Capturing Carbon Dioxide: The Feasibility of Re-Using Existing Pipeline Infrastructure to Transport Anthropogenic CO2

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CAPTURING CARBON DIOXIDE: THE FEASIBILITY OF RE-USING EXISTING PIPELINE INFRASTRUCTURE TO TRANSPORT ANTHROPOGENIC CO_2

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ABSTRACT

Climate change has been attributed to green house gases, with carbon dioxide (CO_2) being the main contributor. Sixty to seventy percent of carbon dioxide emissions originate from fossil fuel power plants. Power companies in the UK, along with oil and gas field operators, are proposing to capture this anthropogenic CO_2 and either store it in depleted reservoirs or saline aquifers (carbon capture and storage, CCS), or use it for 'Enhanced Oil Recovery' (EOR) in depleting oil and gas fields. This would involve extensive onshore and offshore pipeline systems. The decline of oil and gas production of reservoirs beyond economic feasibility will require the decommissioning onshore and offshore facilities post-production. This creates a possible opportunity for using existing pipeline infrastructure. Conversions of pipelines from natural gas service to CO_2 service for EOR have been done in the United States. However, the differing sources of CO_2 and the differing requirements for EOR and CCS play a significant part in allowing the re-use of existing infrastructure. The effect of compositions, the phase of transportation, the original pipeline specifications, and also the pipeline route require major studies prior to allowing re-use.

This paper will first review the requirements for specifying the purity of the CO_2 for CCS and to highlight the implications that the presence of impurities and the current water specifications for pipelines has on the phase diagram and the associated physical properties of the CO_2 stream. A 'best' and 'worst' case impurity specification will be identified. Then an analysis on the impact and subsequent validation, of equations of state based on available experimental data on the phase modelling of anthropogenic CO_2 is presented.

A case study involving an existing 300km gas pipeline in the National Transmission System (NTS) in the UK is then modelled, to demonstrate the feasibility of using this pipeline to transport anthropogenic CO_2. The various issues involved for the selected 'best' and 'worst' case specification are also covered. This is then followed by an investigation of the options for transport in the 'gas' phase and 'supercritical' phases, and also identifying the limitations on re-using pipeline infrastructure for CCS.

1. INTRODUCTION

The power sector accounts for 24% of total greenhouse gases worldwide, with coal and fossil fuels being the major source of CO_2 [1]. This sector is expected to triple its emissions by 2050 [2]. For example, 28% of global electricity generation originates from coal combustion alone [3]. Concentrations of greenhouse gases in the atmosphere are rising beyond the level at which they can be removed from the atmosphere using natural processes such as absorption by the forests, soils, peat, ocean water and carbonate deposits in the deep ocean.

Reduction in the amount of energy we consume with increased energy efficiency can play a major role in the reduction of CO_2 emissions, but the demand for energy and security of supply ensures that many countries continue with the use of coal and gas as their primary sources of fuel. Additionally, developed and developing countries have plans to build hundreds of power stations in the next 10 years; for example, India is planning to double its electricity generating capacity by 2015 [4].

The resulting environmental damage could be mitigated by Carbon Capture and Storage (CCS) schemes, which involves capturing CO_2 from sources such as a power plants or industrial facilities and transporting the CO_2, typically in a pipeline, to a storage site where it is injected underground, either for the sole purpose of storage or for Enhanced Oil Recovery (EOR). The disposal of CO_2 is practical with pipelines, as it can be transported efficiently in large volumes to the reservoirs.

The initial projects proposed for CCS in the UK are aimed at capturing CO_2 from power plants, transporting, and then storing it in an offshore 'sink' in the UK North Sea, such as saline aquifers, or depleting oil and gas fields where the captured CO_2 would be used for the purpose of EOR. The latter coincides with the decline of oil and gas production on the United Kingdom Continental Shelf, and the need to decommission facilities post-production. This creates a possible opportunity for using both the geological structures in the North Sea for carbon sequestration, and the existing engineering infrastructure, especially pipelines.

National Grid is considering the potential to use parts of its existing natural gas pipeline infrastructure for CO_2 transportation. A change of use of parts of the existing transportation system is made possible by the reduction in gas supplies from the UK continental shelf (UKCS) and the development of replacement transportation routes from newly developed import facilities. The depletion of gas supplies from the UKCS therefore presents a unique opportunity to extend the useful life of otherwise depleted gas fields and of under utilised gas transmission pipelines. The most compelling opportunity exists in Scotland where there are already multiple transmission pipelines in place to transport gas from Northern Scotland into England. Predictions of depleting gas supplies into Scotland provide an opportunity to change over one of the 300km pipelines from gas to CO_2 transportation. The use of a limited length of existing assets in Scotland has advantages in that it presents an opportunity to extend the valuable use of existing assets, and it reduces the cost and timescale of implementing CO_2 transportation infrastructure from the Central belt of Scotland to the Northern North Sea.

A problem faced by National Grid is the uncertainty in the CO_2 quality and quantity that will pass through the existing pipelines. Therefore, when conducting a feasibility study, a range of typical and expected compositions and quantities had to be considered.

2. CURRENT PIPELINE QUALITY SPECIFICATIONS

The majority of the CO_2 pipelines operating in the United States are transporting CO_2, principally for EOR. Therefore, the pipeline quality requirements specified for the CO_2 are 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. Hence, it should also be recognised that there is an economic incentive to remove certain impurities for EOR, owing to the revenue stream from the produced oil, which would not be present for storage applications.

The quality specifications for currently operating CO_2 pipelines are summarised in Seevam et al., [5]. The Kinder Morgan ($KMCO_2$) CO_2 quality specification [6] is the specification defined for all supercritical CO_2 pipelines from natural sources owned and operated by $KMCO_2$. The adoption of a universal specification is possible because the majority of the CO_2 transported by $KMCO_2$ is from naturally occurring sources which are relatively pure and fairly consistent in composition. The main issue faced by $KMCO_2$ is the high water content at the source and therefore the CO_2 requires dehydration to prevent corrosion and hydrate formation. The nitrogen and hydrocarbon content in the CO_2 are also carefully controlled as these components can affect the MMP of the CO_2 during EOR operations.

The Denbury CO_2 company pipeline specification is also based on a quality requirement for EOR. The very low concentration of H_2S (0.0015%) in the Denbury specification takes into account the potential for sulphide stress cracking [7]. However, the quality of the anthropogenic CO_2 transported for CCS will depend on the capture process, the technology, the fuel source and also economic considerations.

3. CAPTURE TECHNOLOGY AND CO_2 QUALITY

One method by which an impurity specification can be derived is by a detailed study of the process route, to identify the levels and types of impurities that could be present in the captured CO_2.

There are three main process routes for capturing CO_2 from power plant: post-combustion capture; pre-combustion capture; or IGCC (Integrated Gasification Combined Cycle) and oxyfuel. Within any of these process routes there are then different technologies by which the CO_2 is captured: separation with solvents/sorbents; separation with membranes; and cryogenic separation. The choice of technology depends on parameters such as the volume, concentration and pressure of the CO_2 that is to be captured. Table 1 to Table 3 show the compositions defined for each capture technology in the different literature reviewed [8-10]. It can be observed that a specification of CO_2 for the different capture technology does not exist. However, the general consensus in terms of the purity of CO_2 indicates that post-combustion capture produces CO_2 with high purity followed by pre-combustion and oxyfuel.

The IPCC (International Panel on Climate Change)'s special report [8] identified composition for CO_2 captured from coal and gas fired power plant. This analysis indicates that the CO_2 captured from a post-combustion (Table 1) solvent scrubbing process contains the lowest concentrations of impurities, in particular sulphur compounds (SO_2 and H_2S). However, the IPCC report suggests that for oxyfuel and pre-combustion capture, leaving sulphur compounds in the CO_2 product stream could be economically beneficial as it will reduce the cost of capture.

Component	Post Combustion			
	IPCC		ENCAP	O&R†
Unit vol%	Coal	Gas	Coal	Coal & Gas
CO_2	99.97	99.97	99.95	99.79
CH_4	--	--	--	0.01
N_2	0.0033[*]*	0.0033*	0.021	0.17
H_2S	--	--	--	Trace
C2+	--	--	0.003	0.01
CO	--	--	0.001	0.001
O_2	0.0033*	0.0033*	0.003	0.01
NO_X	0.01	0.01	0.002	0.005
SO_X	0.01	0.01	0.001	0.001
H_2	--	--	--	Trace
Ar	0.0033*	0.0033*	0.021	Trace
HCN	--	--	--	--
COS	--	--	--	--

Table 1: Reviewed Post Combustion CO_2 quality

ENCAP (European Enhanced Capture of CO_2) projects [9] specification is focussed on coal fired power plants burning German lignite coal and, the presence of sulphur in the fuel increases the amount of SO_2 and H_2S in the pre-combustion and oxyfuel capture stream. This is denoted by the 'CO_2+ H_2S' and 'CO_2+SO_2' in Table 2 and Table 3. If it is assumed that the sulphur products are not removed, then the levels of SO_2 and H_2S are raised in the CO_2 product stream.

Oosterkamp and Ramsen (O&R) [10] compiled ranges of impurities [11, 12] for post and pre-combustion capture for both coal and gas fired power plants. The levels indicated in Table 1 to Table 3, in line with the IPCC and ENCAP compositions, are without any further purification after capture. It must be noted that the specifications in the Oosterkamp and Ramsen (O&R) [10] in Table 1 to Table 3 were given in ranges, therefore for the purpose of generating phase envelopes which require exact quantities the amount of CO2 was kept at the minimum required by the specifications whilst the amount of impurities were proportionally normalized based on their respective minimum proportions specified in the literature.

[*] The limit for N_2, O_2 and Ar in the IPCC specification was quoted as a total for all three impurities in combination. For the purposes of comparison, it is assumed that the impurities are present in equal proportion.

Although the impact of these impurities can be considered at an individual level, none of the specifications take into account the interaction of impurities (other than water) and the potential effects that these may have. Nevertheless, it is worth noting that the specifications in terms of water content are currently set to avoid corrosion of pipeline steel.

Comp.	Pre Combustion					
	IPCC †			ENCAP		O&R †
Unit vol%	Coal		Gas	Coal		Coal & Gas
	Lower	Upper		CO_2/ H_2S_2	CO_2+ H_2S	
CO_2	99.14	96.39	95.66	98	95.72	95.6
CH_4	0.01	0.01	2	0.035	0.035	0.021
N_2	0.0033*	0.2*	0.43	0.03	0.03	0.35
H_2S	0.01	0.6	0.01	0.01	2.3	1.99
C2+	--	--	--	--	--	0.059
CO	0.03	0.4	0.04	0.17	0.17	0.23
O_2	0.0033*	0.2	0.43	--	--	Trace
NO_X	--	--	--	--	--	--
SO_X	--	--	--	--	--	--
H_2	0.8	2	1	1.7	1.7	1.8
Ar	0.0033*	0.2	0.43	0.05	0.049	0.03
HCN	--	--	--	$5x10^{-4}$	$5x10^{-4}$	N/A
COS	--	--	--	$5x10^{-4}$	$5x10^{-4}$	--

Table 2: Reviewed pre-combustion CO_2 quality

Component	Oxyfuel				
	IPCC		ENCAP		O&R†
Unit vol%	Coal	Gas	Coal		Coal & Gas
			CO_2/ SO_2	CO_2+ SO_2	
CO_2	95.8	95.87	90.76	90.46	90
CH_4	--	--	--	--	--
N_2	1.23*	1.37*	0.61	0.6	3.94
H_2S	--	--	--	--	Trace
C2+	--	--	--	--	--
CO	--	--	--	--	Trace
O_2	1.23*	1.37*	1.6	1.6	1.69
NO_X	0.01	0.01	--	--	0.14
SO_X	0.5	0.01	0.076	1.5	1.41
H_2	--	--	0.25	0.24	Trace
Ar	1.23*	1.37*	5.7	5.6	2.82
HCN	--	--	--	--	--
COS	--	--	--	--	--

Table 3 : Reviewed oxyfuel CO_2 quality

4. CO_2 PIPELINE WATER SPECIFICATIONS

CO_2 in the presence of water, can form highly corrosive carbonic acid, and it has been reported that carbon steel can corrode at rates of more than 10mm/year in wet pure CO_2 [13,14]. In terms of reusing pipeline infrastructure, corrosion could pose a greater issue if proper pipeline integrity management systems are not put

[†] Upper and lower limits for the IPCC pre-combustion coal specification are based on the published ranges of certain impurities whereby the upper limit assumes the maximum amount of impurities and vice versa

in place during initial (pre- CO_2) operation as the pipeline corrosion allowance on the wall thickness may have reduced and any corrosion related defects maybe be close failure. Therefore, in order to prevent corrosion in transportation pipelines it is necessary either to dry the product prior to transportation to prevent the formation of free water or to specify a more corrosion resistant material. Levels of 2.88 x 10^{-4} to 4.8 x 10^{-4} kg/m^3 of water are accepted by the industry for CO_2 transmission in carbon steel pipelines [15]. For hydrocarbon pipelines, a requirement to dry the gas to 50ppm of water is often used to ensure no free water is in the pipeline. In terms of free water, a number of specifications have been published, particularly drying specifications in Heggum et al. [16]. Based on specific calculations of water solubility for a selected case, it was found that the most stringent drying requirements (e.g. 50ppm proposed (not operational) for Hammerfest LNG) may be relaxed to 600ppm (the present USA Kinder Morgan specification).

The specification of an acceptable level of water in the pipeline is dependent on the solubility of water in the fluid at the operating temperature and pressure. Table 4 reviews some of the published water specifications for operating supercritical CO_2 pipelines. It can be seen that they are all well below the 60% saturation limit in order to ensure that corrosion does not occur. In fact, in many cases, the actual water content achieved in the pipeline is below the specification. For example, CO_2 from the McElmo Dome source, which is transported via the Cortez pipeline, is supplied to a pipeline specification of 30lb/MMscf (0.00048kg/m^3) although in fact a water content of around 15lb/MMscf (0.00024kg/m^3) is actually achieved [13].

The drying requirement specified in the Bati Raman pipeline was based on the specification for drying natural gas and also the design specification used in the CRC pipeline [17]. As previously mentioned, the drying specification for natural gas is likely to be conservative when applied to supercritical CO_2. This conclusion was also drawn by Heggum et al. [16] when commenting on the water specification for the Snøvhit pipeline which is based on the drying requirements for natural gas. They conclude that a "maximum of 600ppm water may be a suitable and sufficient requirement for CO_2 pipelines."

The most stringent water specification in the literature is 20ppm, for the Weyburn pipeline [8]. It is not clear if this is a requirement or whether it results from the nature of the process itself, which happens to produce 20ppm of water, or the fact that the Weyburn pipeline has a high H_2S content. It is interesting to note that the presence of H_2S may actually increase the solubility of water in the CO_2 and therefore have a beneficial effect [18].

The solubility of water is controlled by the pressure and temperature as well as impurities. In the case of transport, the pressures and temperatures are maintained at prescribed levels, therefore consideration has to be given to the amount and type of impurities. This can become even more accentuated in a pipeline network where multiple sources of CO_2 using different capture technologies may exist.

Pipeline/ Company Specification	Water Content		
	lb/ MMSCF	x10^{-4} kg/m^3	ppmv‡
CRC Pipeline[8]	30	4.8	638.32
KMCO$_2$[6]	30	4.8	638.32
Cortez Pipeline[13]	30	4.8	638.32
Sheep Mountain[19]	30	4.8	638.32
Denbury[7]	30	4.8	638.32
Bravo Pipeline[20]	25	4.0	532.15
Bati Raman[21]	4	0.6	85.06
CRC Pipeline[17]	2.31	0.377	50
Snøvhit (proposed)[16]	2.31	0.377	50
Weyburn[22]	0.94	0.15	20

Table 4: Operating pipeline quality specifications NB. The shaded boxes are the values quoted in the literature, the remaining figures quoted are conversions[2] to allow comparison

The Dynamis [18] and Ecofys [23] CCS projects recommend a water content of 500ppm to ensure that no free water is present in the pipeline and therefore to minimise the risk of corrosion and hydrate formation [18]. The Dynamis project did conclude, however, that the 500ppm limit should be reviewed for pipelines which could be operating at temperatures around 4°C. At this temperature, the solubility of water is below 500ppm for pressures below 40bar. The effect of water on the phase properties of CO_2 will be analysed later in this paper using the cubic equation of state.

5. EQUATIONS OF STATE AND THE PHASE DIAGRAM

Modelling of phase behaviour requires the use of an Equation of State (EOS) to provide a relationship between the thermodynamic variables of the system (e.g. temperature, pressure and volume) and to describe the state of the system under a given set of conditions. There are a number of EOS that have been used in determining the phase behaviour of CO_2 [5]. However, there is no consensus in the literature regarding the EOS that should be used for the design of CO_2 pipelines.

Li [24] has conducted a comparative study of all of these EOS and concludes that the selection of the equation of state may have a significant impact on the pipeline design, although without experimental data it was not possible to identify the most accurate

‡ The conversions to ppm used in this section are based on standard conditions of 1 bar and temperature of 15°C which corresponds to a CO_2 density of 1.842 kg/m^3. This is based on the oil and gas pipeline design convention. It is also cautioned that the literature does not generally state whether the specification in ppm is by volume or mass and therefore these conversions should only be used as a guide, reference always being made to the original literature source. The unit used by Gill)[17], Heggum et al[16] and DTI[22] is assumed to be in ppmv, although it is not stated in the original literature.

EOS to use. Following this, Li [25] conducted a study based on collected experimental data and concluded that the Peng Robinson (PR) EOS was most accurate for binary mixtures of CO_2 with H_2S and CH_4 respectively. Indeed, King [24] recommends that the EOS selected should be based on reliable experimental data and concluded that it is advisable to validate the EOS being used for the particular impurity combination under consideration. Table 5 shows the comparison between experimental data and the four different equations of state in predicting the critical point of pure CO_2. It can be observed that the Span and Wagner [27] equation of state has the least deviation from experimental data, in predicting the critical point of pure CO_2. This is because the Span and Wagner equation of state has been semi empirically developed specifically for CO_2. However, this equation is not suitable for predicting phase properties of CO_2 containing impurities. Hence, the Span and Wagner equation of state is not used in this analysis of anthropogenic CO_2.

As the previous section has demonstrated, the captured CO_2 can contain up to twelve different impurities and the experimental validation for these types and levels of impurities does not exist. Therefore, a preliminary assessment of the most appropriate EOS for the modelling of a CO_2 capture stream has been conducted using experimental data for binary acid gas system CO_2-H_2S [28], as this contains at least one of the expected impurities in the captured CO_2 stream. The experimental data for two different concentrations of H_2S was modelled with the Peng Robinson (PR) [29], Benedict Webb Rubin Starling (BWRS) [30] and Soave Redlich Kwong (SRK)[31] equations of state and the results are presented in Figure 1. Although both the PR and SRK EOSs provide a good fit to the experimental data, close inspection indicates that the PR EOS is slightly more accurate over both sets of experiments. Therefore, on the basis of the literature review [32, 33] and the results of Figure 1, the PR EOS [29] has been selected for the following analysis.

Equation of State	Critical Temp. Tc (ºC)	Critical Pressure Pc (bar)	% Deviation from experimental data [29]	
			Tc (ºC)	Pc (bar)
PR	30.86	73.76	-0.29	-0.19
SRK	30.81	73.51	-0.45	-0.27
BWRS	27.56	72.82	-10.95	-1.21
Span & Wagner	30.98	73.77	0.10	0.08
Experimental Data [34]	30.95	73.71	0.00	0.00

Table 5: Comparison of the critical pressures and temperatures of pure CO_2 calculated by the equations of state and experimentally measured values

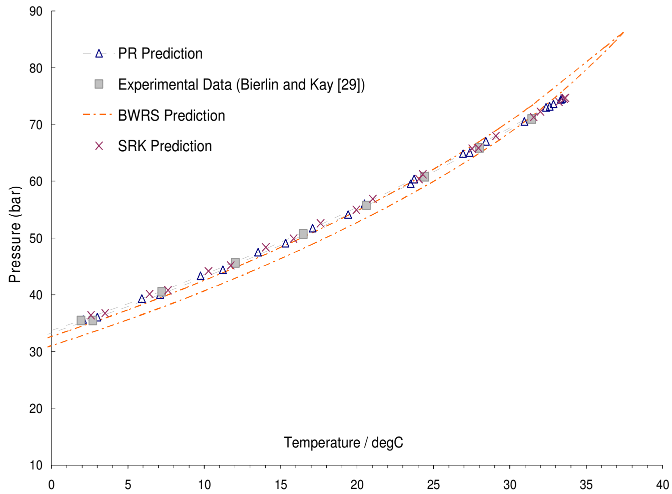

Figure 1: Comparison of experimental results for the 90.02% CO_2-9.98% H_2S system with the three different EOS.

6. DEFINITION OF THE 'BEST' AND 'WORST' CASE COMPOSITION

Long distance CO_2 pipelines operate in the supercritical or dense phase, depending on temperature. This phase is the most efficient phase for pipeline transport of CO_2 as, in this phase, the fluid has the density of a liquid, but the viscosity and compressibility of a gas. Although the CO_2 could be transported by pipeline in its gaseous phase, the low density would require large diameter pipelines and the high pressure drops [32] mean that transport as a gas would only be economical for shorter pipeline lengths. Therefore, for pipeline transport in the dense phase, the CO_2 that is captured has to be compressed to a pressure above the critical pressure.

Two phase flow in pipeline transport should be avoided if possible due to the potential for damage to the pipeline and associated equipment; therefore, it is desirable to transport in the dense or liquid phase above this region, or in the gas phase below this region. The formation of a large two-phase region restricts the available operating envelope of the pipeline.

As shown by Seevam et al [5], one of the effects of impurities is to raise the critical pressure for the system. Therefore a useful indicator of the 'best' and 'worst' case impurity specifications is provided by the critical pressure for that system. Thus, the specification with the highest critical pressure and largest two phase area would be selected as the 'worst' case, and the specification with the lowest critical pressure (i.e. closest to that of pure CO_2) and smallest two phase area would be deemed the 'best' case. Table 6 below shows a comparison of the impurities present for all the specifications including the critical pressure for each of these systems. On this basis, the 'best' case impurity specification is the post-combustion specification published by IPCC [8] and the 'worst' case specification is the oxyfuel specification of Oosterkamp and Ramsen [10]. These specifications are highlighted in Table 6 with their respective compositions shown in Table 7.

Capture Technology	Quality Specification	Two phase area	Critical Pressure (bar)
Post-Combustion	IPCC coal	n/a	73.82
	IPCC gas	n/a	73.82
	Pure CO_2	n/a	73.83
	O&R (Coal and Gas)	n/a	74.04
Pre-Combustion	IPCC Coal Max Purity	149.33	75.81
	IPCC Coal Min Purity	422.46	80.08
	IPCC Gas	322.57	78.9
	ENCAP Coal CO_2/ H_2S	324.30	78.38
	ENCAP Coal CO_2+ H_2S	332.77	78.53
	O&R Coal & Gas	370.87	79.13
Oxyfuel	IPCC Coal	284.32	78.62
	IPCC Gas	279.83	78.39
	ENCAP Coal CO_2/ SO_2	430.03	83.77
	ENCAP Coal CO_2+ SO_2	604.00	84.9
	O&R Coal & Gas	719.46	86.69

Table 6: The critical pressure and size of the two phase region for the different anthropogenic CO_2 quality specifications reviewed

Another conclusion that can be drawn from Table 6 is that, of the three capture technologies, post-combustion capture produces CO_2 streams with critical pressures that are very close to that of pure CO_2. However, there is significantly more variation in the critical pressures for the published specifications for pre-combustion and oxyfuel capture.

Component (vol%)	'Best' case (IPCC)	Worst' case (O&R)
CO_2	99.97	90.00
N_2	0.0033*	3.94
O_2	0.0033*	1.69
NO_X	0.01	0.14
SO_X	0.01	1.41
Ar	0.0033*	2.82

Table 7: the defined 'best' and 'worst' case specification

Figure 2 shows the phase envelopes for the 'best' and 'worst' case specifications plotted using the PR EOS. As might be expected from the calculation of the critical pressure:

- The 'best' case specification has a phase envelope similar to pure CO_2 with a critical pressure of 73.82bar and critical temperature of 31.02°C. This capture stream would therefore be expected to exhibit physical property characteristics to pure CO_2.
- The 'worst' case shows an increase in critical pressure to 86.69bar and a decrease in critical temperature to 28.57°C. Figure 2 also indicates that a large two-phase is formed for this case.

It is also worth noting that the phase envelope generated for the 'best' and 'worst' case specification did not include water as a component as the stringent drying requirements would mean that the amount of water present would be to small to have an effect on phase behaviour. This is further discussed in the following section.

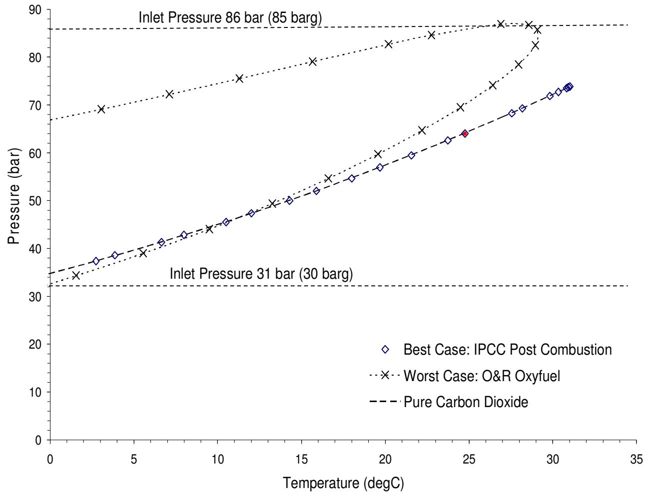

Figure 2: Phase envelope for the 'best' and 'worst' case specification with the inlet pressures used in the case study

7. EFFECT OF CO_2 WATER SPECIFICATION

In order to demonstrate the effect of the water specification shown in Table 4 on the phase behaviour or bubble and dew point of the anthropogenic CO_2, a small amount of water was introduced to the stream and the mixture flashed at different constant temperatures to obtain the dew point and bubble point pressure which in turn related to points on the phase envelope. The modified 'worst' case composition to include water as a component is shown in Table 8, whereby the 640ppmv (0.064vol%) water specification is based on existing specifications for high pressure CO_2 pipelines and the 225ppmv (0.025vol%) of water for low pressure gaseous transport, as per the recommended 60% saturation limit of water in CO_2 pipelines [20][35].

Component	Worst' case specification with 640ppmv (0.064vol%) water	Worst' case specification with 225ppmv (0.0225vol%) water
CO_2	89.936	89.978
H_2O	0.0640	0.0225
NO_X	0.1400	0.1400
SO_X	1.4100	1.4100
Ar	2.8200	2.8200
N_2	3.9400	3.9400
O_2	1.6900	1.6900

Table 8: The modified single branch 'worst' case specification to include the supercritical (0.064vol%) and gaseous phase (0.0225vol%) water specifications

At pipeline operating temperatures and pressures, it is difficult to determine the phase boundaries for systems containing water as it always forms a two phase system, whereby water will be present in the liquid and gaseous phases of CO_2 and at the same time CO_2 is present in the liquid and gaseous phase of the water due to the complex thermodynamic behaviour of strongly associating polar molecules such as water which can lead to unstable phase calculations [36, 37].

In acid-gas CO_2 applications it has been shown that the presence of an aqueous phase is difficult to model with cubic[§] EOS and research is currently being carried out in the area [38]. Therefore, cubic EOS find it difficult to determine the phase boundary in the presence of water. However, it is possible to perform dew and bubble point flashing at given pressures and temperatures using cubic EOS for very low concentrations of water whereby the water does not drop out or become insoluble as the saturation limit is reached [39].

The 'worst' case specification with 0.064vol% water, and without water, was flashed at different temperatures to obtain the bubble and dew point pressures. The results are presented in Figure 3, and also compared with that of pure CO_2 containing the same amount of water. The following were observed for the supercritical pipeline water specification of 0.064vol%:

- The bubble point pressure for the 'worst' case specification does not change in the presence of water.
- The dew point pressure shows deviation when water is present in the 'worst' case specification and also in a binary mixture with CO_2 at lower temperatures of 5^o and 10^oC.
- The amount of water soluble in CO_2 reduces with decreasing pressure and temperature whereby the solubility of water in the lower pressure gas phase at temperatures below 15°C is lower than that of the dense or supercritical phase of CO_2[16][26], thus causing water to condense out of the gas phase.

Therefore, a similar specification of 0.064vol% of water should not be used for gaseous phase CO_2 at pressures below 40 bars when low temperatures are anticipated. It is also worth noting that the dew points for pure CO_2 and the worst case specification at 5°C, 10°C and 15°C are the same, which highlights that at these pressures and temperatures, water will condense for both the 'worst' case and the pure CO_2 for the 0.064vol% water specification. Nevertheless, certain impurities such as CH_4, which lowers the solubility limit of water, will increase the amount of water condensed in the gaseous phase [16].

§ 'Cubic' implies that the equation , which, if expanded , would contain volume terms raised to either the first,, second or third power [40]

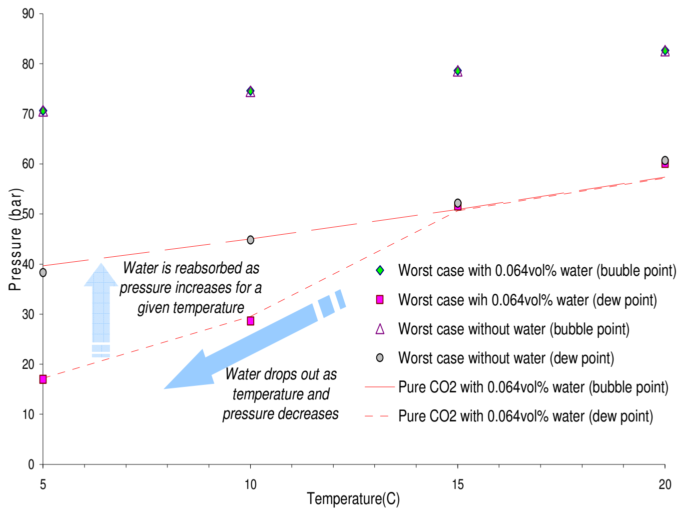

Figure 3: Bubble and dew point flashing of the 'worst' case specification with 0.0064 vol% of water based on the supercritical pipeline specifications for water content (*Note: Pure CO_2 without water has a Vapour Liquid Equilibrium Line (VLE) similar to the bubble point lines of pure CO_2 containing 0.064% H_2*O)

A similar analysis was conducted for the single branch 'worst' case specification using the lower, gaseous phase water specification of 0.0225vol%. The results of the analysis were as follows:

- In contrast to the supercritical or dense phase CO_2, the dew point pressures for the 'worst' case specification containing 0.0225vol% water remains the same in both the presence and absence of water, at all pressures and temperatures, as no condensation is observed at lower pressures and temperatures.
- A similar trend to that of pure CO_2 containing 0.0225vol% of water was observed and therefore suggests that higher water content may be possible.

Consequently, in order to avoid problems with the presence of free water in the pipeline, it is assumed that these stringent requirements, depending on the phase of transport (e.g. 0.064vol% of water for dense phase or supercritical CO_2 and 0.0225vol% of water for gaseous CO_2) will be adopted by CO_2 pipeline operators. Given that the low water specifications of 0.0225vol% have no effect on the bubble and dew point of the 'worst' case specification, the phase behaviour and physical property analysis that follows will not consider water as a component in the anthropogenic CO_2 as it is not deemed to have any significant effect on pipeline hydraulics.

8. REUSING EXISTING INFRASTRUCTURE: CASE STUDY

In order to evaluate the effects of elevation, temperature, inlet pressure and flow rate on the hydraulic analysis of a CO_2 pipeline, an existing gas pipeline in the National Transmission System

(NTS) was selected. The pipeline[**] profile is illustrated in Figure 4. The hydraulic modelling of the case study pipeline has been conducted for CO_2 transport at inlet pressures of 30barg and 85barg. The inlet pressure of 85barg is the design pressure and Maximum Allowable Operating Pressure (MAOP) of the pipeline and represents the maximum pressure that can be achieved at any point on the pipeline. The operating parameters assumed are presented in Table 9

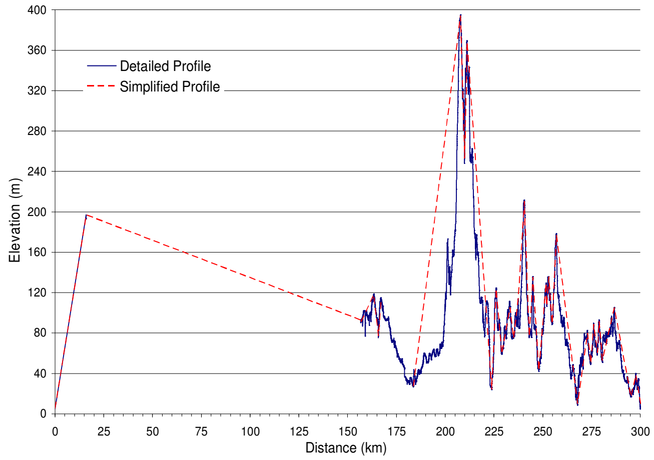

Figure 4: Case study pipeline elevation profile

Flow Rate	Minimum (Qmax)	3000 Te/day (34.72 kg/s)
	Maximum (Qmin)	6000 Te/day (69.44 kg/s)
Ground Temperature	Minimum	4.1°C
	Maximum	13.5°C
Compressor discharge temperature		40°C
Lower Inlet Pressure		30 barg
Upper Inlet Pressure		85 barg

Table 9 : Case study pipeline operating specifications

The hydraulic modelling of the case study pipeline was conducted using the PipeSim® pipeline simulation software with the Beggs and Brill flow model and the Moody friction factor [41]. The CO_2 physical properties were calculated using the PR EOS. The selection of the EOS has been described previously. The analysis that has been conducted is a static analysis and does not take into account transient effects. For each scenario considered, a pressure and temperature profile was calculated and compared with the expected results for a pure CO_2 pipeline. It is highlighted that, as an existing pipeline was used for the modelling, the pipeline diameter has not been optimised for the flow rates considered. In addition, the original design constraints in terms of allowable operating stress had to be observed.

[**] Internal Diameter (ID) : 888.6 mm; Outer Diameter (OD) : 914.4 mm; Wall thickness : 12.7 mm; Roughness : 0.05 mm; Pipe Grade : X60; Pipeline Length : 300.3km

OPTIONS FOR TRANSPORT OF ANTHROPOGENIC CO_2

Before proceeding to the detailed hydraulic modelling of the case study pipeline, it is useful to review the impact of the chosen operating temperatures and pressures on the expected phase behaviour of the transported CO_2. The phase diagrams for the 'best' and 'worst' case specifications of CO_2 compositions are presented in Figure 2.

At an inlet pressure of 30barg, the CO_2 will be in the gas phase for all values of temperature. If the operating pressure is raised above 32barg and the temperature drops below 0°C, then it is possible that the CO_2 could enter the two-phase region for the 'worst' case specification.

At an inlet pressure of 85barg, the CO_2 will be in the supercritical and/or dense phase region for both the pure CO_2 and the 'best' case specification unless the operating pressure drops below 74 barg, in which case a phase change to gas or liquid could occur, depending on temperature. However, for the 'worst' case CO_2 specification, the CO_2 starts in the gas phase and could enter the two-phase or liquid region as the temperature and pressure drops in the pipeline. Increases in pressure above 86.69barg, the critical pressure for the 'worst' case specification, will cause a 'phase' change to the supercritical or dense phase depending on the temperature. Therefore, it would be recommended that, for transportation of the 'worst' case CO_2 specification, the inlet pressure should be determined such that the CO_2 does not enter the two-phase region at any location along the pipeline. However, for this particular pipeline, the maximum pressure is constrained by the allowable stress in the pipeline

Although detailed analysis was conducted as part of the initial study, only the main outcome of this study will be reported here. In terms of gaseous CO_2 transport, the parameters in Table 9 were investigated for the pre-defined 'best' and 'worst' case specification. In addition, the sensitivity to increasing flow rate was also analyzed.

OPTION 1: Gaseous Phase Transport (inlet pressure 30 barg)

Figure 5 show the pressure profiles for both the maximum and minimum flow rates for the 'best' and 'worst' case scenarios at a ground temperature of 4.1°C. It can be seen that the pressure drop along the pipeline increases with increasing flow rate. However, for the flow rates considered, the maximum pressure drop predicted along the pipeline is only 4.8barg for the maximum flow rate and 3.2barg for the minimum flow rate. The largest pressure drops were predicted at the highest point of the pipeline. The composition of the CO_2 does not have a significant impact on the pressure drop, although at the higher flow rate it can be seen that the 'best' case composition results in a slightly lower pressure drop. The temperature was seen to tend to the ambient ground temperature with fluctuations attributed to the changing elevation with the lowest temperatures predicted at the highest point in the pipeline.

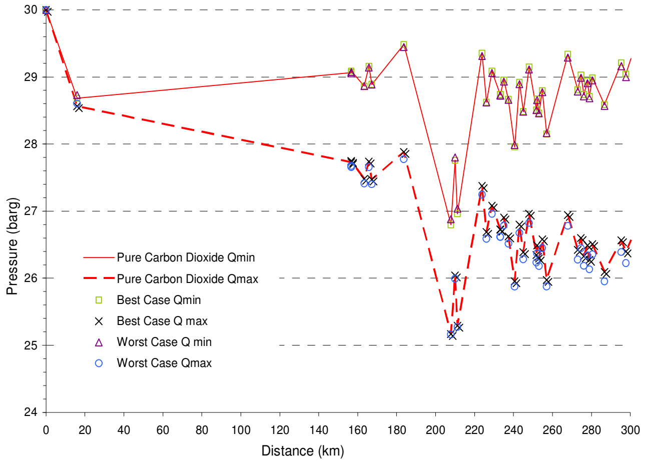

Figure 5: Pressure profiles for the maximum and minimum flow rates at a fixed ground temperature of 4.1°C

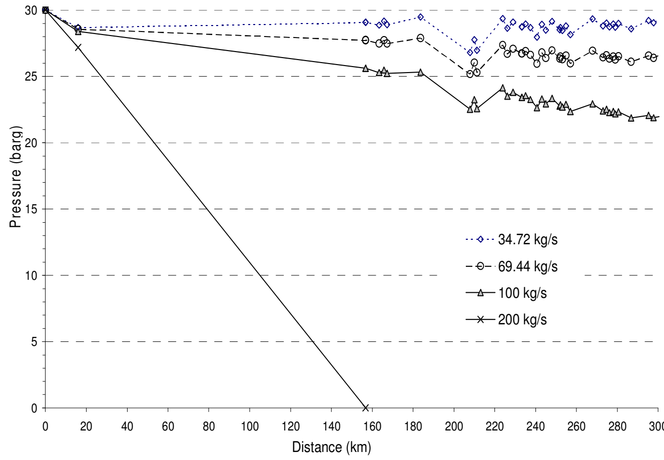

Figure 6: Sensitivity analysis for flow rate on pressure profile for an inlet pressure of 30barg, ground temperature of 4.1°C and 'worst' case composition

Similar trends in the pressure and temperature were observed when the pipeline was modelled with a ground temperature of 13.5°C. As seen previously, the difference in flow rate dominates the differences in the pressure profile with composition having a secondary, minor effect at higher flow rates. The temperature profile shows little influence of either flow rate or composition and is again tending towards the assumed ground temperature. It is highlighted that for all combinations of pressure and temperature along the pipeline route and for the 'best' and 'worst' case compositions for the transported CO_2, reference to the phase diagram of Figure 2 indicates that the fluid remains in the gaseous phase

As might be expected, the ambient temperature had a far greater effect on the temperature profile than the pressure profile. Indeed, for the maximum flow rate modelled, neither ground temperature nor composition has a significant effect on the pressure profile along the pipeline. It was also found that, the temperature of the pipeline tends towards the ambient temperature with no effect of composition.

In order to investigate the sensitivity of the pressure profile to flow rate, the modelling was conducted for a number of different flow rates; 34.72kg/s, 69.44kg/s, 100kg/s and 200kg/s. The modelling was conducted at a ground temperature of 4.1°C and for the 'worst' case composition, as it has been concluded that neither ground temperature nor composition significantly affect the pressure profile. The resultant pressure profiles are presented in Figure 6 which indicates that for flow rates up to 100kg/s, the total pressure drop along the pipeline is less than 10barg.

It is also interesting to note that as the pressure drop increases between 69.44 and 100kg/s, the lowest pressure in the pipeline is no longer at the lowest point in the pipeline but at the outlet. This phenomenon is due to the fact that at higher flow rates the pressure drop is governed by friction losses rather than gravity. At a flow rate of 200kg/s, recompression would be required prior to 150km as the pressure has dropped to an unviable level.

OPTION 2: Supercritical Phase Transport (inlet pressure 85 barg)

A similar analysis was carried out at an inlet pressure of 85 barg. Figure 7 show the pressure profiles for both the maximum and minimum flow rates for the 'best' and 'worst' case scenarios at a ground temperature of 4.1°C. Comparing the pressure profiles predicted for an inlet pressure of 30barg (Figure 5), it can be seen that at the higher inlet pressure of 85 barg, the flow rate has little effect on the pressure profile.

However, it is observed that the composition of the CO_2 has a slightly more significant effect. For the flow rates considered, the lowest pressure predicted along the pipeline for each scenario is presented in Table 10. It can be concluded that, for these scenarios, the effect of impurities is to increase the minimum pressure and therefore to reduce the maximum pressure drop along the pipeline. At these low flow rates the pressure drop is dominated by gravity [42] and therefore the density of the fluid is important. As was demonstrated in Seevam et al [5], impure CO_2 has a lower density than pure CO_2, and therefore the 'worst' case compositions show a slightly improved pressure profile compared with pure CO_2, although it is recognised that the actual differences in the calculated minimum pressures for the different scenarios are very small.

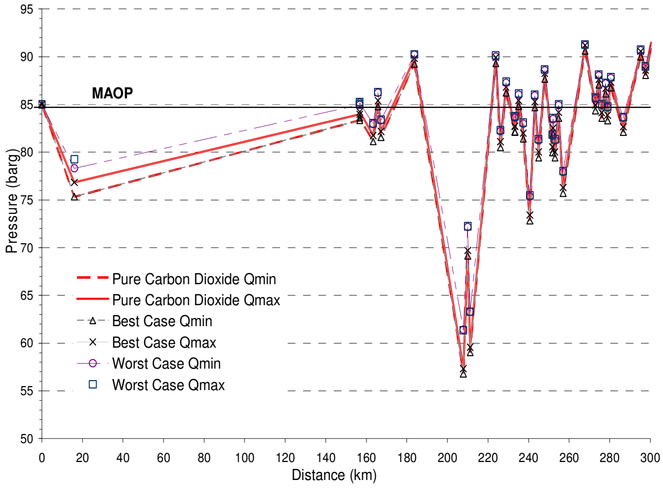

Figure 7: Pressure profiles for the maximum and minimum flow rates at a fixed ground temperature of 4.1°C

Inlet Pressure (barg)	Ground Temperature (°C)	Composition	Flow Rate, Q (kg/s)	Minimum Pressure (barg)
85	4.1	Pure CO_2	34.72	56.8
85	4.1	Best case	34.72	56.8
85	4.1	Worst case	34.72	61.4
85	4.1	Pure CO_2	69.44	57.3
85	4.1	Best case	69.44	57.3
85	4.1	Worst case	69.44	61.3
85	13.5	Pure CO_2	34.72	58.9
85	13.5	Best case	34.72	59.0
85	13.5	Worst case	34.72	64.0
85	13.5	Pure CO_2	69.44	59.2
85	13.5	Best case	69.44	59.2
85	13.5	Worst case	69.44	64.6

Table 10: Minimum pressures predicted for the different ground temperatures, flow rate and composition

As the pressure profile is gravity dominated, Figure 7 indicates that the lowest pressures are observed at the highest points in the pipeline and the highest pressures at the low points. It can also be seen that there are points along the pipeline where the pressure exceeds the MAOP of 85 barg, therefore this operating regime would not be permitted. As with the gas phase transportation, from the assumed compressor outlet temperature of 40°C, the temperature is seen to tend to the ambient ground temperature with fluctuations attributed to the changing elevation with the lowest temperatures predicted at the highest point in the pipeline. Flow rate and composition have no significant effect on the temperature profile. Similar trends in the pressure and temperature plots were observed when the pipeline was modelled with a ground temperature of 13.5°C

It was previously highlighted that for an inlet pressure of 85barg, there was the risk of phase changes and two-phase flow along the pipeline depending on the combination of temperature and pressure and the composition of the CO_2. The pressure and temperature profiles presented in this section indicate that two-phase flow will occur for the 'worst' case composition at the given flow rates, particularly at locations of low temperature and pressure corresponding with high points on the pipeline.

At the flow rates considered for this study, it has been shown that neither flow rate nor ground temperature have a significant effect on the pressure profile although the composition of the CO_2 does have a marginal effect. However, at higher flow rates, where the pressure drop becomes dominated by frictional rather than gravitational effects, it is considered that variations in flow rate and composition, in particular, will have more impact on the pressure profile.

In order to investigate the sensitivity of the pressure profile to flow rate, further analysis was conducted for an inlet pressure of 85barg, a ground temperature of 4.1°C and flow rates of 34.72, 69.44, 100, 200, 300, 400 and 500kg/s for the 'best' and 'worst' case composition scenarios. The sensitivity of the 'worst' case for the different flow rates are shown in Figure 8 for illustration. It is highlighted that for flow rates up to 300kg/s for the 'best' case composition and flow rates up to 200kg/s for the 'worst' case composition, the MAOP of the pipeline is exceeded at a number of locations along the pipeline and therefore these operating regimes are not permissible. At higher flow rates the MAOP criterion is not exceeded, however, the pressure and temperature profiles in the pipeline indicate that the pipeline will be operating under conditions of two-phase flow and/or phase changes depending on composition, which would not be desirable conditions.

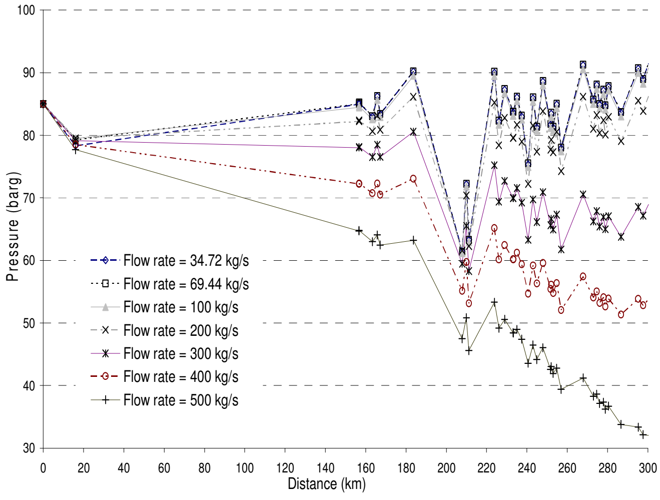

Figure 8: Sensitivity analysis for flow rate on pressure profile for an inlet pressure of 85barg, ground temperature of 4.1°C and 'worst' case composition

Figure 9 shows the relationship between the pressure difference (i.e. the difference between the inlet and outlet pressure) and flow rate for the scenarios considered. A negative value for the pressure difference is due to terrain effects which result in a higher outlet than inlet pressure. At lower flow rates the pressure drop is gravity dominated and, as mentioned previously, the density of the fluid is important. As the flow rate increases, the pressure drop is dominated by friction and impurities have more of an effect in increasing the pressure difference.

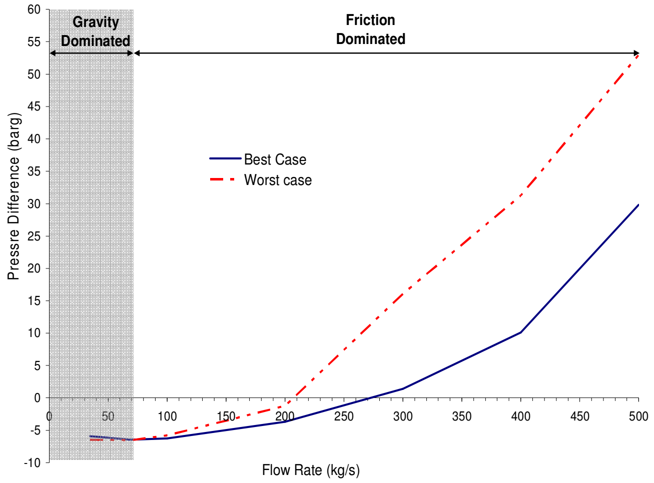

Figure 9: Relationship between flow rate and pressure drop for the 'best' and 'worst' case compositions at a ground temperature of 4.1°C and inlet pressure of 85barg

At higher flow rates, the 'worst' case composition shows a higher pressure difference and lower outlet pressure for the same flow rate. The differences between the 'best' case and 'worst' case become more significant as the flow rate increases. The turning point between a friction dominated and gravity dominated pressure drop is around 70kg/s. Gravity dominated flow rates are often associated with terrain slugging whereas frictionally dominated operations have a higher tendency towards hydrodynamic slugging. Prediction of slugging requires a transient analysis which is outside the scope of this analysis.

9. OTHER KEY CONSIDERATIONS OF REUSING PIPELINE INFRASTRUCTURE FOR CCS

On the basis that re-use of existing infrastructure for CO_2 transportation may be an option in the UK, it is considered pertinent to review the code requirements for pipeline conversion. The procedure outlined in 49CFR195 [43] requires the pipeline operator to determine the design, construction, operation and maintenance history of the pipeline. If this information is not available then appropriate testing has to be conducted to determine the condition of the pipeline and verify that it is safe for operation in the intended service. It may also be necessary to re-hydrotest the pipeline to verify the design pressure. It is highlighted that Denbury have converted part of a natural gas pipeline to transport supercritical CO_2 under these regulations [7].

In the UK, PD 8010-1 [44] contains very similar guidance, establishing that the design and integrity of a pipeline is appropriate for the change in service, which includes a change in fluid. As well as the as-built, operational and maintenance data, PD 8010-1 requires particular attention to be paid to the welding and jointing methods and procedures used and the materials used for pipeline and valves and also the internal and external coating to ensure that they are appropriate for the intended service. Further consideration may be required when blowing down a supercritical CO_2 pipeline whereby the material must be suitable for very low temperature service. Dispersion modelling would also be necessary to understand the behaviour of CO_2 upon release.

Based on the preceding review of the design and operational requirements for CO_2 pipelines, particularly those operating in the dense phase/supercritical region, of particular concern with regard to change of use would be:

- Ensuring that the pressure required for dense phase/supercritical operation does not exceed the design or location factors relevant to CO_2 pipelines, along the pipeline.
- Ensuring that the minimum distance to occupied buildings is adequate for safety considerations. Perhaps reducing block valve spacing may also be considered.
- Ensuring that the pipeline material has adequate toughness to arrest long running fractures.
- Ensuring that the coating materials and any non-metallic materials are suitable for dense phase or supercritical CO_2 service.

10. DISCUSSION

This paper has presented a wide-ranging hydraulic evaluation of the transportation of anthropogenic CO_2 containing impurities in pipelines that have originally been designed and operated for hydrocarbon service. The preceding sections contain detailed discussions and conclusions; therefore, this section will only highlight the key issues

10.1 CO_2 Pipelines: Now and the Future

Current CO_2 pipelines are conservatively designed [45] (for example the very high pressures used to maintain the CO_2 in the supercritical region) and are mostly used to transport CO_2 from natural sources for the purpose of EOR. EOR is a highly lucrative business, and provides a cost incentive that accommodates the extra costs incurred by this conservatism.

Future pipelines built for carbon capture and storage projects are likely to transport a different type of CO_2: the CO_2 captured from fossil fuel power plants will contain impurities. The type and quantity of impurities will depend on the capture technology used, the type of fuel, the storage option and also an economic balance between clean-up and transport costs. Networks may also play an important role in determining the amount of impurities present due to the presence of multiple sources of anthropogenic CO_2.

10.2 CO_2 Compositions

This review of CO_2 purity specifications has indicated that, at the present time, there is no published pipeline quality CO_2 specification. However, the review has also identified some of the potential barriers to being able to do this, most specifically economic constraints.

In principle it is possible to remove impurities to very low levels but, for storage purposes, there may be no economic incentive to achieve these low levels. In addition, it has been shown that the type and quantity of impurities will change for different fuel types and capture processes. Although the impact of these impurities can be considered at an individual level, none of the specifications take into account the interaction of impurities and the potential effects that these may have. However, it has been shown that the current water specification recommended based on corrosion avoidance does not have an effect on the phase behaviour and pipeline hydraulics.

10.3 Inlet Pressures and Flow Rates

Based on the analysis carried out for the case study, the assumed maximum and minimum flow rates for pipeline transport at 85 barg are too low for any significant differences to be seen in terms of pressure profile or composition. At these low flow rates, the pressure drop is dominated by gravity and the elevation and fluid density become important factors. Indeed, for the flow rates considered, the gravitational effects result in locations along the pipeline where the pressure in the pipeline is above the MAOP. Such operation would not be allowable. If the flow rate in the pipeline is increased then the effect of friction begins to dominate and variations in flow rate and composition, in particular, have more impact on the resultant pressure profile. Indeed, at higher flow rates the MAOP criterion is not exceeded, although the predicted pressure and temperature conditions mean that the pipeline will be operating in a regime where two phase flow could result and/or phase changes could occur along the pipeline length

On the basis of the modelling conducted our case study pipeline would be suitable for transporting the specified flow rates of the 'best' and 'worst' case compositions of CO_2 at an inlet pressure of 30barg. The pressure profile along the pipeline was dominated by the flow rate, with composition having a secondary, minor effect at higher flow rates. The temperature profile showed little influence of either flow rate or composition and tended towards the assumed ground temperature. In fact, the pipeline is able to accommodate flow rates higher than those assumed in this study.

10.4 Other Considerations

In order to re-use pipeline infrastructure all the aspects required in designing and operating new CO_2 pipelines as mentioned previously, need to be considered, with additional consideration in terms of the integrity of the existing infrastructure, the pressure ratings of the pipeline, the route and also the suitability of pipeline capacity with the amount of CO_2 that is to be captured from both an economic and technical view. This would in turn play a significant role in selecting between the gaseous and supercritical phase of transportation and the viability of reusing existing pipeline infrastructure to transport anthropogenic CO_2 for CCS.

11. CONCLUSION

- EQUATION OF STATE: A review of EOS relevant to CO_2-impurity combinations has indicated that the PR EOS is the most appropriate for use in CO_2 pipelines. However, it is highlighted that no experimental work has been conducted on the phase behaviour of supercritical CO_2 containing the impurities to be found in power station capture. The EOS is therefore selected on the basis of limited experimental verification.

- CO_2 QUALITY SPECIFICATIONS: The 'best' case and 'worst' case CO_2 specification has been identified from the published literature by calculating the critical pressure for each of the specifications reviewed. On this basis, the 'best' case specification was that published by IPCC [8] for post-combustion capture, and the 'worst' case was that published by Oosterkamp and Ramsen [10] for oxyfuel capture. The 'best' case specification has similar behaviour phase characteristics to pure CO_2. However, the 'worst' case specification exhibits a large two- phase region which limits the operating envelope of a pipeline carrying this capture stream.

- WATER SPECIFICATIONS FOR CO_2 PIPELINES: The existing water specification of 640 ppmv for supercritical pipelines does not have an effect on the phase behaviour of the defined 'worst' case specification of CO_2. However, this specification is not suitable for gaseous transport of anthropogenic CO_2 at lower temperatures. The 225ppmv water specification recommended for gaseous CO_2 based on the 60% saturation limit of water in CO_2 pipelines does not have an effect on the phase properties of the anthropogenic 'worst' case specification of CO_2 and is therefore deemed more suitable Hence, the drying requirements for natural gas may not be appropriate and may be overly conservative for supercritical CO_2 as the saturation behaviour is different. This water specification should also be utilised when re-using existing pipeline infrastructure for CO_2 transportation.

- CASE STUDY PIPELINE: As a result of this study it is concluded that the case study pipeline is not suitable for operation at an inlet pressure of 85barg because the low flow rates and terrain conditions will result in pressures in excess of the MAOP. In addition, the inlet pressure is below the critical pressure for the 'worst' case composition and therefore there is the potential for phase changes and two-phase flow during pipeline operation. Consequently, it is recommended that if this pipeline is to be re-used for CO_2 transportation, that transport in the gas phase is considered.

- RE-USING PIPELINE INFRASTRUCTURE FOR CCS: Considerations must be given to the level of impurities in the anthropogenic CO_2, the amount of CO_2 that is to be captured and transported, the critical pressure of the mixture, the potential for two-phase flow and the existing MAOP of the pipeline in order to determine the change of use requirements.

10. RECOMMENDATIONS

Given the various publications in the literature for CO_2 composition, a pipeline specification of CO_2 quality for the UK should be determined. Central to defining this quality will be an understanding of the economic implications of clean up cost versus transportation cost of CO_2 with and without impurities. In addition, a pipeline CO_2 quality specification needs to be based on the validation of anthropogenic CO_2 phase properties including water, in order that the phase behaviour can be reliably predicted. This would require phase determination and water solubility experiments to be conducted that would further validate the equations of state for the quality of CO_2 that is to be transported from power plants in the UK. Following this, guidance should be put in place in terms of re-using existing infrastructure for CCS by the appropriate parties.

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