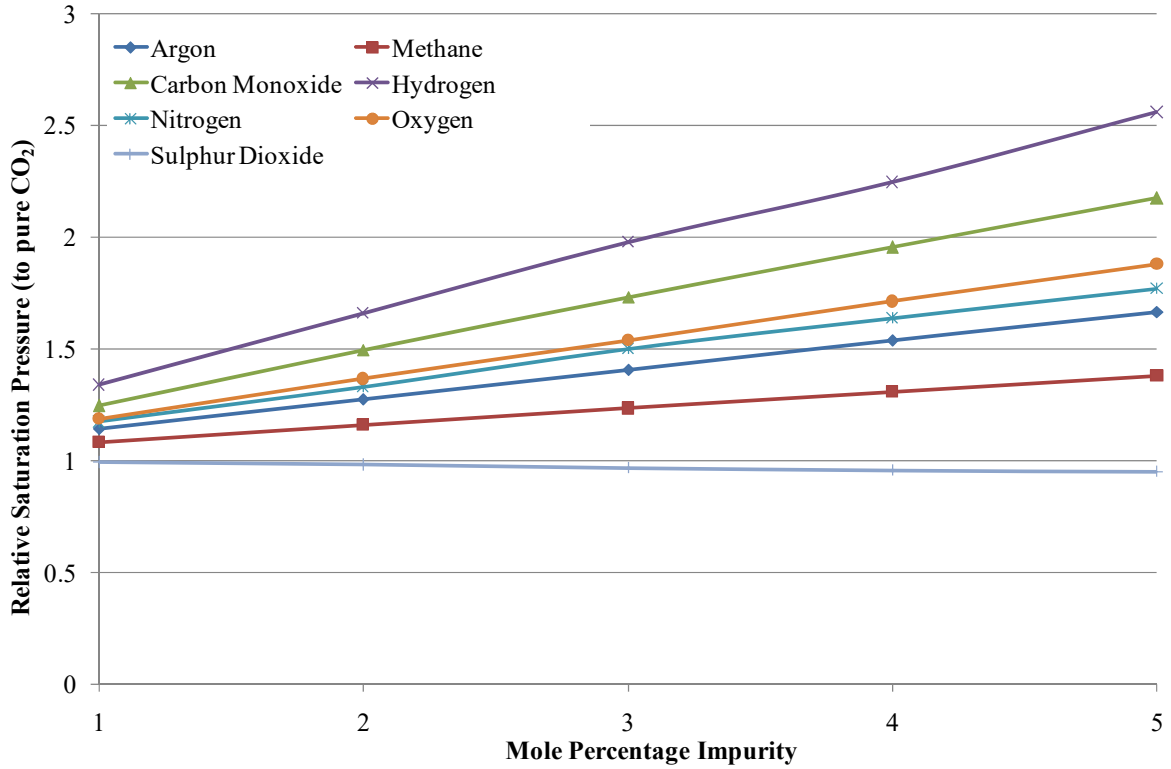(Cosham and Eiber 2007)

Figure 7: *Relative saturation pressures (compared with pure CO_2) for binary CO_2-%X mixture when decompressing from 100bar,5^oC*
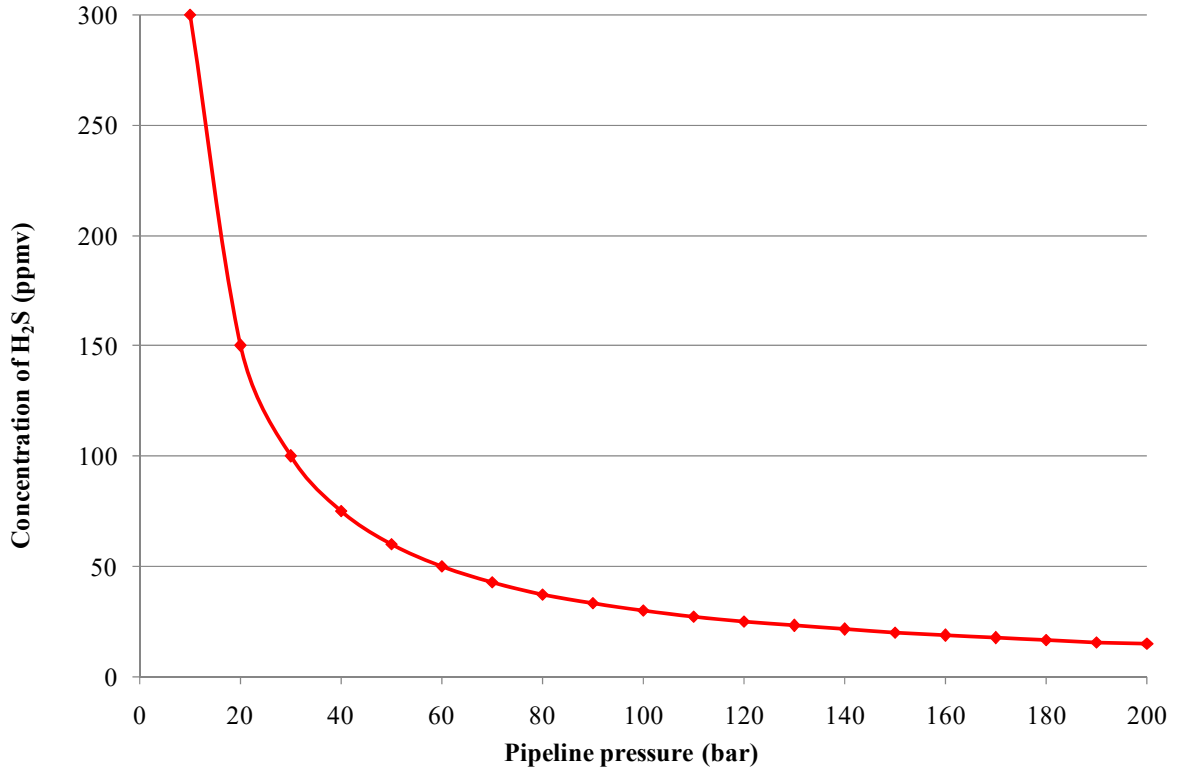

Figure 8: *Concentration of H_2S required to prevent sour cracking*