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GHGT-12

## Impact of CO<sub>2</sub> impurity on CO<sub>2</sub> compression, liquefaction and transportation

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### Abstract

The impurities present in carbon dioxide (CO<sub>2</sub>) streams for Carbon Capture and Storage (CCS) schemes are extremely important for CO<sub>2</sub> pipeline and ship transportation affecting, for instance, the range of operation, safety considerations, fracture, cracking, corrosion control, dispersion in the event of a release, fluid density, operating pressure and temperature and the quantity of CO<sub>2</sub> that can be transported. The range and levels of potential impurities present in captured CO<sub>2</sub> from CO<sub>2</sub> capture facilities will differ between sources and also between the capture technologies installed at the CO<sub>2</sub> emission sources. However, the potential CO<sub>2</sub> specifications that could enter the transport and storage systems, particularly from industrial sources, remain relatively under-researched. Consequently, the effect of these potential impurities in CO<sub>2</sub> streams on CO<sub>2</sub> transportation also needs to be understood. This paper summarises the main findings of an IEAGHG study, “Impact of CO<sub>2</sub> Impurity on CO<sub>2</sub> Compression, Liquefaction and Transportation”, commissioned to identify potential impurities and address the consequences of their impact on CO<sub>2</sub> transportation.

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**Keywords:** Impurity; CO<sub>2</sub> Compression; CO<sub>2</sub> liquefaction; Transportation

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## 1. Introduction

The impurities present in CO<sub>2</sub> streams are extremely important for CO<sub>2</sub> pipeline and ship transportation affecting, amongst other things, the range of operation, safety considerations, fracture control, cracking, corrosion control, dispersion in the event of a release, fluid density, operating pressure and temperature and the quantity of CO<sub>2</sub> that can be transported. The range and levels of potential impurities emitted from Carbon Capture and Storage (CCS) facilities will differ between different power plant and industrial sources and also between the capture technologies installed at the source. However, the potential CO<sub>2</sub> specifications that could enter the transport and storage systems, particularly from industrial sources, remain relatively under-researched. Therefore, it is of critical importance to improve the understanding of the effect of these potential impurities, which have not been widely studied, on CO<sub>2</sub> compression, liquefaction and transportation in relevant conditions.

This paper, reviews the CO<sub>2</sub> impurities that could be present from different capture technologies and develops twelve CO<sub>2</sub> scenario compositions for analysis. The physical and transport properties of the scenarios are evaluated including the bubble point, density, Joule-Thomson coefficients, speed of sound, viscosity and thermal conductivity. The effects of the impurities on CO<sub>2</sub> compression in terms of performance and energy requirements are also explored. Additionally, this work identifies the effects of impurities on the operating conditions for both pipeline and ship based transportation. Finally, the effect of the impurities on the selection of materials is discussed.

## 2. Review of possible impurities present in captured CO<sub>2</sub>

Although there is some public domain information in the literature on impurities that are likely to enter CO<sub>2</sub> transport systems (e.g.[1]-[11]), it is also widely acknowledged that state-of-the-art understanding in industry and from pilot plant operations is not fully reflected in public domain literature. The project team have, therefore, combined a critical review of the literature with a questionnaire used to elicit feedback from relevant experts that is not readily available in the public domain to explore possible impurities that may be present in captured CO<sub>2</sub>. This section provides an overview of the scenarios developed for use in this study based on this work.

Two general types of impurities can be considered. These are (1) those that may be present at %vol levels and, hence, have an impact on thermodynamic properties etc and (2) those that are likely to be present only at much lower (e.g. ppm) levels, but that may have important impacts on material performance, safety etc. The primary purpose of this section is to identify a realistic set of potential impurities present at the %vol level in CO<sub>2</sub> produced by a range of CO<sub>2</sub> capture processes<sup>1</sup>.

Although the scope of work is not exhaustive, it does aim to be sufficiently comprehensive to allow a range of plausible “worst case” scenarios that could be faced by future CO<sub>2</sub> transport systems operating within CCS projects to be identified. It should be noted that this section does not take into account downstream constraints that may limit pipeline specifications<sup>2†</sup>. The remainder of this paper will explore the implications of potential impurities being present in CO<sub>2</sub> entering CO<sub>2</sub> transport systems, so that better informed judgements can be made on which impurities, if any, need to be removed before CO<sub>2</sub> transport.

Table 1 presents the scenarios used in the remainder of this study, building on the work outlined above. The intention of this work is to provide scenarios that are “worst case” but also plausible given current understanding of likely constraints on CO<sub>2</sub> transport and storage systems. In most cases, values are similar to those reported in the review of possible impurities present in captured CO<sub>2</sub> carried out by the project team, but indicative values have been selected since these scenarios are intended to indicate illustrative CO<sub>2</sub> compositions entering CCS transport and storage systems. This approach also increases potential for comparison between scenarios (e.g. where identical CO<sub>2</sub> purity is obtained, but the impurities are different).

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<sup>1</sup>The compositions reported and discussed in this section are typically provided on a dry basis.

<sup>2</sup>For example, at the time of writing, there is an emerging body of work on acceptable O<sub>2</sub> levels in the sub-surface that may lead to substantially tighter CO<sub>2</sub> transport specifications that would not be met by some of the scenarios considered in this study.

In many cases, it is possible to improve CO<sub>2</sub> purity produced in the CO<sub>2</sub> capture scenarios considered in this study. There is, however, often expected to be a cost trade-off between improving purity of CO<sub>2</sub> entering CO<sub>2</sub> transport systems rather than designing a CO<sub>2</sub> transport (and storage) system that is able to handle some impurity in the CO<sub>2</sub>. Overall, this study should make a substantial contribution to the evidence base that can be used by CCS project developers to determine which approaches are best to manage CO<sub>2</sub> impurities within CCS systems.

Table 1. CO<sub>2</sub> purity scenarios for developed in this study.

Scenario number	Scenario	Component (all values % by volume)							
		CO <sub>2</sub>	O <sub>2</sub>	N <sub>2</sub>	AR	H <sub>2</sub>	CO	H <sub>2</sub> S	CH <sub>4</sub>
1	REF	100							
2	CO2 MEM1	93		7					
3	CO2 MEM2	97	3						
4	ADS1	90	1	9					
5	ADS2	95		5					
6	Ca LOOP (also OXY-like)	95	1	2	2				
7	OXY1	90	6	3	1				
8	OXY2	96.5	0.5	2.5	0.5				
9	PRE	98				2			
10	H2 MEM	96		1		1	0.5	1.5	
11	CH4-RICH	98							2
12	ULCOS	96		0.5			3.5		

Acronyms: ADS-adsorption; Ca LOOP-Calcium looping; CO2 MEM-CO2 membrane; H2 MEM-H2 membrane; OXY-oxyfuel; PRE-pre-combustion; REF-reference

### 3. The impact of impurities on CO<sub>2</sub> physical properties

This section investigates the effect of the addition of the components identified in the scenarios developed in Section 3 on the physical properties of CO<sub>2</sub>. In particular, the effects on the location of the phase boundaries, density, speed of sound, Joule-Thomson coefficient, viscosity and thermal conductivity relative to pure CO<sub>2</sub>, for the combination of impurities in each scenario. The twelve scenarios identified represent a plausible range of ‘worst case’ scenarios for steady-state operation. The pressures and temperature ranges to cover the physical properties were selected to be representative of dense phase pipeline operation, a pressure of 15MPa was chosen and a temperature range of 0 to 50°C.

Based on the effects of the impurities, worst case scenarios are developed for dense phase transportation taking into account the effect of the impurities on the thermodynamic and transport properties.

This paper uses the reference equations of state for each component [12]-[19], and solving routines identical to REFPROP [20]. Mixing rules for compositions with more than one component are taken from GERG2008 [21]. Transport properties cannot be calculated from equations of state and are not defined in the two-phase region. To calculate viscosity [22]-[25] are used and [26]-[29] are used to calculate thermal conductivity.

Since not all experimental work covers the regions of interest in this paper, the thermodynamic and physical properties of the mixtures are modelled. Furthermore, there is extremely limited experimental data available for the properties of potential captured CO<sub>2</sub> streams. In addition, for some impurity combinations, due to the lack of experimental data, the equations of state are operating in regions where they are expected to be less robust.

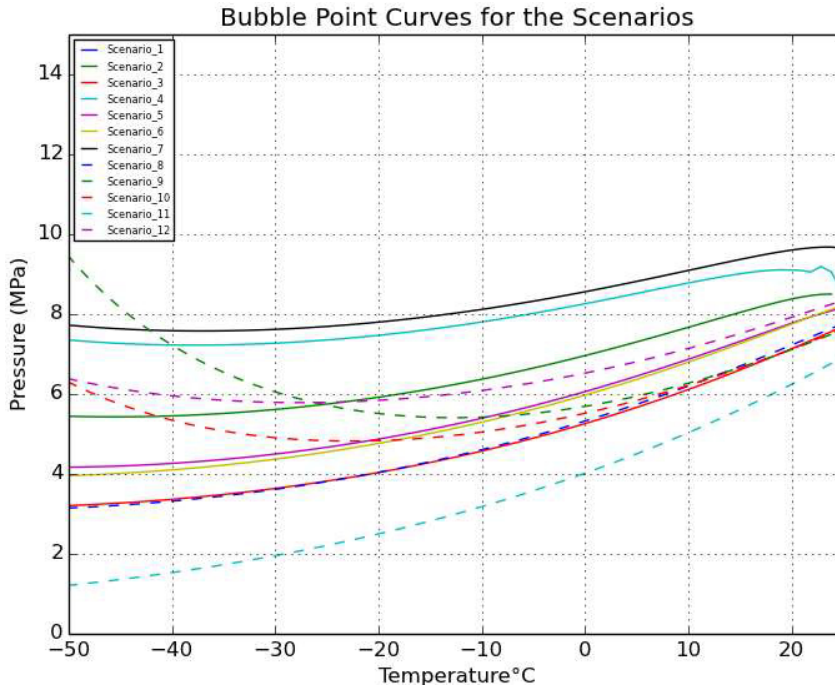


Fig. 1. The bubble point curves of the scenarios.

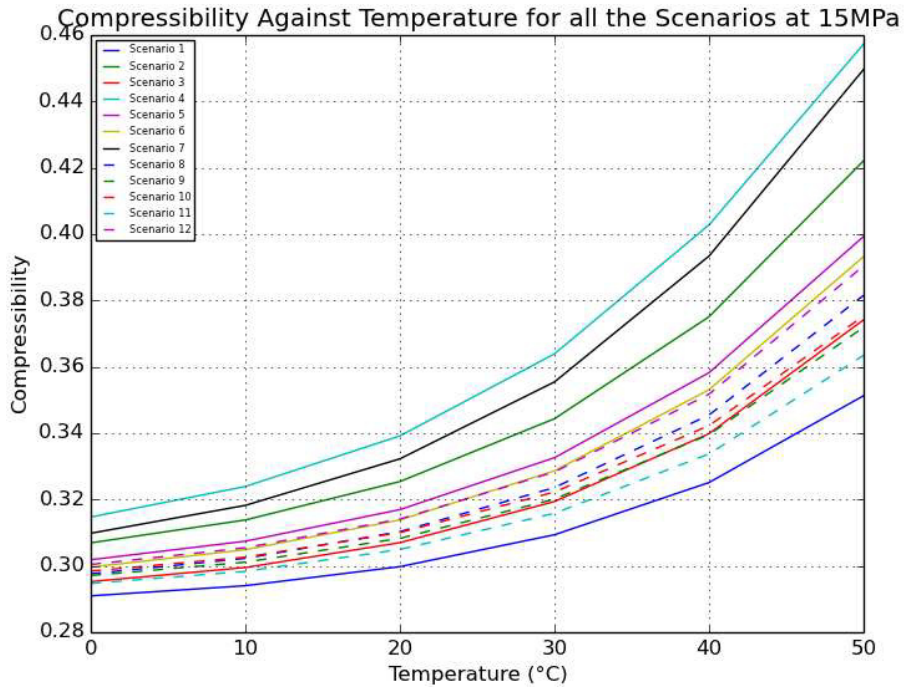


Fig. 2. The compressibility of the scenarios.

Physical and transportation properties of the scenarios are demonstrated in Figs. 1 to 7. In the dense phase Scenarios 4 (ADS1), 7 (OXY1) and 2 (CO<sub>2</sub>MEM) tend to produce the least desirable qualities for dense phase pipeline transportation. These CO<sub>2</sub> streams have the lowest proportions of CO<sub>2</sub> and have the highest bubble point curves, compressibility, Joule-Thomson coefficient and the lowest densities, speed of sound and thermal conductivities. However, it is worth noting that these scenarios also have the lowest viscosities.

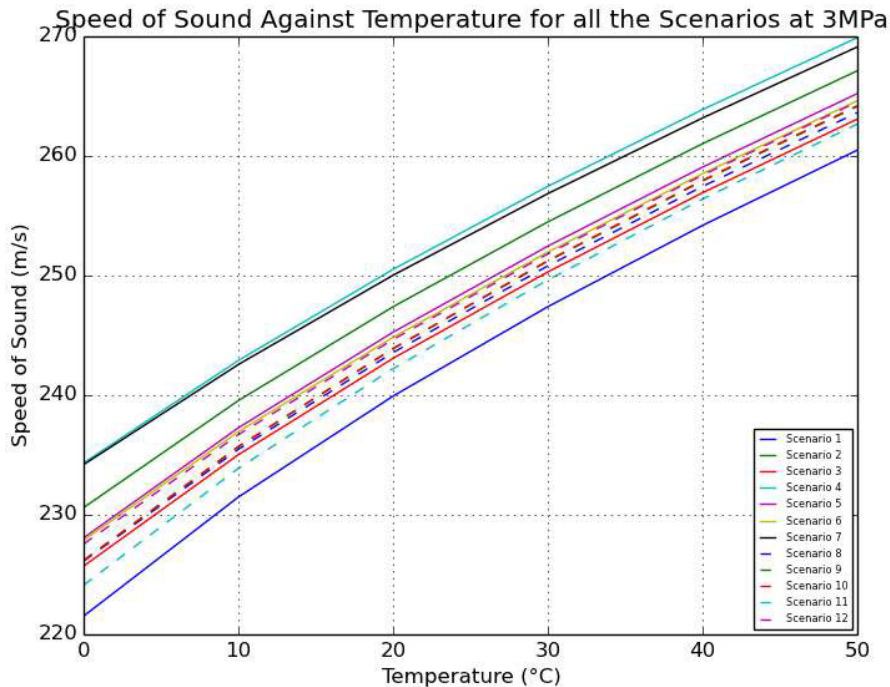


Fig. 3. Speed of sound in gaseous phase for the scenarios.

Apart from pure carbon dioxide, Scenario 11 (CH<sub>4</sub>-RICH) has the most desirable qualities for dense phase pipeline transportation with the lowest dew point curve, Joule-Thomson coefficients and compressibility and the greatest density and speed of sound. That is balanced with the fact that it has the lowest thermal conductivity and the highest viscosities. It should also be noted that, even though it has a high carbon dioxide purity (98%), Scenario 9 (PRE) has shown relatively undesirable dense phase pipeline transportation characteristics because hydrogen has large effects in small quantities. For these reasons, Scenarios 4 (ADS1), 7 (OXY1) and 2 (CO<sub>2</sub>MEM) are selected for the worst cases for dense phase pipeline transportation. It also expected that these scenarios will show the highest compression power requirements for compression to dense phase due to their relatively high compressibility.

#### 4. Impact of impurities on CO<sub>2</sub> compression

Using commercially available pipeline simulation software [30], the energy requirement and cost for a set of compressors for each scenario relative to a base case of pure CO<sub>2</sub> was evaluated and compared. The compression costs were calculated using the approach outlined in [31] and the compression base case was modelled on case B<sub>0</sub> from [33].



The choice of base case sets the number of compression stages<sup>‡</sup> and the compression ratio at each stage. It should be noted, however, that the number of compression stages is process-specific and different project developers may adapt the number of compression stages used to better integrate the CO<sub>2</sub> capture and compression processes (e.g. by reducing the number of stages in cases where a relatively high inlet pressure is delivered by the capture process).

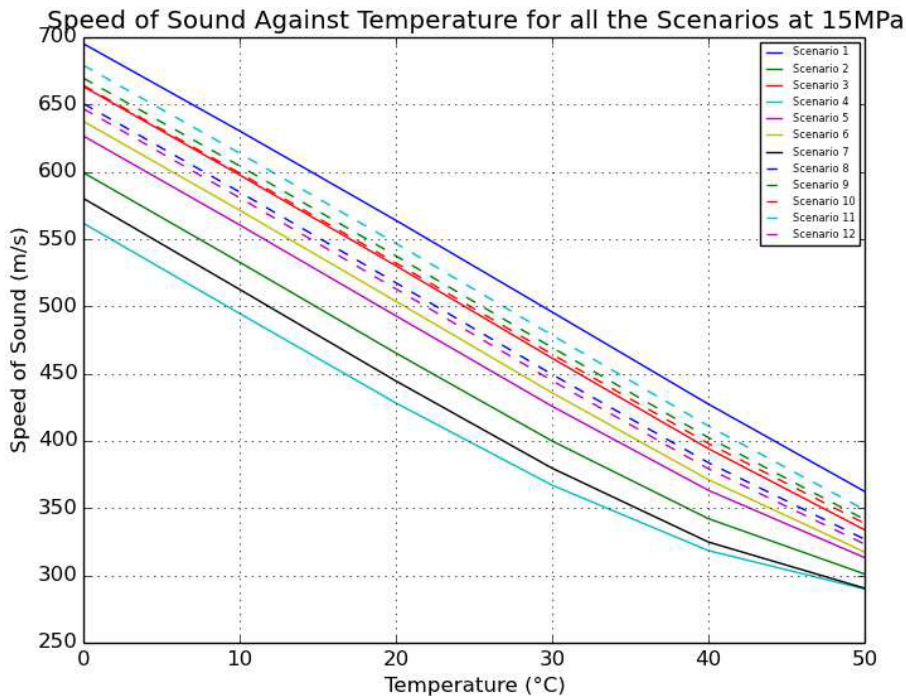


Fig. 4. Speed of sound in dense phase for the scenarios.

The inlet pressure and temperature were selected to be 1.6bar and 38°C respectively. These initial conditions are broadly representative of current recognized capture technologies and allow comparisons to be made between the scenarios. It should be noted that for specific CO<sub>2</sub> capture options actual compressor entry conditions should be used since these can have a noticeable impact on CO<sub>2</sub> compressor power requirements and costs.

In the analysis reported here a constant mass flow rate of 700,000 kg/h is assumed to be entering the compressor and that the CO<sub>2</sub> flow delivered to the pipeline in the dense phase has a pressure of 110bar and temperature of 30°C. This information is summarized in the Table 2.

For simplicity, this study has assumed a constant composition throughout the CO<sub>2</sub> compression process. As seen in Fig.8, CO<sub>2</sub> composition only has a small effect on CO<sub>2</sub> compression requirements. Further work could take into account variations in CO<sub>2</sub> composition during CO<sub>2</sub> compression.

The total power requirements and individual compressor power requirements for each case relative to pure CO<sub>2</sub> are shown in Fig. 8. These are the data obtained assuming a compressor with an isentropic efficiency of 85%. To draw clearer conclusions, the total power requirements of the anthropogenic CO<sub>2</sub> streams were normalized against the total power requirement of the REF case and the results are demonstrated in Fig.8.

ADS1 showed to be the worst case scenario of all, with slightly below 7% extra energy requirements. Sorting the energy requirement of the anthropogenic scenarios, if only the composition varies (i.e. given that inlet conditions are

<sup>‡</sup>Which varies between 4-6 stages in the literature for CO<sub>2</sub> compression.

assumed constant), then, in descending order, the scenarios that cause the most significant changes to compression power requirements are as follows ADS1, OXY1, CO2MEM1, ADS2, PRE, Ca LOOP and ULCOS, H2MEM, OXY2, CH4RICH and CO2MEM2. This is in agreement with the compressibilities calculated in Section 3.

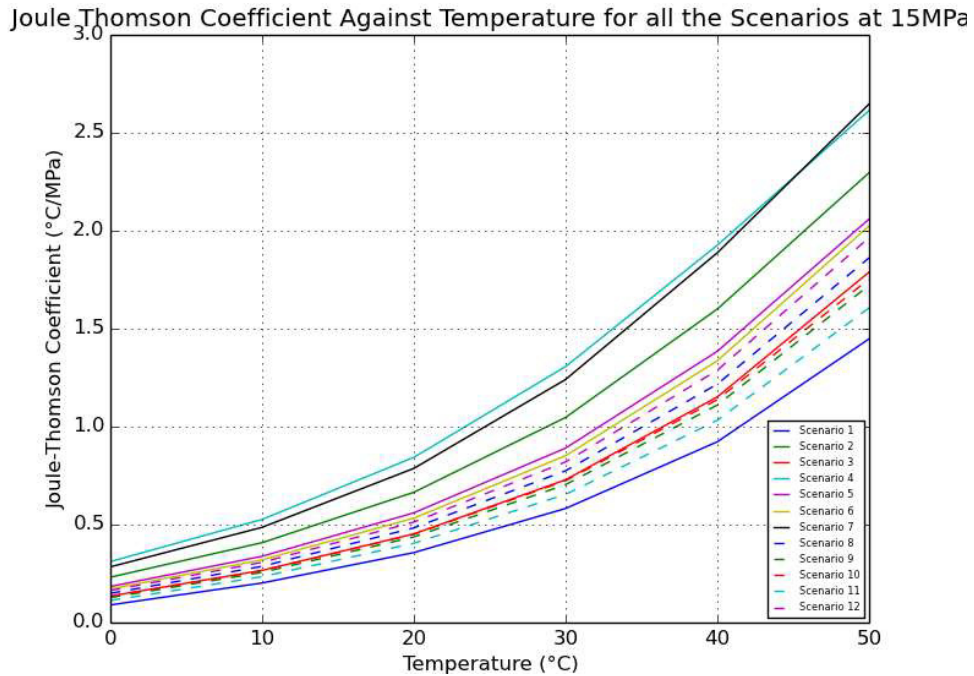


Fig. 5. Joule-Thomson Coefficient for the scenarios.

## 5 Impact of impurities on pipeline specification and hydraulics

The importance of the effect of impurities on CO<sub>2</sub> transportation was previously discussed by many scholars [33]-[35]. As demonstrated in Section 3, the impurities are expected to influence a wide range of thermodynamic and other properties relevant to CO<sub>2</sub> pipeline transport, including the density of the stream, the specific pressure drop and the critical point. As a consequence, the pipeline design parameters such as diameter, wall thickness, inlet pressure, Minimum Allowable Operational Pressure (MAOP) and the distance between booster stations are potentially subject to change. These all will also have an impact on the cost of transportation. CO<sub>2</sub> is generally transported in pipelines in the dense phase at temperature and pressure ranges between 12°C and 44°C and 85bara and 200bara. The lower pressure limit is set by the phase behaviour of CO<sub>2</sub> and should be sufficient to maintain single phase conditions while the upper pressure limit is mostly due to economic and material concerns. Regarding the temperatures, the upper temperature limit is determined by the compressor station discharge temperature and the temperature limits of the external pipeline coating material, while the lower limit is determined by the winter ground temperature of the surrounding soil [36].



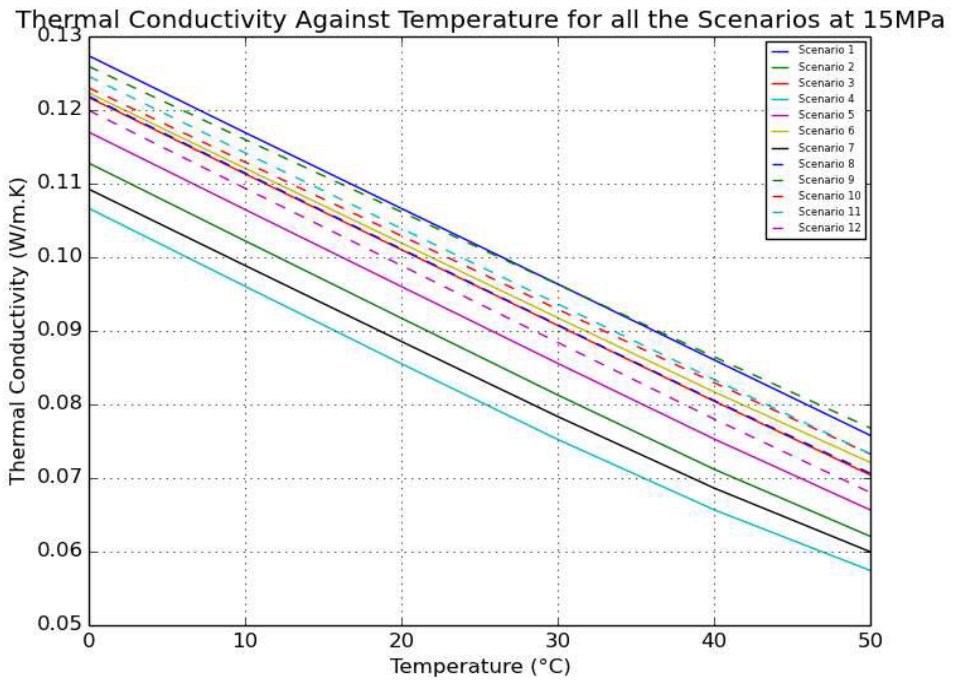


Fig. 6. Thermal conductivity of the scenarios.

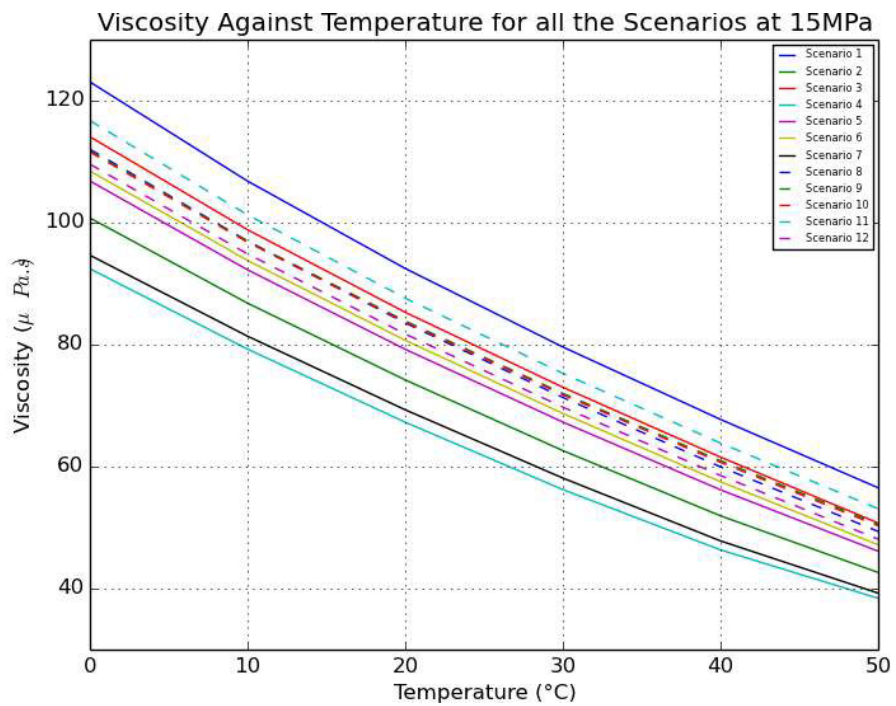


Fig. 7. Viscosity of the scenarios.

Table 2: Electrical consumption at different stages along the post combustion case B<sub>0</sub> from Appendix 1 of IEAGHG 2011/07)

Stage	State	Temperature (°C)	Pressure (bar)	Power to compress (MW) IEAGHG 2011/07)	Evaluated Isentropic Power to compress 546855 kg/h CO <sub>2</sub> flow stream (MW)
1	1	38	1.6	21.7	21.2
	2	184	7		
2	3	19	6.6	24.1	21.9
	4	176	34		
3	5	24	32.7	8.0	7.8
	6	97	70		
4	7	40	69.6	3.7	3.7
	8	81	111.2		
	9	73	111		
SUM				57.5	54.7

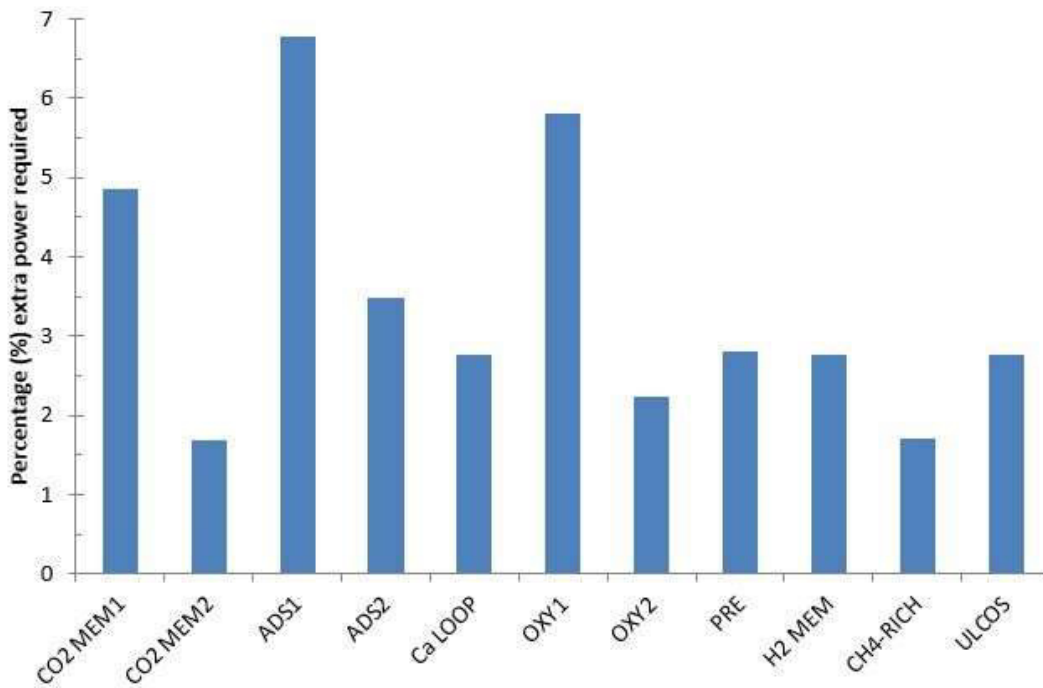


Fig. 8. The extra power requirement for anthropogenic CO<sub>2</sub> stream composition (relative to the case of pure CO<sub>2</sub>) assuming 1.6bara and 38°C entry conditions for all streams.

To study the impact of the impurities on the cost of transportation, a set of assumptions have been made as listed in Table 3. Within this study, the analysis considered designing pipelines that transport the (anthropogenic) CO<sub>2</sub> stream from the capture site, where the CO<sub>2</sub> stream enters the pipeline at 110bar and 30°C to an onshore storage site or a terminal a distance of 150km away from the capture site. A single point to point pipeline on a flat terrain is considered, with the center of the pipeline buried 1.1m below the ground level. The surrounding soil temperature is 5°C and the conductivity of the steel pipeline and the soil are taken to be 60.55 and 2.595W/m<sup>2</sup>K respectively.

Table 3: Initial conditions considered for transport of CO<sub>2</sub> in dense phase

Parameter	Value	Unit
Rate of Undulations	0	/1000
Horizontal Distance	150	km
Elevation Difference	0	m
Roughness	0.0457	mm
Ambient Temperature	5	°C
Inlet Pressure	110	bar
Mass flow rate	700	Ton/hr
Inlet Temp (°C)	30	°C
Burial depth	1.1	m
Steel Heat Transfer Coefficient	60.55	W/m <sup>2</sup> /K
Soil Heat Transfer Coefficient	2.595	W/m <sup>2</sup> /K

Using the parameters in Table 3, the pipeline geometry requirements for dense phase transportation for the worst case scenarios and a pure CO<sub>2</sub> case were calculated and are summarized in Table 4.

Table 4: Comparison of the pipeline dimensions, pressure and temperature losses for dense phase transportation of a pure CO<sub>2</sub> and the worst anthropogenic cases.

	Calculated Pipe Parameters (mm)			P <sub>i</sub> bar	T <sub>i</sub> °C	P <sub>f</sub> bar	T <sub>f</sub> °C	Hoop Stress (MPa)
	ID	W	OD					
REF	490.4	8.8	508	110	30	84.9	15.4	317.5
ADS1	588.0	11.0	610	110	30	96.8	17.1	305.0
OXY1	588.0	11.0	610	110	30	97.2	17.5	305.0
PRE	490.4	8.8	508	110	30	83.3	15.8	317.5

In order to transport 700Ton/hr (194.4kg/s) of pure CO<sub>2</sub> in dense phase, a pipeline of 508mm outside diameter would be required. The minimum thickness for this pipeline to comply with the maximum allowable tangential stress is 8.8mm. The maximum allowable tangential stress calculated as 324MPa and the designed stress limit is 317.5MPa. The choice of optimum wall thickness also keeps the pipeline weight to a minimum. This setup results in a 25.1bar pressure drop along the length of the pipeline which is equivalent to 16.8kPa/km and is in agreement with allowable pressure drops limits in pipeline engineering [37]. The delivery pressure is such that two phase flow in the pipeline is prevented. There is almost a 15°C drop in the temperature of the fluid, which makes the fluid slightly denser at the delivery point. This, in turn, causes a slight reduction in the erosional velocity. The erosional velocity ratio (flow mean velocity to erosional velocity) is around 0.3. The same design considerations as reference case have been applied in pipeline design for the worst case anthropogenic scenarios. The cases ADS1 and OXY1 require pipelines OD sizes of 610mm with wall thicknesses of 11mm. This keeps the hoop stress under 305MPa.

## 6 Effect of impurities on materials selection

It is highlighted that there is little published work on the types and levels of trace elements that could be present in the final captured CO<sub>2</sub>. It could be considered that any components which could be present in the streams delivered to the CO<sub>2</sub> capture plant could also be carried through to the exported CO<sub>2</sub> stream at very low levels. The types and levels of these trace elements therefore becomes very hard to quantify as coal and biomass can contain many different types of elements at low levels and some capture options might also add trace elements due to the nature of the process. Consequently, the approach that has been taken for this study has been to consider the effect that the trace elements could have on the various aspects of pipeline transportation and comment on the levels required for these conditions to occur.

In order to identify a worst case composition from the scenarios identified in this current work, the saturation pressures have been calculated for each composition based on decompression from the pipeline operating conditions of 150bara and 30°C. The results are presented in Table 5. From this analysis, it can be seen that the OXY1

composition is the most onerous composition to transport in terms of fracture control and will require careful consideration when designing the pipeline to ensure fracture arrest.

Table 5: Saturation pressures for scenario compositions for a pipeline decompressing from 150bar and 30°C.

Scenario	CO <sub>2</sub>	O <sub>2</sub>	N <sub>2</sub>	Ar	H <sub>2</sub>	CO	H <sub>2</sub> S	CH <sub>4</sub>	Saturation Pressure (bar)
REF	100								
CO2 MEM1	93		7						82.0
CO2 MEM2	97	3							69.5
ADS1	90	1	9						82.2
ADS2	95		5						75.5
Ca LOOP	95	1	2	2					79.8
OXY1	90	6	3	1					86.7
OXY2	96.5	0.5	2.5	0.5					77.2
PRE	98				2				62.3
H2 MEM	96		1		1	0.5	1.5		77.1
CH4-RICH	98							2	59.0
ULCOS	96		0.5			3.5			82.5

The solubility of water in pure CO<sub>2</sub> has been studied extensively as a function of temperature and pressure. The specification of water in currently operating pipelines ranges between 640ppmv and 20ppmv [38] to avoid the formation of free water in the pipeline at the operating conditions. However, whilst it is known that the presence of impurities will affect the solubility of water in CO<sub>2</sub>, there has been little research into the absolute effects of these impurities and the published data is limited. The CO<sub>2</sub>-H<sub>2</sub>O-CH<sub>4</sub> system has been studied by a number of researchers [39]-[41] and the experimental results and thermodynamic models indicate that the addition of CH<sub>4</sub> requires a more stringent water content to be specified as the solubility of water decreases with increasing CH<sub>4</sub> content. Similar results have been seen in the CO<sub>2</sub>-H<sub>2</sub>O-N<sub>2</sub> system where it has been shown that at a temperature of 40°C, an addition of 10% N<sub>2</sub> can lower the solubility of water in CO<sub>2</sub> by up to 26% [42]. It is highlighted that this composition is similar to the ADS1 composition. Conversely, in the CO<sub>2</sub>-H<sub>2</sub>O-H<sub>2</sub>S system, de Visser and Hendriks [43] showed that, on the basis of thermodynamic calculation, the solubility of water would increase with the addition of H<sub>2</sub>S. Although these ternary systems provide useful information on the potential effects of individual components, the data on representative CO<sub>2</sub> streams as presented in the scenarios in this paper is extremely limited. Pereira et al [44] studied a system of CO<sub>2</sub> and 5.05% N<sub>2</sub> -3.07% O<sub>2</sub>, 2.05% Ar at a pressure of 150bar and have shown that the addition of these impurities reduced the solubility of water by 20% compared to pure CO<sub>2</sub>. This composition is similar to the OXY1 scenario considered in this paper and therefore water content for this scenario would have to be very carefully specified at the pipeline operating conditions to avoid associated degradation mechanisms.

## 7 Ship transportation

An efficient transport mode for CO<sub>2</sub> over relatively long distances is by sea. At atmospheric pressure, impure CO<sub>2</sub> will be in either the gas or solid phase. For transportation by ship it is desirable to keep the product in liquid form. A specialised ship is therefore required with a suitable product containment system to keep the CO<sub>2</sub> in the liquid phase. A liquid state maximises the payload capability (the amount of cargo that can be carried) of the ship.

In order for the pressure requirement to be met for product to be kept in liquid phase, liquid carbon dioxide (LCD) will need to be transported in Type C tanks. Currently Type C tanks have typical application for smaller liquefied natural gas (LNG) ships which are usually suitable for coastal trade for areas which lack conventional gas pipelines. For example, 1000m<sup>3</sup> capacity ships currently operate in remoter coastal areas of Norway. However, larger vessels are currently being developed with Type C tanks. TGE Marine are currently constructing two 30,000m<sup>3</sup> carriers, with class approval in principle, and already operate a 7,500 m<sup>3</sup> vessel, the Coral Methane [45]. An advantage of Type C is the minimisation of the boil-off-gas (BOG). Some ships do not carry any BOG re-processing facility.

To enable containment of CO<sub>2</sub> mixtures in liquid form, the containment system must keep the product (above the triple point pressure) at pressures and temperatures that are above the bubble and melting point lines. This zone varies for different impurity scenarios. As seen in Section 3, some of the impurity scenarios can be transported in the liquid phase around -57°C and 1 to 1.5MPa, with the others requiring high pressures. The melting points are fairly invariant for the feasible containment pressures and range from -57°C to -73°C. Increasing the tank pressure further will move more scenarios further into the liquid phase. This improves the capabilities of the containment system for different impurity scenarios but some scenarios require unfeasible storage pressures. These scenarios would require further clean up in order to be transported by ship.

Care must be taken to avoid formation of solids (dry ice) in the storage tank and when loading/unloading. This may indicate that higher tank pressures would be required. The suggested containment pressures/temperatures are similar to previously reported values [46], [47].

It is, however, feasible to transport certain impurities of CO<sub>2</sub> by ship. An equivalence to Type C LNG ships shows that the operating pressures and temperatures are within existing ship design scope. A suitable pressure/temperature combination for high purity CO<sub>2</sub> scenarios is 0.6MPa and -57°C. As noted above, increasing the tank pressure moves less pure scenarios into the liquid phase and improves the capabilities of the containment system for different impurity scenarios, although the majority of the worst case scenarios will require storage at unfeasible pressures. Overall, the general arrangement and fundamental design parameters of an LCD ship would likely be similar to a Type C LNG ship. The density of different impurity scenarios varies significantly. This would need to be considered for stability and sea-keeping during the ship design. It will also affect the payload capacity of the ship and would therefore impact on transportation costs.

## 8 Buffer storage and liquefaction

Intermediate buffer storage could add valuable flexibility into the CO<sub>2</sub> transportation system allowing for temporary storage on route to storage or utilisation; it is a vital component for the loading of CO<sub>2</sub> onto ships. Buffer storage could consist of saline aquifers and tanks along the route of a pipeline or at a CO<sub>2</sub> terminal at the shore. However, these options could run into difficulties with health and safety regulators as well difficulties in public acceptance of onshore CO<sub>2</sub> storage, as seen in the Dutch CCS case in Barendrecht [48].

Liquefaction of CO<sub>2</sub> is not a novel technology. However, liquefaction of impure anthropogenic CO<sub>2</sub> is not straightforward. Supplied CO<sub>2</sub> would be liquefied via dehydration and refrigeration processes. For CO<sub>2</sub> mixtures to be in the liquid state they must be stored at pressures and temperatures on the liquid side of the bubble point and melting point curves. Additional impurities to a pure CO<sub>2</sub> stream cause a 2-phase region to open up. Large quantities of these impurities tend to increase the size of the envelope, especially if they have properties that are very different to CO<sub>2</sub>, and the envelope opens out away from critical point, i.e. at lower temperatures the bubble and dew point curves are further apart. Wider envelopes also have the dew and bubble point lines further apart and will require higher pressures to reach the liquid phase. There has been very little work done on low temperature CO<sub>2</sub> mixtures near the solid phase and impurities will affect the melting line, although there has been work done on the equation of state for solid carbon dioxide [12], [49], [50] and the impurities in their pure form. The lack of data on the melting point line for CO<sub>2</sub> mixtures leads to uncertainties in the liquid storage region. In order for mixtures with large amount of impurities to be on the liquid side of the bubble point curve at low temperatures, large pressures are required. Therefore buffer storage of these types of mixtures is unlikely. For mixtures with a small amount of impurity, the properties of the mixtures will be very similar to pure CO<sub>2</sub> and therefore the storage conditions and tank properties will also be similar to those of pure CO<sub>2</sub>. However, storage sites such as saline aquifers will allow for temporary storage of these kinds of mixtures in the dense or supercritical phase.

The liquefaction states of CO<sub>2</sub> transport by ships that were specified for this study were (i) 50°C, 7bara and (ii) -130°C and 7bara. A closer look at the condition (ii) reveals that all of the streams would be at their solid state for this condition; while in condition (i), many of the scenarios are either in the 2-phase region or in the gaseous phase (see Fig. 1). Therefore it can be concluded that the decision on the conditions under which anthropogenic streams should be transported depends on the phase envelope of each stream.

## 9 Conclusions

Based on the work conducted in this study, it has been possible to identify twelve worst case, but plausible, scenarios which are representative of a range of CO<sub>2</sub> capture processes. These scenarios are summarized in Table 1. It should be remembered that although these scenarios are considered plausible, it is also likely that many of the impurities reported in Table 1 could be removed if this was considered to be the most cost effective approach for a particular CCS project.

In the dense phase the ADS1, OXY1 and CO<sub>2</sub>MEM1 scenarios tend to produce the least desirable qualities for dense phase pipeline transportation. These CO<sub>2</sub> streams have the lowest proportions of CO<sub>2</sub> and have the highest bubble point curves, compressibility, Joule-Thomson coefficient and the lowest densities, speed of sound and thermal conductivities. However, it should be noted that these scenarios have the lowest viscosities. Apart from pure carbon dioxide, the CH<sub>4</sub>-rich scenario has the most desirable qualities for dense phase pipeline transportation with the lowest dew point curve, Joule-Thomson coefficients and compressibility and the greatest density and speed of sound. That is balanced with the fact that it has the lowest thermal conductivity and the highest viscosities. The ADS1 composition shows the highest compression energy requirements amongst all of the scenarios studied and this was 7% more than the base scenario. It is highlighted that this extra energy requirement is only at the compressor stages and does not represent the overall energy requirement for the whole process unit. Also, the results reported here assumed identical entry CO<sub>2</sub> compressor pressure and temperature but variations in these entry conditions can be expected in reality and should be considered in further work.

In terms of dense phase transport, only the worst case scenarios (ADS1 and OXY1) require increased pipeline sizes over the reference case of pure CO<sub>2</sub> for the design conditions considered. This will affect the capital cost of these pipelines.

For fracture control, the saturation pressure of the CO<sub>2</sub> stream is a critical variable that will determine the required pipeline dimensions and toughness to prevent a long-running ductile fracture. Hydrogen in particular has the most potent effect in raising the saturation pressure. The OXY1 scenario was the most onerous scenario composition to transport due to the high levels of oxygen and nitrogen which also raise the saturation pressure. Corrosion and stress corrosion cracking of plain carbon steel will not occur without the presence of water. The effect of impurities on water solubility is therefore critical. There is little information on water solubility available in the literature, but it has been shown that water specification for the ADS1 and OXY1 scenarios would require careful specification.

For ship transportation, it would be necessary to liquefy the scenario compositions studied in this paper. High pressure and low temperature conditions are required to maintain the fluid in its liquid phase. Although it is feasible to transport high purity CO<sub>2</sub> streams by ship, this renders the worst case scenario compositions considered in this study uneconomical for transportation in the cryogenic liquid phase. For high purity CO<sub>2</sub> streams, an equivalence to Type C LNG ships shows that the operating pressures and temperatures are within existing ship design scope. A suitable pressure and temperature combination for CO<sub>2</sub> streams with a very high purity is 0.6MPa and -57°C. Increasing the tank pressure moves the scenarios into the liquid phase. However, most of the scenarios considered in this study require an unfeasibly large pressure for ship transportation in the liquid phase and would require further cleanup. Type C vessels have, thus far, been used as containment on relatively small LNG ships. Therefore, there are significant design and approval consequences if Type C vessels are applied for LCD in large volumes.

On the capture side, it should be noted that there can be differences between what systems actually achieve and what they are guaranteed to achieve and this may be particularly the case in the early stages of CCS implementation. Additionally, the focus of this study is on steady-state performance at design conditions. Further work could consider the potential for more challenging CO<sub>2</sub> specifications to be supplied to CO<sub>2</sub> transport systems in non-steady state conditions and particularly in upset conditions.

Particularly for CO<sub>2</sub> capture from industrial sources, it may be valuable to review plant permits (rather than more generic Best Available Technology documents considered for this study) to improve understanding of the flows entering CO<sub>2</sub> capture and, hence, potentially also CO<sub>2</sub> transport and storage systems.

There is also scope for somewhat more significant variations in pressure and temperature of the CO<sub>2</sub> stream exiting the CO<sub>2</sub> capture plant than the quantitative analysis in this study considered, with several configurations under development for several CO<sub>2</sub> capture technology options. Further work could, therefore, usefully explore what



the best approach to setting pressure and temperature at the exit of the CO<sub>2</sub> capture plant might be given the implications this will have for CO<sub>2</sub> transport (and also compression or liquefaction).

Further work could consider a broader range of CO<sub>2</sub> compression scenarios with, for example, different intercooling temperatures assumed (e.g. depending on cooling source assumed to be available) and a broader variety of heat exchanger options than were included in the analysis. A tailored, optimized compression route could also be designed for each scenario based on the impurities existing in the CO<sub>2</sub> stream.

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