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DEPT. OF RESOURCES, ENERGY AND TOURISM

# **DRET CCS Task Force Support**

## **Carbon Dioxide Specification Study**

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DRET CCS TASK FORCE SUPPORT  
CARBON DIOXIDE SPECIFICATION STUDY

## SYNOPSIS

The Commonwealth Department of Resources, Energy and Tourism (DRET) have requested WorleyParsons to provide specialist support for carbon dioxide (CO<sub>2</sub>) pipeline networks as part of their review into carbon capture and storage (CCS).

This scope of work is an assessment into possible CO<sub>2</sub> pipeline stream specifications based on pipeline operating restrictions. To consider restrictions to pipeline operations, it is necessary to understand the potential impurities from industrial plants operating either pre-combustion, post-combustion or oxyfuel capture methods for CCS. An extensive review of current literature and CO<sub>2</sub> pipeline operations has been carried out for this study, which also focuses on the economic impact of varying stream compositions, possible constraints due to operational, health and safety, or legislative requirements, and differences between CCS for permanent underground storage and enhanced oil recovery (EOR) operations.

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### PROJECT 401001-00514 - DRET CCS TASK FORCE SUPPORT

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## EXECUTIVE SUMMARY

A literature review of existing studies has been conducted to evaluate available schemes to capture, transport and store carbon dioxide (CO<sub>2</sub>), the impact of different impurities, overall health and safety issues, and guidelines and regulations for Carbon Capture and Storage (CCS)

Two major CO<sub>2</sub> storage schemes are used at present (a) Enhanced Oil Recovery (EOR) and (b) Permanent Underground Storage. EOR is mainly used to recover more oil from depleting wells as well as to store some CO<sub>2</sub>. This is a proven technology, but principally focused on oil recovery. In the permanent underground storage scheme, CO<sub>2</sub> is captured from different industries, transported at high pressure and stored underground at site(s) for the sole purpose of permanent storage (geo-sequestration). Though the injection technology is well developed, the long term impact of stored CO<sub>2</sub> and several impurities are not yet fully established. In addition, it is important to note that in the case of EOR, 'leakage' from the injection area either into the oil (the objective) or to other surrounding rock and even to atmosphere has not been of major concern, whereas for geo-sequestration, it is essential that there is no migration of CO<sub>2</sub>.

Selection of a proper carbon capture method is important and depends on the type of industries and impurity tolerance for storage purposes. Commonly available methods are (a) Pre-combustion Scheme, (b) Post-combustion Scheme, and (c) Oxyfuel Combustion Scheme.

Pre-combustion capture is often associated with the Integrated Gasification Combined Cycle (IGCC) process. In this method, oxygen (from an Air Separation Unit) is used for the gasification process in which the partial combustion / oxidation process converts coal to syngas, primarily consisting of carbon monoxide and hydrogen, and this contributes to a very high internal power consumption. A shift reaction then converts the required amount of CO to CO<sub>2</sub> with the addition of steam and the aid of a specialised catalyst, and the CO<sub>2</sub> is separated by either a chemical or physical solvent. The fuel used for power generation is very rich in hydrogen (normally diluted with nitrogen to a certain degree), though combustion technologies for hydrogen rich fuel are not yet fully developed. Depending on the process used for the removal of the CO<sub>2</sub> from the syngas, impurities such as H<sub>2</sub>S can be separately removed so that only very low levels remain in the CO<sub>2</sub> stream. In addition, while some H<sub>2</sub> and CO does remain in the CO<sub>2</sub> stream, the process can be configured to greatly minimise these levels.

In post-combustion capture, CO<sub>2</sub> is separated from the flue gas. This method has relatively low power consumption, but requires large equipment due to very high volumetric flow. The level of impurities is relatively low and CO<sub>2</sub> purity of 99 vol% is achievable.

In the oxyfuel method, combustion of fuel is performed in an oxygen rich environment. This is comparable to post-combustion method with low volumetric flow. Since the oxygen is provided from an Air Separation Unit, internal power consumption is high. The level of impurities is generally high and normally rich in SO<sub>x</sub>, argon and oxygen. The CO<sub>2</sub> level in the captured gas is approximately 90 vol%.



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Impurities in the CO<sub>2</sub> can have a significant impact on the fluid physical properties and associated transport aspects, depending on the levels. The main problem is the increase in critical pressure with the increase in impurities. CO<sub>2</sub> is transported in the “dense phase” (i.e. above the gas critical pressure where the gas acts more like a liquid) to reduce frictional pressure drop, and the increase in critical pressure directly increases frictional losses, hence the power consumption. The critical pressure of pure CO<sub>2</sub> is approximately 73 bar and increases to 86 bar if contaminated with 5 vol% of H<sub>2</sub> or 5 vol% of NO<sub>2</sub>. Also, it is preferable to keep the fluid temperature as low as possible. A fluid temperature above 35°C rapidly decreases the density when the pressure is close to the critical pressure, resulting in a two-phase flow through the pipeline, which causes both operational (larger pressure drop in the pipeline) and maintenance (e.g. damage to compressors) issues.

The main factor that dictates pipeline corrosion is the presence of free water in the CO<sub>2</sub> stream, either carried over from the upstream process facilities or formulated within the pipeline due to pressure drop. It is presumed that CO<sub>2</sub> corrosion will not take place unless there is presence of free water. Hence, drying of CO<sub>2</sub> to water concentrations below the dewpoint for operating conditions is thus regarded as effective corrosion prevention. If free water is permitted, then it would be necessary to either increase the wall thickness of the pipeline allowing for predicted corrosion rates or utilising corrosion resistant materials where in contact with the CO<sub>2</sub> stream. This is not considered a cost effective solution for pipeline systems of significant length.

There are health and safety issues associated with CO<sub>2</sub> transportation due to the presence of impurities, though CO<sub>2</sub> itself is non-toxic at atmospheric concentration. Since CO<sub>2</sub> is denser than air and an asphyxiate, a pipeline leakage can potentially develop dangerous levels of CO<sub>2</sub> in low lying areas. Additionally, impurities like H<sub>2</sub>S and CO have a higher toxicity risk than CO<sub>2</sub> itself, and additional precautionary measures will need to be implemented.

Several variations in CO<sub>2</sub> composition due to capture techniques, pipeline operating restraints and storage implications have been discussed in this study. As a result of the wide range of potential impurities possible in a CO<sub>2</sub> stream, it is not recommended to introduce legislation defining acceptable CO<sub>2</sub> composition for all possible CCS projects. Instead, it is recommended that each CCS system define their own CO<sub>2</sub> specification that carefully considers the cost and safety for the particular constraints present in the CCS system.



## 1. INTRODUCTION

The Commonwealth Department of Resources, Energy and Tourism (DRET) have requested WorleyParsons to provide specialist support for carbon dioxide (CO<sub>2</sub>) pipeline networks as part of their review into carbon capture and storage (CCS).

In recent years, there has been a worldwide increase in energy demand coupled with a continued reliance on fossil fuel resources, which has contributed to a significant increase in atmospheric levels of CO<sub>2</sub> [1]. Currently, 40% of all human (anthropogenic) CO<sub>2</sub> generation originates from the burning of fossil fuels in power stations, with the power sector expected to triple its emissions by 2050 [2]. Furthermore, anthropogenic sources of CO<sub>2</sub> from industrial processes such as ammonia plants are expected to come on-line in the relatively near future [3] along with other existing industrial sources such as blast furnaces (for steel making) and cement kilns. Although reducing energy consumption with increased energy efficiency can play a major role in the reduction of CO<sub>2</sub> emissions, the demand for energy and security of supply ensures that many countries will continue with the use of coal and gas as their primary source of fuel. As such, there has been profound interest in the area of CCS as a potential approach for reducing CO<sub>2</sub> emissions.

Reliable data on CO<sub>2</sub> emission compositions and its physical properties are required for a successful process design with the most reliable source being experimental data as well as data from operating CCS facilities. However, the collection of such data is costly, time-consuming and limited to the test conditions. Furthermore, there are many factors that contribute to varying CO<sub>2</sub> stream compositions (i.e. impurity levels), the most prominent being the capture technique used at the emission source.

In essence, current theoretical models have not been fully validated by full scale testing, especially considering the extended timeframe that CO<sub>2</sub> has to remain safely stored underground.

### 1.1 Study Scope

This scope of work is an assessment into possible CO<sub>2</sub> pipeline stream specifications based on pipeline operating restrictions. To consider restrictions to pipeline operations, it is necessary to understand the potential impurities from industrial plants operating either pre-combustion, post-combustion or oxyfuel capture methods for CCS. An extensive review of current literature and CO<sub>2</sub> pipeline operations has been carried out for this study, which also focuses on the economic impact of varying stream compositions, possible constraints due to operational, health and safety, or legislative requirements, and differences between CCS for permanent underground storage and enhanced oil recovery (EOR) operations.



## 2. ABBREVIATIONS

Abbreviation	Description
Ar	Argon
CAPEX	Initial Capital Expenditure
CCS	Carbon Capture and Storage
CH <sub>4</sub>	Methane
C <sub>2</sub> H <sub>6</sub>	Ethane
CO	Carbon Monoxide
CO <sub>2</sub>	Carbon Dioxide
COAG	Council of Australian Governments
CTL	Coal-To-Liquid
DOT	U.S. Department of Transportation
DRET	(Commonwealth) Department of Resources, Energy and Tourism
EOR	Enhanced Oil Recovery
H <sub>2</sub>	Hydrogen
H <sub>2</sub> O	Water
H <sub>2</sub> S	Hydrogen Sulphide
HC	Hydrocarbon
HSE	Health, Safety and Environment
IGCC	Integrated Gasification Combined Cycle
IPCC	Intergovernmental Panel on Climate Change
MCMPR	Ministerial Council on Mineral and Petroleum Resources
MEA	Mono-Ethanol-Amine
MMP	Minimum Miscibility Pressure
MSDS	Material Safety Data Sheet
N <sub>2</sub>	Nitrogen
NO	Nitric Oxide
NOHSC	National Occupational Health and Safety Commission
NO <sub>x</sub>	Oxides of Nitrogen Compounds
NH <sub>3</sub>	Ammonia
O <sub>2</sub>	Oxygen





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Abbreviation	Description
OPEX	Operations and Maintenance Expenditure
ppm	Parts Per Million
SO <sub>2</sub>	Sulphur Dioxide
SO <sub>x</sub>	Oxides of Sulphur Compounds
STEL	Short Term Exposure Limit



### 3. LITERATURE REVIEW

An extensive literature review has been conducted to identify, interpret and assess various CCS techniques and developments currently being undertaken worldwide, both on a commercial and demonstration / pilot plant operating scale.

The first section of this review provides an overview of existing and developing CCS work with specific focus on CO<sub>2</sub> transport for enhanced oil recovery operations and carbon capture and storage (CCS) in underground geological formations.

The second section presents an overview of three distinct CO<sub>2</sub> capture techniques that are considered to be potential methods for CCS. A brief overview of each technique, namely pre-combustion, post-combustion and oxyfuel combustion methods will be discussed, along with the possible CO<sub>2</sub> composition emitted from each method.

The final sections address CO<sub>2</sub> pipeline stream specifications that are currently being incorporated in existing CO<sub>2</sub> pipelines as well as those developed from on-going research in this area. The operational and economic impact of varying stream compositions on the pipeline and facilities due to the presence of impurities from different upstream capture methods is reviewed.

#### 3.1 Overview of CCS Developments

The heightened awareness of greenhouse gas effects towards climate change and the proposed introduction of the Carbon Pollution Reduction Scheme have provided greater incentives for research and development in the field of CCS. While CO<sub>2</sub> has been captured on a commercial scale for several decades by separating it from natural gas production for use during enhanced oil recovery (EOR) operations in depleting oil and gas fields, the current focus has shifted to capturing CO<sub>2</sub> from coal/gas-fired electricity generating facilities for storage (CCS) in depleted reservoirs or saline aquifers [3]. This change of focus is mainly due to the large role played by coal/gas-fired power plants in overall CO<sub>2</sub> emissions.

The following subsections will briefly discuss each of the CO<sub>2</sub> end usage processes, i.e. EOR and CCS for permanent storage, and will also provide discussions illustrating the differences between them in terms of CO<sub>2</sub> quality requirements.



### 3.1.1 Enhanced Oil Recovery (EOR)

The process and operation of enhanced oil recovery has been undertaken for over 30 years (mainly in the United States) and is regarded as a proven technology in the oil and gas industry. Thus, the transportation of CO<sub>2</sub> by pipeline has also been accomplished for several decades, mainly from naturally occurring, relatively pure CO<sub>2</sub> sources for onshore EOR processes [2]. As a result, there are existing CO<sub>2</sub> stream specifications available as reference from currently operating CO<sub>2</sub> pipelines, which will be discussed further in Section 3.3.

The EOR process involves supercritical CO<sub>2</sub> being injected into an oil / gas field in a cycle alternating with water injection so as to maximise the amount of oil removed [4]. The CO<sub>2</sub> in the EOR process serves two distinct purposes: (1) it acts to reduce both density and viscosity of the oil; and (2) it greatly increases the displacement efficiency (under sufficiently high reservoir pressure) of the oil through its high miscibility property [5]. This particular physical quality of CO<sub>2</sub> in the supercritical state allows it to approach, or enter, a miscible state with the oil that remains trapped in pore spaces of a production reservoir, causing the oil droplets to expand, become detached from the adjoining rock, and join the CO<sub>2</sub> in diffusing through the pore space [3].

Based on the above concept, CO<sub>2</sub> pipelines for EOR are primarily focused on serving downstream interests of production. Experience from the utilisation of CO<sub>2</sub> for EOR shows that there are few operational problems as long as the fluid is pure and the water content is controlled [6]. The following aspects have been identified as important considerations for CO<sub>2</sub> quality during EOR operations.

- The injected stream should have a CO<sub>2</sub> purity level of at least 95%. If purity is below 95%, the pressure required to achieve miscibility rises substantially (magnitude dependent on the impurities present) to uneconomical or unattainable levels for the reservoir, which increases injection costs and raises the risk of formation damage (e.g. build-up of asphaltenes) [4].
- Slight impurities such as nitrogen (N<sub>2</sub>), sulphur dioxide (SO<sub>2</sub>) and hydrogen sulphide (H<sub>2</sub>S) can enhance the effectiveness of CO<sub>2</sub> interaction at the miscibility front and hence improve EOR efficiency [4].
- CO<sub>2</sub> solubility decreases dramatically as the proportion of N<sub>2</sub> rises [4].
- Positive impurity additions are sulphur oxides (SO<sub>x</sub>), ammonia (NH<sub>3</sub>) and H<sub>2</sub>S, while negative additions include methane (CH<sub>4</sub>), ethane (C<sub>2</sub>H<sub>6</sub>), argon (Ar), hydrogen (H<sub>2</sub>), oxygen (O<sub>2</sub>), and carbon monoxide (CO) [7].
- CO<sub>2</sub> containing O<sub>2</sub> reacts with the oil and causes negative overheating at the injection point [7].

As stated earlier, CO<sub>2</sub> pipeline compositions for existing EOR operations are presented in Section 3.3.



### 3.1.2 Permanent Underground Storage (CCS)

To reduce the magnitude of CO<sub>2</sub> release from various industrial sources, the CCS scheme provides a potentially attractive option by capturing the CO<sub>2</sub> from its anthropogenic sources, transporting it via a pipeline system, and injecting it underground at site/s for the sole purpose of permanent storage. The disposal of CO<sub>2</sub> is practical with pipelines, not only due to the experiences from EOR operations, but also because it can be transported efficiently in large volumes to the reservoirs, and is in effect, potentially the cheapest and safest option for transportation of large volumes [2]. The injection technology used for CCS is also essentially the same as to that currently in existence for EOR operations, although the geological storage requirements are different between the two purposes.

A CCS pipeline for transporting captured CO<sub>2</sub> from one or more emission sources for permanent geologic storage is, in certain respects, different to EOR pipelines. The CCS scheme is operationally subordinate to the generation of electricity and the requirements for reliable operation of the power grid into which the power plant delivers the power [3]. Therefore, its focus is serving upstream interests (i.e. on the source of CO<sub>2</sub> supply at the electricity generating facility) in comparison to downstream serving EOR pipelines (as discussed in Section 3.1.1). As such, the quality of CO<sub>2</sub> in CCS pipelines will be predominantly dictated by the CO<sub>2</sub> capture and removal method employed at the industrial facilities with secondary consideration of pipeline and storage constraints. This will be further discussed in Section 3.2.

There are three general types of geological formations that have been proposed for use as permanent CO<sub>2</sub> storage, namely depleted oil and gas formations, deep unmineable coal seams and deep saline aquifers. Details on each type of geological formation are outside the scope of this study, although the following issue regarding the effects of CO<sub>2</sub> pipeline composition based on geological formations, more specifically for saline aquifers, should be considered.

The long-term timeframe in which CO<sub>2</sub> is stored underground implies that the CO<sub>2</sub> can react with the surroundings over time, unlike the CO<sub>2</sub> injected during EOR operations in which it is recovered for recycle and reuse. The CO<sub>2</sub> may react and be held in another form through [4]:

- (1) Solubility trapping in an aqueous phase either dissolved in brine or as bicarbonate ions (e.g. reaction with silicate minerals can form calcium, magnesium and iron carbonate precipitates).
- (2) Mineral trapping in solid minerals resulting from reactions with the rock.

Therefore, different levels of impurities in the injected CO<sub>2</sub> stream can inadvertently influence the nature in which the CO<sub>2</sub> reacts with the geological formations over time. However, the interaction of a given CO<sub>2</sub> stream with a particular geological formation may differ based on the possible combinations of minerals or chemicals in the CO<sub>2</sub> stream and in the target formation [3]. As a result, certain sites may be suitable for some CO<sub>2</sub> specifications, but not for others. There is only limited information and resources available on this issue, although Statoil has been operating commercial scale permanent storage of CO<sub>2</sub> since 1996 in saline aquifers [4].



### 3.1.3 Comparisons between EOR and CCS for Permanent Storage

There is considerable experience of CO<sub>2</sub> pipeline transport, but there are several major differences between past experiences (i.e. EOR pipelines), and the conditions under which the future CCS pipelines will operate. Areas of difference include specification of CO<sub>2</sub> composition, regulations, risk, routing, design, purpose, operation and maintenance [2]. This section will outline the main differences to consider in terms of CO<sub>2</sub> quality between EOR operations and CCS for permanent underground storage.

The main differences in CO<sub>2</sub> quality is governed by the purpose and nature in which CO<sub>2</sub> is used. For EOR operations, the quality of CO<sub>2</sub> is dictated by the requirements to extract the maximum quantity of oil or gas from the reservoirs without compromising the integrity and safety of the operation. For example, low N<sub>2</sub> content is important for EOR to keep the minimum miscibility pressure (MMP) low [2]. Therefore, the interaction between CO<sub>2</sub> and the hydrocarbon reserves is an important factor in determining the CO<sub>2</sub> quality, which is illustrated by the different pipeline specifications in existence from varying EOR projects (refer to Table 2 in Section 3.3).

In contrast, the CO<sub>2</sub> quality for permanent underground storage (CCS) is primarily influenced by (1) the upstream CO<sub>2</sub> capture method used at the emission source (details discussed in Section 3.2); (2) the interaction mechanisms involved between the CO<sub>2</sub> fluid and underground formations (e.g. brine, minerals, rocks, etc.) due to the long-term storage objective; and (3) the impact of the CO<sub>2</sub> on pipeline integrity and operating and maintenance costs.

Another key characteristic of an EOR pipeline is that it is sized and operated to transport and inject the least amount of CO<sub>2</sub> needed to extract the greatest amount of oil, and to recycle and reuse as much of the injected CO<sub>2</sub> as possible [3]. In comparison, CCS pipelines will strive to transport the maximum amount of CO<sub>2</sub> that can be removed (economically) from the emission source and geologically stored [3]. While EOR operations recycle and reuse as much of the initially-injected CO<sub>2</sub>, a large percentage of the injected CO<sub>2</sub> – of the order of fifty percent or more – cannot be recovered for reuse under current technology and remains stored in the underground formation as an incident of the oil production operation [3]. Hence, the incidental storage of CO<sub>2</sub> during EOR operations is physically indistinguishable from the incremental storage of anthropogenic CO<sub>2</sub> that occurs if depleted oil formations are utilised as a permanent storage source [3].

The details given above suggests that experiences from EOR pipeline operations in terms of CO<sub>2</sub> specification are an appropriate source of information, given that vast quantities of CO<sub>2</sub> are already stored incidentally as part of the EOR process. However, this perception cannot be taken for granted for CCS as other factors such as the type and economies of the capture method used, the type of geological formation the CO<sub>2</sub> is injected into, the impact on transportation OPEX and CAPEX, and the long-term interaction behaviour between the CO<sub>2</sub> and underground formations, can also significantly influence CO<sub>2</sub> quality specifications.



## 3.2 Overview of Carbon Capture Methods

A critical step within the CCS scheme is the capture method used to remove the CO<sub>2</sub> component from industrial emissions (e.g. flue gas) prior to transportation for subsequent injection into nominated sites for permanent storage. There are three primary approaches to CO<sub>2</sub> capture – pre-combustion, post-combustion and oxyfuel combustion – that have been identified as potential techniques for use in CCS. The chemical composition of the CO<sub>2</sub> stream produced will tend to vary with many factors, including the capture technique used and the composition of the specific fuel source (i.e. coal, natural gas and oil) at each industrial facility. The presence and type of other components (impurities) will also differ considerably between the three capture methods.

As the concept of CCS and its associated capture techniques are still in the early phases of development, there have been some technical uncertainties about the level of capture that can be achieved from each method. Presently, the post-combustion capture methods are the most mature, while pre-combustion integrated gasification combined-cycle (IGCC) and oxyfuel techniques appear to be promising.

Power plants with CO<sub>2</sub> capture will emit a CO<sub>2</sub>-depleted flue gas to the atmosphere. The concentrations of the most harmful substances in the flue gas will be similar to the flue gas from plants without CO<sub>2</sub> capture [12].

In addition, certain contaminants may be combined with the CO<sub>2</sub> stream destined for geological storage as the preferred means of disposing toxic substances that would otherwise be stored in solid form above ground [3]. The type and amount of other components introduced in the CO<sub>2</sub> depends on the fuels used and the type of capture method (and type of solvent) used [10]. This, however, may raise other issues such as future liability of the involved parties and possible environmental effects [10]. In summary, the CO<sub>2</sub> stream captured at a given power plant will not be 100% pure but will include various other impurities. As a result, contractual quality standards will have to be developed to protect the interests of all participants in a CCS transaction and ensure that the CO<sub>2</sub> stream is also suitable for the downstream facilities [3].

Other industrial processes such as steel, cement, ammonia and ethanol production facilities are also potential candidates for CO<sub>2</sub> capture. Capture from steel or cement production will be similar to post-combustion or oxyfuel combustion capture techniques [1]. Ammonia and ethanol production plants are especially attractive since they generate a relatively pure stream of CO<sub>2</sub> as a by-product [1]. Also, CO<sub>2</sub> removed from natural gas streams is another candidate for CCS.

The following subsections will briefly describe each of the three capture techniques (focusing on primarily coal/gas-fired power plants) identifying the main concepts and methods, with a brief summary of expected CO<sub>2</sub> emissions from each capture technique given in the final section.



### 3.2.1 Pre-Combustion Method

The pre-combustion capture method, which is often associated with the Integrated Gasification Combined Cycle (IGCC) process, involves the generation of syngas (primarily carbon monoxide plus hydrogen) from coal (Figure 1) or natural gas (Figure 2), followed by a shift reaction to convert a required amount of CO to CO<sub>2</sub> (depending on capture requirements) with the addition of steam [1] and the use of a specialised catalyst. CO<sub>2</sub> is then separated from the hydrogen-rich component using either a chemical or physical solvent, after which the hydrogen can be either burned in a turbine [1] or used for chemical production. This process essentially increases the concentration of CO<sub>2</sub>, thus improving the CO<sub>2</sub> capture efficiency downstream and increasing the amount of carbon that can be removed.

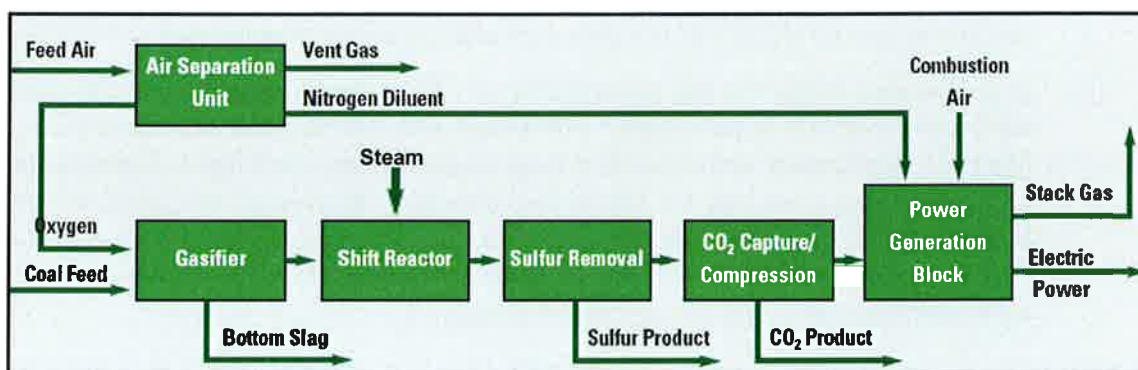


Figure 1 – Pre-Combustion Capture from IGCC Coal-Fired Power Plant [1]

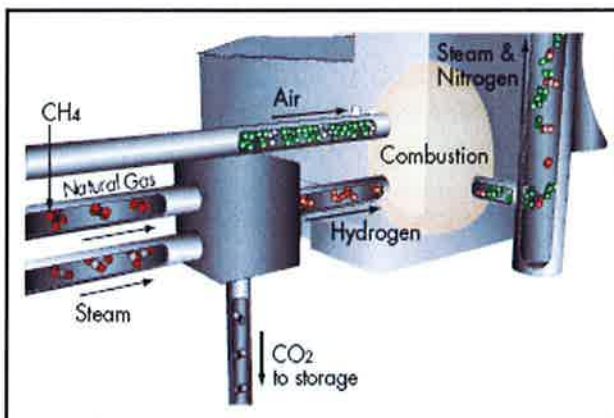


Figure 2 – Pre-Combustion Capture from IGCC Gas-Fired Power Plant [8]



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Examples of planned CCS projects using pre-combustion technique include [1]:

- ZeroGen, based in Australia using coal as feedstock.
- Monash Energy, based in Australia using coal as feedstock.
- Fort Nelson, based in Canada using gas as feedstock.

CO<sub>2</sub> from pre-combustion physical solvent scrubbing processes typically contains about 1-2% of H<sub>2</sub> and CO, traces of H<sub>2</sub>S and other sulphur compounds [12]. It may also contain N<sub>2</sub> and CH<sub>4</sub>, dependant on the solvent used for CO<sub>2</sub> capture [10]. IGCC plants with pre-combustion capture can also be designed to produce a combined stream of CO<sub>2</sub> and sulphur compounds (primarily H<sub>2</sub>S), so as to reduce costs, avoid the production of solid sulphur and dispose together with the CO<sub>2</sub> at the storage sites [12]. However, this option will only be considered in circumstances where the combined stream can be transported and stored in a safe, cost effective and environmentally acceptable manner [12].

In comparative terms, the low concentration of CO<sub>2</sub> in the flue gas from power stations using post-combustion methods, in combination with almost atmospheric pressure, means that a large volume of gas has to be handled, which results in large equipment sizes and higher capital costs [4]. In addition, it has been suggested that the use of pre-combustion techniques with IGCC is more cost-effective because the CO<sub>2</sub> can be captured at relatively higher pressures compared to post combustion [1]. This essentially results in reduced compression requirements for pipeline transport, which is a significant factor on a cost and operational basis.

### 3.2.2 Post-Combustion Method

Post-combustion capture refers to the separation of CO<sub>2</sub> from the flue gas of a combustion process, where fuel sources can be hydrocarbons such as coal (Figure 3), natural gas (Figure 4) or oil [1]. The flue gas leaving the boiler is cleaned with a scrubber to remove SO<sub>2</sub> as well as particulate matter. This process allows the removal of SO<sub>2</sub> to acceptable levels, which is typically less than 10 ppm, to reduce corrosion and fouling of the downstream system as well as susceptibility to high levels of exposure [1]. The cleaned flue gas then enters an absorption column that contains an amine solution (e.g. monoethanolamine or MEA), whereby the CO<sub>2</sub> is absorbed into the amine solution, and then separated for pipeline transport. Note that other CO<sub>2</sub> capture methods exist beside chemical absorption such as physical adsorption, membrane separation and cryogenic separation [1].





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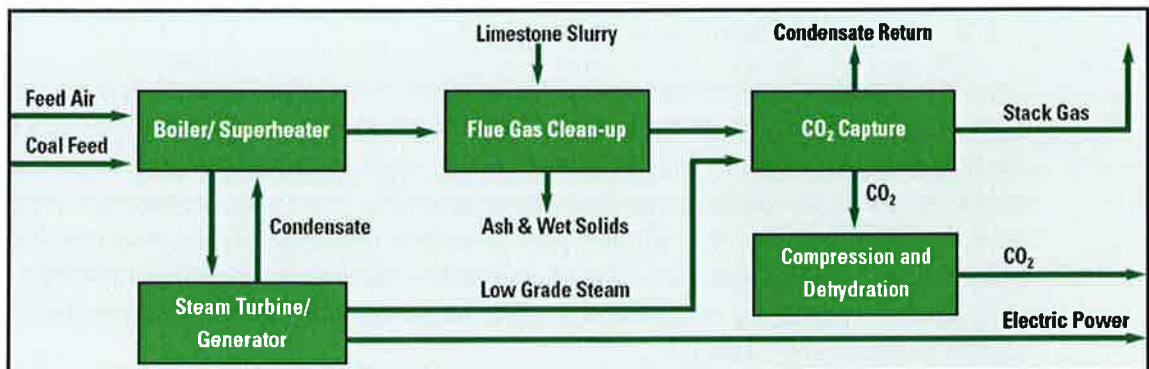


Figure 3 – Post-Combustion Capture from Coal-Fired Power Plant [1]

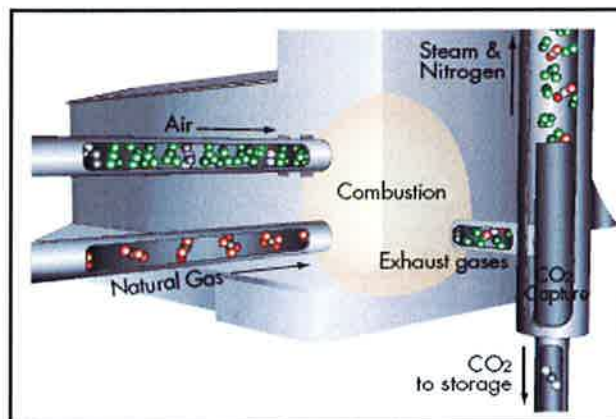


Figure 4 – Post-Combustion Capture from Gas-Fired Power Plant [8]

Examples of planned/operating CCS projects using post-combustion technique include [1]:

- Williston, based in USA using coal as feedstock.
- Sargas Husnes, based in Norway using coal as feedstock.
- Tenaska, based in USA using coal as feedstock.

CO<sub>2</sub> from post-combustion solvent scrubbing processes normally contains low concentrations of impurities, with many of the existing post-combustion capture plants producing high purity CO<sub>2</sub> [12]. In addition, post-combustion solvent absorption processes require low concentrations of sulphur compounds in the feed to avoid excessive solvent loss, and the flue gas may contain traces of solvent as well as ammonia produced by decomposition of the solvent [12]. Flue gases from coal combustion will contain CO<sub>2</sub>, N<sub>2</sub>, O<sub>2</sub> and water, but also air pollutants such as SO<sub>x</sub>, NO<sub>x</sub>, particulates, hydrochloric acid, hydrogen fluoride, mercury, other metals, and trace organic and inorganic contaminants [10].



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### 3.2.3 Oxyfuel Combustion Method

Oxyfuel combustion involves the combustion of fuel such as coal (Figure 5) and natural gas (Figure 6) in an oxygen-rich environment (instead of air) to dramatically increase the CO<sub>2</sub> concentration of the resulting flue gas, which in turn facilitates the CO<sub>2</sub> separation process downstream as well as lower emissions of NO<sub>x</sub> compared to air-blown combustion [1]. The oxyfuel combustion method is similar to the post-combustion method, with the main difference being the oxygen feed from the air separation unit. However, the flue gas from oxyfuel combustion may require significant cleaning (and therefore, cost) before transport if it is expected to meet the same minimum requirements for CO<sub>2</sub> composition as post-combustion capture [1].

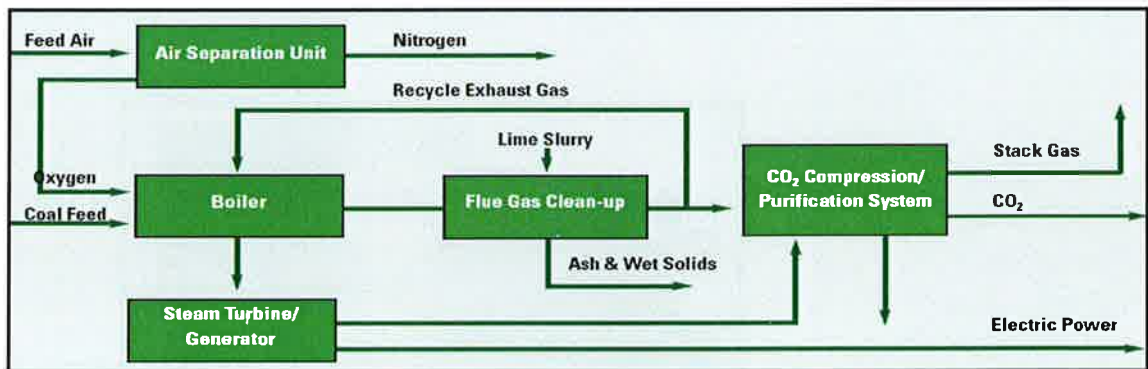


Figure 5 – Oxyfuel Combustion Capture from Coal-Fired Power Plant [1]

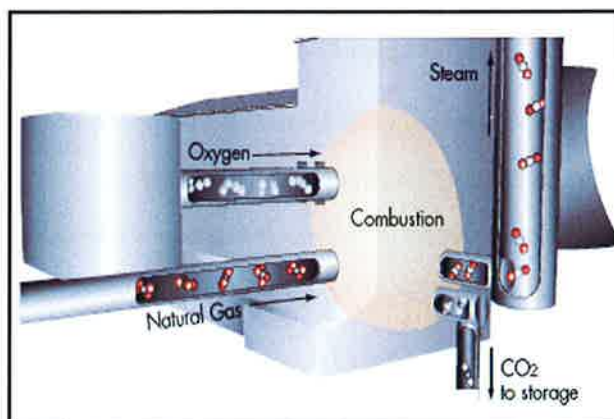


Figure 6 – Oxyfuel Combustion Capture from Gas-Fired Power Plant [8]



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Examples of planned/operating CCS projects using oxyfuel combustion technique include [1]:

- Callide-A Oxy Fuel, based in Australia using coal as feedstock.
- Vattenfall Oxyfuel, based in Germany using coal as feedstock.
- Total Lacq, based in France using oil as feedstock.

The CO<sub>2</sub>-rich gas from oxyfuel methods contains O<sub>2</sub>, N<sub>2</sub>, Ar, SO<sub>x</sub>, NO<sub>x</sub> and various other trace impurities [12]. On economic terms, a non-condensable component level of less than 4% (volume basis) can be considered as a reasonable CO<sub>2</sub> purification level for general cost balance in the oxyfuel (coal) combustion CCS chain [11]. On an operational basis, the CO<sub>2</sub> gas will normally be compressed and fed to a cryogenic purification process to reduce the impurities concentrations to the levels required to avoid two-phase flow conditions in the transportation pipelines [12]. 99.99% purity can also be achieved by including distillation in the cryogenic separation unit [12]. Alternatively, the SO<sub>x</sub> and NO<sub>x</sub> content may be left in the CO<sub>2</sub> stream in circumstances where that is environmentally acceptable and when the total amount of all impurities left in the CO<sub>2</sub> is low enough to avoid two-phase flow conditions in transportation pipelines [12].

### 3.2.4 Summary of CO<sub>2</sub> Quality per Carbon Capture Methods

This section will briefly focus on the main components in the CO<sub>2</sub> stream from each of the three capture techniques. A more detailed analysis on the range of CO<sub>2</sub> stream compositions is provided in Section 4.1.

Table 1 (adapted from [13]) identifies the various components (denoted by 'X') that can influence or become critical factors in CO<sub>2</sub> pipeline transport. Those components marked in yellow indicate that these components may also become critical in the case of a mixture of CO<sub>2</sub> streams from different capture techniques. The effects of these components will be discussed later in this section.

**Table 1 – Identification of Potentially Critical Components in CO<sub>2</sub> Transport**

Component	Pre-Combustion (IGCC)	Post-Combustion	Oxyfuel
Water	X	X	X
SO <sub>2</sub>			X
H <sub>2</sub> S	X		
NO			X
CO	X		
Ar			X
O <sub>2</sub>			X
H <sub>2</sub>	X		



### 3.3 Existing CO<sub>2</sub> Specifications

Although certain aspects involved in CCS, such as the capture techniques described in Section 3.2, are still in the early phases of development, there is considerable experience available in terms of CO<sub>2</sub> pipeline operations from the EOR industries. It is estimated that there are over 3,100 km of CO<sub>2</sub> transporting pipelines of varying diameters worldwide with a capacity of approximately 44 Mt per year of CO<sub>2</sub> [2]. As such, valuable information with respect to CO<sub>2</sub> quality and specifications are available from EOR projects, which presently constitutes as best practice since there are no widely accepted standards for the quality of CO<sub>2</sub> for the purpose of CCS [10].

There are no regulations or legislation concerning the quality of CO<sub>2</sub> for pipeline transportation and storage so pipeline operators transporting CO<sub>2</sub> for EOR contractually require facility operators to provide a CO<sub>2</sub> stream of a certain composition [1]. This is done for a variety of reasons, including health and safety, corrosion prevention, and EOR operator requirements [1]. As such, the CO<sub>2</sub> specifications set for existing pipelines are case specific and depend on the trade agreement (contract) between the producer of CO<sub>2</sub> and the client [10].

Various regulatory organisations have begun to define CO<sub>2</sub> quality terms and conditions for CO<sub>2</sub> transport and storage. The U.S. Department of Transportation (DOT) defines pipeline CO<sub>2</sub> as a fluid consisting of more than 90 percent CO<sub>2</sub> molecules compressed to a supercritical state [1] & [3]. While there is no established standard for permitted levels of impurities in CO<sub>2</sub> (including moisture content) for CCS, the pipeline-quality CO<sub>2</sub> compositions adhered to by the major EOR pipeline operators are a reference for determining compositions suitable for CCS [1].

For EOR, the CO<sub>2</sub> concentration typically ranges from 95 to 99 percent so as to enhance miscibility within the oil [1]. Other constituents are also important factors to consider, for example, non-condensable gases such as O<sub>2</sub>, N<sub>2</sub> and CH<sub>4</sub> can raise the pressure at which the supercritical (dense) phase is reached [1]. More detailed discussions on the effect of each type of impurity are given in Section 4.3.

The following table (Table 2) provides a detailed overview of the CO<sub>2</sub> specifications in place from various existing CO<sub>2</sub> pipelines.



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**Table 2 – CO<sub>2</sub> Compositions from Existing CO<sub>2</sub> Pipelines and Research**

Comp.	WRI <sup>[1]</sup>	Canyon Reef Carriers <sup>[2] [14]</sup>	Weyburn <sup>[2] [10]</sup>	Dakota Gasification <sup>[15]</sup>	Cortez <sup>[2] [14]</sup>	Central Basin <sup>[2] [14]</sup>
Source	-	Anthropogenic	Anthropogenic	Anthropogenic	EOR	EOR
CO <sub>2</sub>	> 95 vol%	95 vol%	96 vol%	96.8 vol%	95 vol%	98.5 vol%
CH <sub>4</sub>	N/A	5 vol%	0.7 vol%	0.3 vol%	1-5 vol%	0.2 vol%
N <sub>2</sub>	< 4 vol%	< 0.5 vol%	< 300 ppm (wt)	-	4 vol%	1.3 vol%
H <sub>2</sub> S	< 20 ppm (wt)	100 ppm (wt)	0.9 vol%	1.1 vol%	0.002 vol%	< 20 ppm (wt)
C2+	N/A	-	2.3 vol%	1.0 vol%	Trace	-
CO	-	-	0.1 vol%	-	-	-
O <sub>2</sub>	< 10 ppm (wt)	-	< 50 ppm (wt)	-	-	< 10 ppm (wt)
S	< 30 ppm (wt)	-	-	-	-	-
H <sub>2</sub> O	< 30 lbs/MMcf	50 ppm (wt)	< 20 ppm (vol)	Bone Dry	240 ppm (wt)	240 ppm (wt)
HC	< 5 vol%	N/A	N/A	N/A	N/A	N/A

[Table 2 continues next page]

Comp.	Permian Basin <sup>[3]</sup>	Kinder Morgan <sup>[10] [15]</sup>	Bravo Dome <sup>[14]</sup>	Jackson <sup>[14]</sup>	Sheep Mountain <sup>[2] [14]</sup>
Source	EOR	EOR	EOR	EOR	EOR
CO <sub>2</sub>	> 95 mol%	95 vol%	99.7 vol%	98.7-99.4 vol%	96.8-97.4 vol%
CH <sub>4</sub>	N/A	N/A	-	Trace	1.7 vol%
N <sub>2</sub>	< 4 mol%	< 4 vol%	0.3 vol%	Trace	0.6-0.9 vol%
H <sub>2</sub> S	< 1500 ppm (wt)	10-200 ppm (wt)	-	Trace	-
C2+	N/A	N/A	-	-	0.3-0.6 vol%
CO	-	-	-	-	-
O <sub>2</sub>	< 10 ppm (wt)	< 10 ppm (wt)	-	-	-
S	< 1450 ppm (wt)	-	-	-	-
H <sub>2</sub> O	< 0.48 g/m <sup>3</sup>	< 30 lbs/MMcf	-	-	120 ppm (wt)
HC	< 5 mol%	< 5 vol%	N/A	N/A	N/A



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Notes:

1. The specifications sourced from [1] (World Resource Institute) are not that of an existing pipeline but rather a guideline.
2. The specifications sourced from [3] apply to all pipelines injecting CO<sub>2</sub> into the Permian Basin. The hydrocarbon dewpoint shall not exceed -28.9°C for all pipelines connected to the Permian Basin. Glycol cannot exist as a liquid state at pipeline conditions and contain no more than  $4 \times 10^{-5}$  L/m<sup>3</sup>.
3. Glycol shall not exceed 0.3 gal/MMscf for Kinder Morgan [10].
4. The water content limit for the Weyburn pipeline is not a specification but occurs as a result of the low temperature Rectisol process (methanol absorption) used for CO<sub>2</sub> recovery.



## 4. CO<sub>2</sub> COMPOSITIONAL CONSIDERATIONS

### 4.1 Possible CO<sub>2</sub> Specifications

As discussed in Section 3.2, the CO<sub>2</sub> composition is influenced by the particular type of capture technique used at the emission source. The following tables (Table 3 and Table 4) have summarised typical concentrations of impurities in dried CO<sub>2</sub>, given as percentage by volume (vol %) for the three capture techniques from different literature sources.

**Table 3 – Potential Impurities from Different Capture Techniques [1], [12]**

	SO <sub>2</sub>	NO	H <sub>2</sub> S	H <sub>2</sub>	CO	CH <sub>4</sub>	N <sub>2</sub> /Ar/O <sub>2</sub>	Total
<b>Coal-Fired Power Plants</b>								
<i>Post-Combustion</i>	<0.01	<0.01	-	-	-	-	0.01	0.01
<i>Pre-Combustion</i>	-	-	0.01-0.6	0.8-2.0	0.03-0.4	0.01	0.03-0.6	2.1-2.7
<i>Oxyfuel</i>	0.5	0.01	-	-	-	-	3.7	4.2
<b>Gas-Fired Power Plants</b>								
<i>Post-Combustion</i>	<0.01	<0.01	-	-	-	-	0.01	0.01
<i>Pre-Combustion</i>	-	-	<0.01	1.0	0.04	2.0	1.3	4.4
<i>Oxyfuel</i>	<0.01	<0.01	-	-	-	-	4.1	4.1

Notes:

1. Given specifications for pre-combustion capture based on IGCC process.
2. The SO<sub>2</sub> concentration for oxyfuel and the maximum H<sub>2</sub>S concentration for pre-combustion capture are for cases where these impurities are deliberately left in the CO<sub>2</sub> to reduce the costs of capture. Given values for coal-fired plants based on coal with a sulphur content of 0.86% (which is directly proportional to the fuel sulphur content).
3. The oxyfuel case includes cryogenic purification of the CO<sub>2</sub> to separate some of the N<sub>2</sub>, Ar, O<sub>2</sub> and NO<sub>x</sub>. Removal of this unit will increase impurity concentrations but reduce costs.
4. For all techniques, the impurity concentrations given in the table can be reduced with higher capture costs.



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**Table 4 – Potential Impurity Combinations from Different Capture Techniques [2], [14]**

Comp.	Pre-Combustion (IGCC)		Post-Combustion		Oxyfuel	
CO <sub>2</sub>	> 95.6 vol%	<i>95.60</i>	> 99 vol%	<i>99.79</i>	>90 vol%	<i>90.00</i>
CH <sub>4</sub>	< 350 ppmv	<i>0.02</i>	< 100 ppmv	<i>0.01</i>	0	<i>0.00</i>
N <sub>2</sub>	< 0.6 vol%	<i>0.35</i>	< 0.17 vol%	<i>0.17</i>	<7.0 vol%	<i>3.54</i>
H <sub>2</sub> S	< 3.4 vol%	<i>1.00</i>	Trace	<i>0.00</i>	Trace	<i>0.00</i>
C2+	< 100 ppmv	<i>0.01</i>	< 100 ppmv	<i>0.01</i>	0	<i>0.00</i>
CO	< 0.4 vol%	<i>0.23</i>	< 10 ppmv	<i>0.00</i>	Trace	<i>0.00</i>
O <sub>2</sub>	Trace	<i>0.00</i>	< 100 ppmv	<i>0.01</i>	<3.0 vol%	<i>1.80</i>
NO <sub>x</sub>	0	<i>0.00</i>	< 50 ppmv	<i>0.01</i>	<0.25 vol%	<i>0.15</i>
SO <sub>x</sub>	0	<i>0.00</i>	< 10 ppmv	<i>0.00</i>	<2.5 vol%	<i>1.50</i>
H <sub>2</sub>	< 3.0 vol%	<i>2.76</i>	Trace	<i>0.0</i>	Trace	<i>0.00</i>
Ar	< 500 ppmv	<i>0.03</i>	Trace	<i>0.0</i>	<5.0 vol%	<i>3.01</i>

Notes:

1. Italic values are normalised figures based on its relative volume percentage in the CO<sub>2</sub> stream.
2. H<sub>2</sub>S in the pre-combustion case assumes no separation processes used. Reductions to 10 ppm or less are achievable by current technologies.

The above tables show the potential impurity ranges from different capture techniques that can be present in the CO<sub>2</sub> stream. In comparison to Table 2 in Section 3.3, CO<sub>2</sub> with impurities such as SO<sub>x</sub>, NO<sub>x</sub> and argon have not been transported before by pipeline, and therefore, their effects on pipeline design parameters are not fully understood [2]. It is also highlighted that water is not considered in the specifications as it is assumed the CO<sub>2</sub> will be adequately dehydrated due to stringent limitations to avoid pipeline corrosion and only trace amounts will be present (refer to Section 4.3.1 for further details on water specifications).

It has been identified from various literature sources that the effect of impurities on the transportation of CO<sub>2</sub> using pipelines is of great significance, with the CO<sub>2</sub> quality directly influenced by the type of capture technique used at the emission source. The following graphs illustrate the effect of impurities on the pressure (Figure 7) and temperature (Figure 8) profiles of an arbitrary 500 km pipeline. The figures present pure CO<sub>2</sub>, binary combinations of CO<sub>2</sub> with 5% of selected impurities, and the combination of all impurities that make up the potential CO<sub>2</sub> stream from the three capture techniques (based on Table 4) [2]. Section 4.2 will further describe the effects of impurities in more detail.





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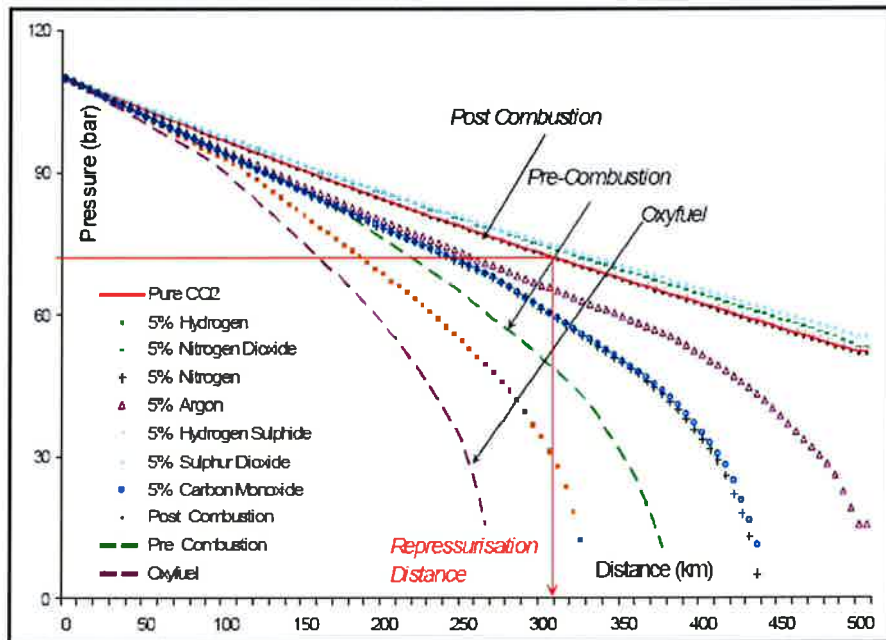


Figure 7 – Pressure Profile for Various CO<sub>2</sub> Quality Specifications [2]

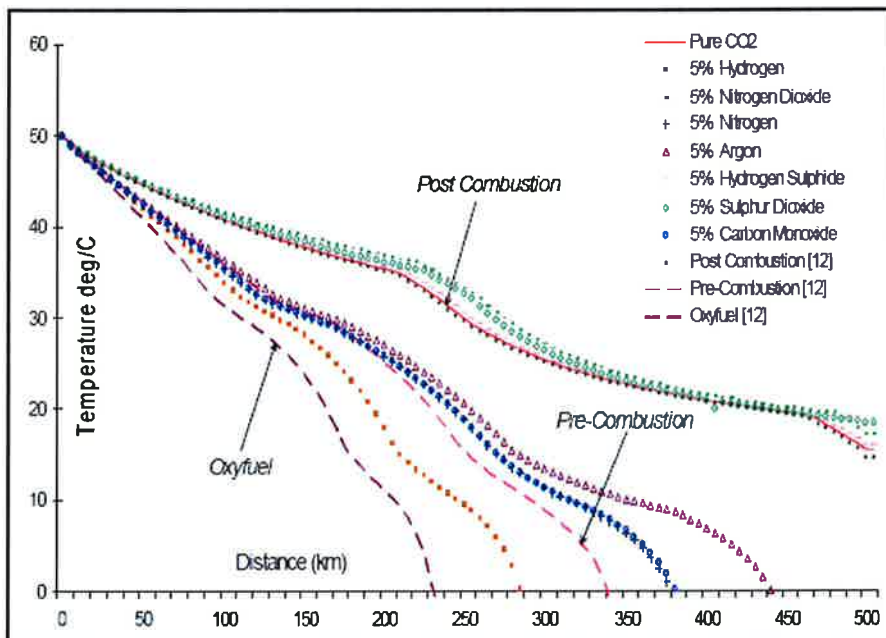


Figure 8 – Temperature Profile for Various CO<sub>2</sub> Quality Specifications [2]



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The binary combination of CO<sub>2</sub> with 5% N<sub>2</sub>, H<sub>2</sub> and CO respectively shows the largest pressure and temperature drops along the pipeline [2]. In terms of temperature, there seems to be a significant decrease in temperatures below 5°C, which is a major concern in the event of a leak or pipeline rupture where the sudden expansion causes a large temperature drop that may cause initiation of brittle fracture.

Furthermore, the binary combination of CO<sub>2</sub> with 5% SO<sub>2</sub>, NO<sub>2</sub> and H<sub>2</sub>S respectively have a less significant pressure and temperature drop relative to pure CO<sub>2</sub> [2]. The pressure profile for these binary impurity combinations is actually raised above that of pure CO<sub>2</sub> and can be considered as a positive effect in terms pipeline hydraulics [2]. In addition, restrictions on SO<sub>x</sub> and NO<sub>x</sub> emissions will have an effect on the quantity of these impurities in the capture stream [2].

The following conclusions can be drawn in terms of CO<sub>2</sub> transport from different capture techniques and their corresponding impurities in CO<sub>2</sub> [2]:

1. Post-combustion: The most pure CO<sub>2</sub> stream (99.9%) from the post-combustion capture method shows a similar temperature and pressure profile to that of pure CO<sub>2</sub>.
2. Pre-combustion: The pre-combustion capture method results in a pressure and temperature profile close to the CO<sub>2</sub> - 5% H<sub>2</sub> combination, which is expected as the pre-combustion capture stream consists of approximately 3% H<sub>2</sub> (believed to dominate the phase properties). However, as previously notes, this assumes no separation processes used after CO<sub>2</sub> capture and lower concentrations are achievable by current technologies.
3. Oxyfuel: The oxyfuel capture method has the least pure stream of CO<sub>2</sub> (90%), which results in the largest drop in pressure and temperature profile. The presence of N<sub>2</sub>, O<sub>2</sub> and Ar, all of which have a high pressure drop profile when compared to pure CO<sub>2</sub>, has also contributed to this large drop in pressure and temperature along the pipeline. Cleaning technologies such as cryogenic purification are available to reduce the impurity levels and increase the CO<sub>2</sub> content, although this will significantly increase the CAPEX of this capture technique.

The increasing interest in CCS as a method of reducing CO<sub>2</sub> emissions has stimulated the growth in research and development of CO<sub>2</sub> properties, its interactions with possible impurities, and the effects of these impurities on pipeline and storage specifications and requirements.

There is currently no legislation or regulations that place restrictions on the quality and specification of CO<sub>2</sub> for transport and storage. Legislation is not recommended for CO<sub>2</sub> composition because each CCS network will have different restraints. Each network can develop contractual specifications for CO<sub>2</sub> composition to address these particular constraints. Experiences from EOR operations as well as health, safety and environmental (HSE) (Section 5) considerations provide guidance for CCS CO<sub>2</sub> specifications. Current developments are largely based around these aspects, for example, the Dynamis CO<sub>2</sub> quality specification based on the pre-combustion capture technique (Table 5) illustrates this point.



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Table 5 – Dynamis CO<sub>2</sub> Quality Specification [10]

Component	Concentration	Limitation
Water	500 ppm	Design and operational considerations
H <sub>2</sub> S	200 ppm	Health and safety considerations
CO	2000 ppm	Health and safety considerations
CH <sub>4</sub>	Aquifer: < 4 vol% EOR: < 2 vol%	Past experiences
N <sub>2</sub>	< 4 vol%	Past experiences
Ar	< 4 vol%	Past experiences
H <sub>2</sub>	< 4 vol%	Past experiences, although further reduction is recommended
CO <sub>2</sub>	> 95.5%	Balanced with other compounds in CO <sub>2</sub>

Captured CO<sub>2</sub> contains impurities that may require specific handling or treatment. However, it is difficult to determine the exact levels of impurities that may be present in the captured CO<sub>2</sub> as this will be affected not only by the capture technique (as discussed in Section 3.2), but also by economics (i.e. increased capture cost associated with the removal of impurities to lower levels), and safety considerations [2].

While not strictly a transport issue, the impact of CO<sub>2</sub> injection with impurities is also unknown on a large scale and will most likely affect the requirements for CO<sub>2</sub> purity [1]. For the sole purpose of storage, the threshold for impurities can be different from those specified in EOR operations.

However, there are potential financial advantages to leaving some impurities in the CO<sub>2</sub> stream [7]. CO<sub>2</sub> quality can be seen as an opportunity to co-capture other main pollutants from power plant operations (such as SO<sub>x</sub>) and store them together with the CO<sub>2</sub>, which can create a concept of near-zero emissions and also avoid costly and energy-demanding flue gas cleaning equipment [7]. However, the risks associated with transporting impurities must be weighed against any negative technical and/or HSE effects.



## 4.2 Physical Properties of CO<sub>2</sub>

Understanding the physical properties of CO<sub>2</sub> is vital for all processes involved in the CCS scheme, especially for pipeline transportation. This section will outline the key issues and considerations involved with CO<sub>2</sub> transport.

### 4.2.1 Phase Behaviour of Pure CO<sub>2</sub>

It is imperative that the CO<sub>2</sub> pipeline be maintained as a single-phase flow by avoiding abrupt pressure drops as it creates problems for compressors and other pipeline operations. Research into existing CO<sub>2</sub> pipelines as well as available literature has identified the requirement for the CO<sub>2</sub> fluid to exist in the supercritical or dense phase region for efficient transport in pipelines. The phase diagram for pure CO<sub>2</sub> is given in Figure 9.

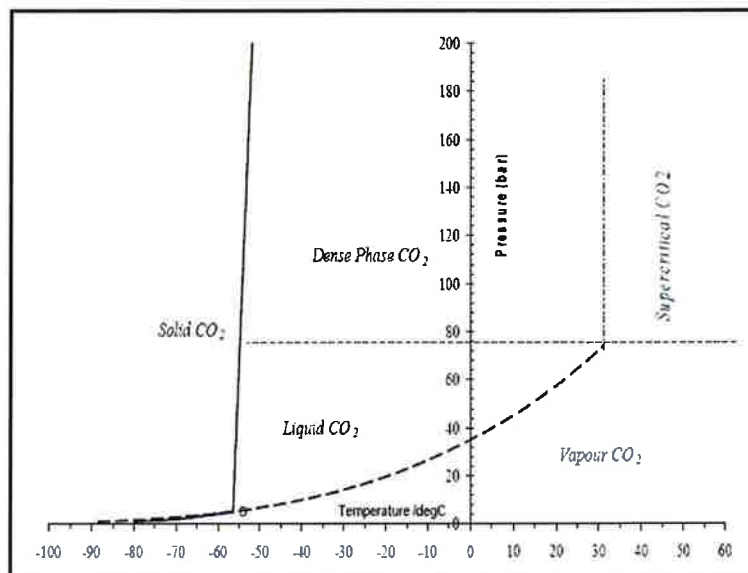


Figure 9 – Phase Diagram for Pure CO<sub>2</sub> [2]

At pressures and temperatures above the critical point (at 74 bar and 31°C), CO<sub>2</sub> no longer exists in distinct gaseous and liquid phases but as a supercritical phase with a density of a liquid but the viscosity of a gas [2]. At pressures above, but temperatures below critical, the CO<sub>2</sub> exists as a (dense) liquid whose density increases with decreasing temperature [2].

Current operating practice for CO<sub>2</sub> pipelines is to maintain the pressure well above the critical pressure to avoid any possibility of a phase change to occur. However, the presence of impurities in anthropogenic CO<sub>2</sub> alters the physical and transport properties of CO<sub>2</sub> due to the changes in the phase behaviour, critical temperature and critical pressure [2].



## 4.2.2 Effect of Impurities on CO<sub>2</sub> Phase Behaviour

Currently, extensive research is being carried out on the effects of impurities on the physical and transport properties of CO<sub>2</sub>. Section 4.1 had demonstrated the significant effects of impurities on the pressure and temperature profile of an arbitrary pipeline. This section will primarily focus on the phase behaviour of CO<sub>2</sub> with various impurities.

The following plots illustrate the effect of impurities on the phase behaviour of the CO<sub>2</sub> stream. Figure 10 illustrates binary combinations with CO<sub>2</sub>, Figure 11 for ternary combinations with CO<sub>2</sub>, and Figure 12 for the different capture techniques described in Section 3.2. Note that Figure 12 is based on the specifications detailed in Table 4.

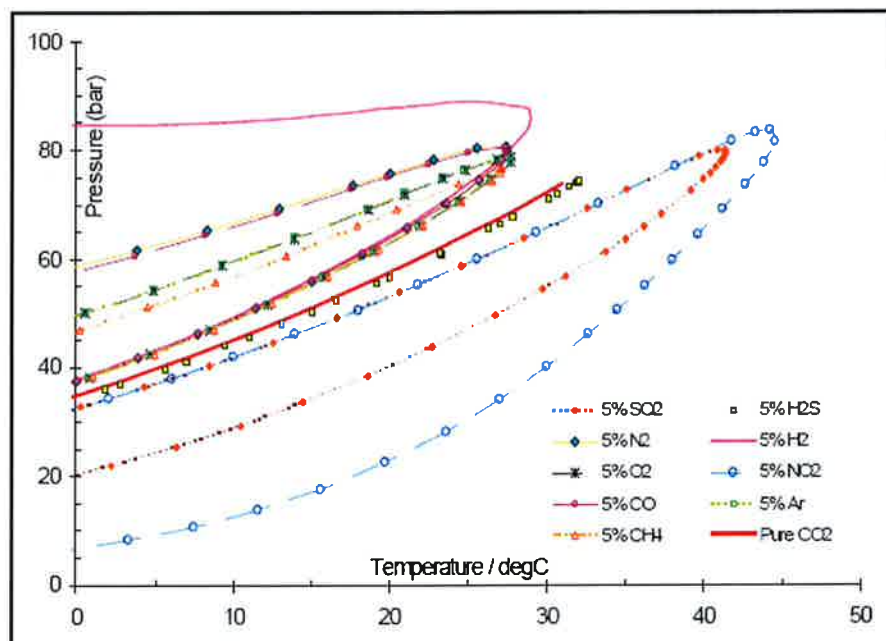


Figure 10 – Phase Diagram for Various Binary CO<sub>2</sub> Specifications [2]



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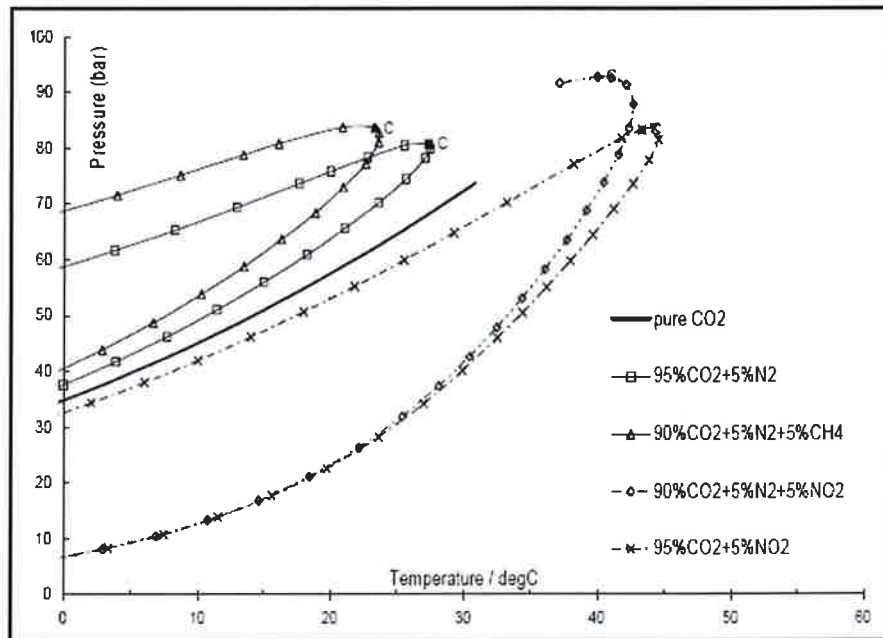


Figure 11 – Phase Diagram for Various Ternary CO<sub>2</sub> Specifications [2]

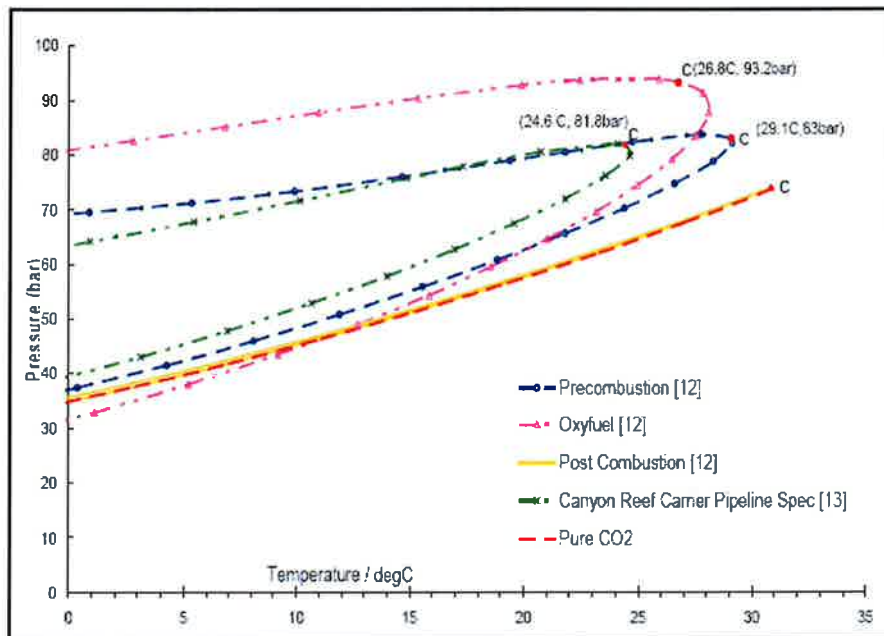


Figure 12 – Phase Diagram for Different Capture Techniques [2]



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As shown in all three diagrams, the phase behaviour governing the physical properties of CO<sub>2</sub> changes significantly when impurities are introduced into the system, which is dictated by the type, amount and combination of impurities present, as the impurities interact with the CO<sub>2</sub> and each other [2]. The effect of impurities is generally to increase the width of the phase envelope, which results in the formation of a two phase gas-liquid region [2]. Some impurity combinations tend to cause a large increase on the envelope (e.g. H<sub>2</sub> and NO<sub>2</sub>) whilst others show much smaller increase (e.g. N<sub>2</sub> and H<sub>2</sub>S), though generally, the critical pressure increases but the critical temperature decreases when compared to pure CO<sub>2</sub> [2]. However, the increase in critical pressure decreases the supercritical area, thus reducing the optimum pipeline operating region [2]. In addition, the determination of the correct inlet pressure is critically dependent on the impurities present, which generally reduce pipeline capacity and may become an issue in a pipeline network with multiple sources of CO<sub>2</sub> [2].

Furthermore, the post-combustion method shows the least change in the critical temperature and pressure due to the high CO<sub>2</sub> purity achievable from this method. The oxyfuel impurity combination had the greatest effect on the area of the two-phase region, and the highest decrease in critical temperature with the maximum increase in critical pressure when compared to pure CO<sub>2</sub> [2].

### 4.2.3 Effect of Impurities on CO<sub>2</sub> Density

Following on from Section 4.2.2, this section will primarily focus on the changes in CO<sub>2</sub> density with various impurities. Density is an important physical property in terms of pipeline transportation as this parameter dictates the pressure drop through the pipeline system as well as the pipeline size and throughput.

Figure 13 shows the change in density of pure CO<sub>2</sub> as a function of pressure and temperature. As evident, at pressures close to the critical point, a small change in temperature or pressure yields a very large change in the density of CO<sub>2</sub> (steep non-linearity in the density), which can result in a change of phase and fluid velocity within the pipeline, producing unwanted slug flow in the system [1]. A slug flow occurs when high density liquid and low density gas co-exists in the pipeline, and this becomes a source of potential damage to compressors [2].



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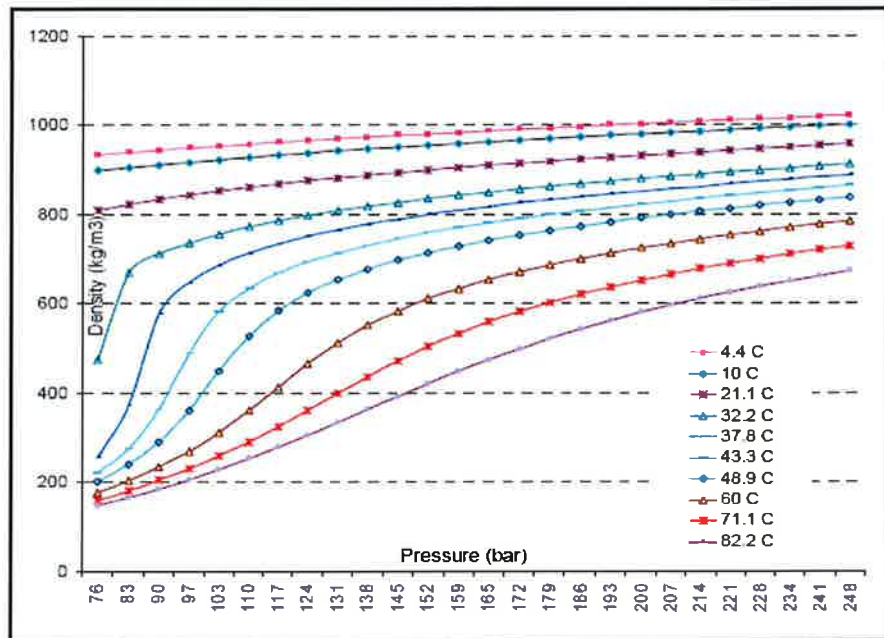


Figure 13 – Densities for Pure CO<sub>2</sub> [2]

In addition to the fact that both temperature and pressure significantly alter the density of CO<sub>2</sub>, the incorporation of impurities also have a similar effect, with the following diagrams showing the effects of various impurities on CO<sub>2</sub> as a function of pressure (Figure 14) and temperature (Figure 15).





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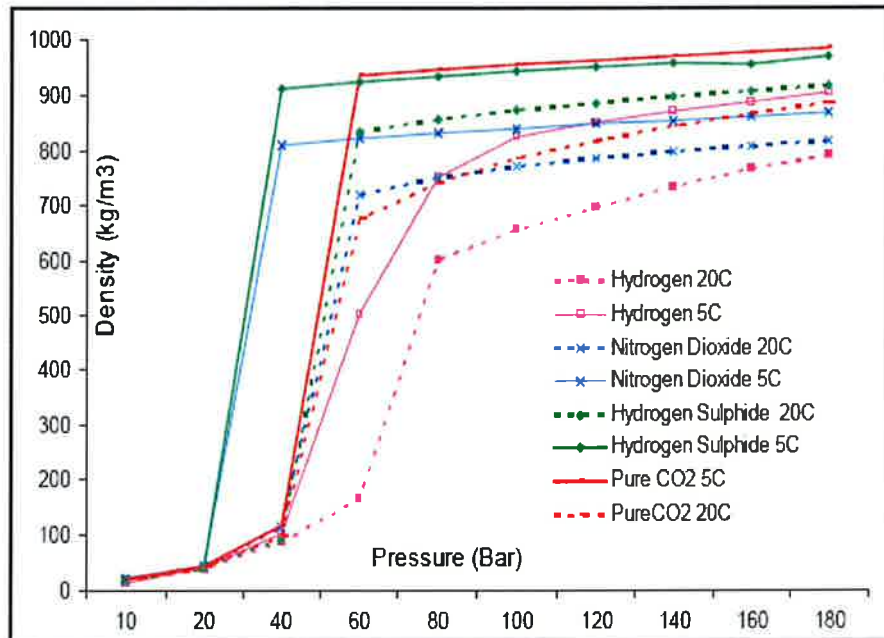


Figure 14 – Densities for Various CO<sub>2</sub> Specifications as Function of Pressure [2]

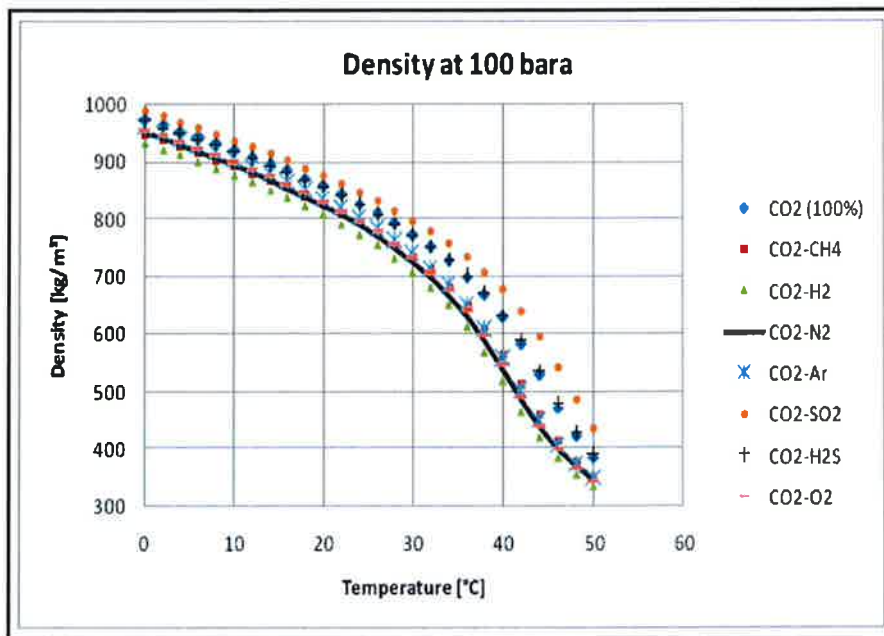


Figure 15 – Densities for Various CO<sub>2</sub> Specification as Function of Temperature [14]



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Based on Figure 13, Figure 14 and Figure 15, temperature, pressure and the input of impurities have a profound effect on the resulting CO<sub>2</sub> density. However, temperature has a more significant effect on density than pressure for both pure CO<sub>2</sub> and CO<sub>2</sub> containing impurities [2]. Increasing the temperature of the fluid decreases the density and this will have a significant effect on pipeline operation [2]. In terms of impurities, N<sub>2</sub>, O<sub>2</sub>, H<sub>2</sub>, Ar and CH<sub>4</sub> all reduce density while SO<sub>2</sub> and H<sub>2</sub>S increase the density.

#### 4.2.4 Other Impurity Effects – Compressibility and Vapour Pressure

Two more important changes to the physical properties of CO<sub>2</sub> from impurities are compressibility and vapour pressure.

Figure 16 shows that the compressibility of CO<sub>2</sub> is non-linear in the range of pressures common for pipeline transport and is highly sensitive to impurities such as H<sub>2</sub>S and CH<sub>4</sub> [5].

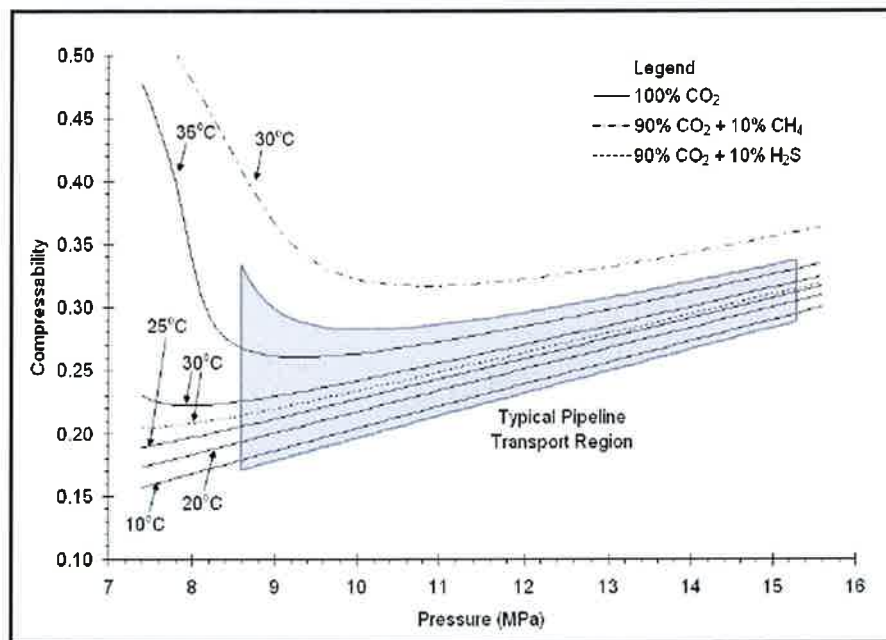


Figure 16 – Compressibility of CO<sub>2</sub> [5]

Also, impurities in the CO<sub>2</sub> stream have a marked effect upon vapour pressure. By raising the vapour pressure of the stream, a higher minimum entrance pressure or shorter recompression / booster station intervals are needed to keep the fluid in the dense phase [14].



## 4.3 Impact of Impurities

### 4.3.1 Water (H<sub>2</sub>O) Content Guidelines

Perhaps the most important impurity to consider in the CO<sub>2</sub> specification is the allowable water content due to its detrimental corrosion and hydrate formation effects on the pipeline infrastructure. CO<sub>2</sub> reacts with free water to form carbonic acid (sweet corrosion), which is highly corrosive, so the CO<sub>2</sub> must be dehydrated sufficiently low to avoid water condensation, under any circumstances, before transport [1], [3]. Accordingly, existing CO<sub>2</sub> pipeline quality specifications generally prohibit the inclusion of free water and sharply limit the presence of water vapour in CO<sub>2</sub> tendered for transport, even though the injection of water into a deep saline storage formation might itself not pose any problems [3].

The current water specification used for existing CO<sub>2</sub> pipelines differ from one to another. The following water content limitations have been stated in literature:

- CO<sub>2</sub> dehydration to levels below 50 ppm of water (near complete dehydration) [1], [10].
- CO<sub>2</sub> dehydration to levels between 7 and 30 lbs/MMscf [19].
- A concentration limit of water to no more than 60% of the solubility limit between CO<sub>2</sub> and water at worst conditions [10].
- A maximum allowable water content of typically  $0.4 \times 10^{-3} \text{ kg/m}^3$  (400 ppm) [18].

Note however that the risk of H<sub>2</sub>S hydrate formation in the presence of dissolved water has not been considered as a criterion for the definition of the water concentration limit [10].

It is also recognised that the solubility of water in CO<sub>2</sub> is dependant on the operating pressure, temperature and composition of the fluid, and therefore, it is necessary to determine the solubility limits of water in anthropogenic CO<sub>2</sub> as it influences corrosion and hydrate formation [2]. Note that if the CO<sub>2</sub> is in the dense liquid or supercritical phase, the amount of water that can be contained in CO<sub>2</sub> as a function of pressure is equal to the solubility limit; in the vapour phase, it is the water dewpoint [6]. Figure 17 and Figure 18 show the amount of water that CO<sub>2</sub> can contain as a function of temperature and pressure in pure CO<sub>2</sub> based on two different literature findings.



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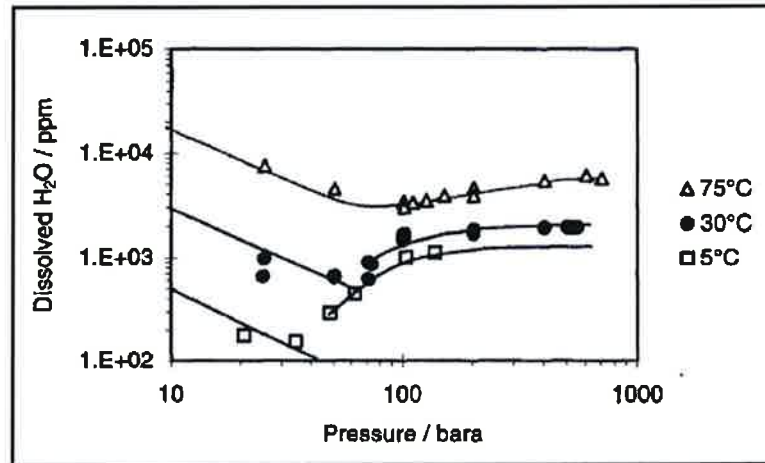


Figure 17 – Solubility of Water in CO<sub>2</sub> [6]

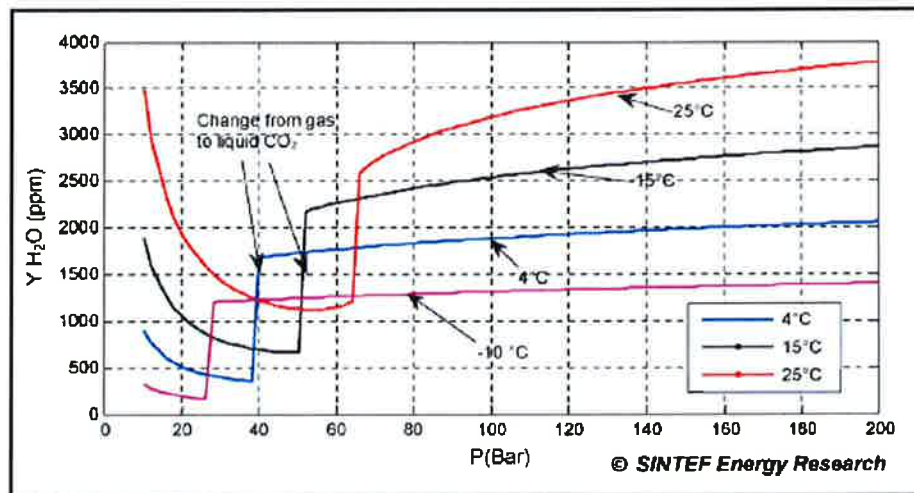


Figure 18 – Solubility of Water in CO<sub>2</sub> [10]

Based on Figure 17, the solubility at high pressure and temperature is several thousands ppm, though it drops to a few hundred ppm at the supercritical pressure at low temperature. Figure 18 shows that the water solubility limit is significantly lower when CO<sub>2</sub> is in the gaseous phase rather than in liquid phase. Furthermore, the diagram illustrates how water solubility decreases with temperature [10].

In addition, the solubility is further affected by the presence of other components that are likely to be present in the CO<sub>2</sub> stream. For example, CH<sub>4</sub> lowers (downward shift) the water solubility in CO<sub>2</sub> at high pressures in comparison to pure CO<sub>2</sub> by approximately 30%, while adding H<sub>2</sub>S increases the solubility of water [10], [16]. However, at H<sub>2</sub>S concentrations of 200 ppm, the effect on the water solubility is negligible [10].



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The presence of free water enhances the occurrence of corrosion and hydrates formation and therefore has to be avoided. Essentially, the water concentration limit should prevent free water formation over the total pressure and temperature range of CO<sub>2</sub> that is transported by pipeline [10]. Also, a decrease in solubility of the CO<sub>2</sub> in water results in the slowing down effect of the corrosion reaction rate [20].

### 4.3.2 Hydrogen Sulphide (H<sub>2</sub>S) Content Guidelines

Hydrogen sulphide (H<sub>2</sub>S) is another impurity (produced during the gasification of coal) that must be considered during CCS operations, mainly due to health and safety factors. H<sub>2</sub>S is toxic, and exposure to low concentrations of H<sub>2</sub>S (<50 ppm) can cause eye, nose or throat irritation [1]. At levels above 500 ppm, H<sub>2</sub>S can lead to a loss of consciousness or even death [1]. Therefore, the current concentration limit of H<sub>2</sub>S in CO<sub>2</sub> is based on health and safety considerations because of the high toxicity of H<sub>2</sub>S. The concentration of H<sub>2</sub>S in the CCS stream is limited to 200 ppm [10]. This limit of 200 ppm is supportable in terms of safety and gives a reasonable safety margin [10]. Lowering the H<sub>2</sub>S concentration limit to 100 ppm will require substantial additional investment upstream at the capture stage, and existing scoping works indicate that the 200 ppm H<sub>2</sub>S level is achievable without adversely affecting the design of the removal system [10]. However, some existing pipelines have specified a H<sub>2</sub>S concentration limited to less than 100 ppm in the CO<sub>2</sub> flow [18].

On another note, including the H<sub>2</sub>S with CO<sub>2</sub> leaving the facility can result in cost savings because the operator will not need to install a sulphur recovery unit/equipment (e.g. Claus plant) or find an alternative method for disposing of sulphur-based compounds [1]. As an example, facilities in Canada have been disposing of H<sub>2</sub>S through injection in geologic formations since 1989 [1]. However, in this scenario, the costs for pipeline monitoring will increase because of the presence of H<sub>2</sub>S in the pipeline [1].

Another important factor to consider when handling H<sub>2</sub>S is dehydration of the gas because H<sub>2</sub>S reacts with water to form sulphuric acid (with the presence of SO<sub>2</sub> or SO<sub>3</sub>), which is highly corrosive and may also result in pipeline cracking (sulphide stress cracking) , increasing the potential for leaks [1], [14]. Furthermore, H<sub>2</sub>S when present reacts with carbon steel to form a thin film of iron sulphide on the surface of the steel, which may be dislodged at times and cause fouling problems downstream [22], although this is not limited to CO<sub>2</sub> pipelines only. H<sub>2</sub>S in wells may also give rise to other sulphur containing components, such as mercaptans, and also elemental sulphur, in which the latter may cause precipitation problems.

In terms of operational issues, the maximum amount of hydrates formed through CO<sub>2</sub>, CH<sub>4</sub> and/or H<sub>2</sub>S due to the presence of dissolved water in the CCS stream will be too small to cause operational problems [10]. Hence, there are no strong arguments to propose a stricter limit for H<sub>2</sub>S than required by health and safety considerations [10].



### 4.3.3 Hydrocarbon (HC) Content Guidelines

The main hydrocarbon that may be present in the CO<sub>2</sub> stream is methane (CH<sub>4</sub>), although trace amounts of ethane are also possible. In general, hydrocarbons reduce the density and increase the pressure required to inject the CO<sub>2</sub> in the supercritical phase due to the increase in critical pressure. This has negative effects towards equipment (i.e. compression power) and operational costs. Methane is also significantly more volatile than the CO<sub>2</sub> component, which results in the broadening of the phase envelope [17]. Furthermore, the decreasing effect of CH<sub>4</sub> on the solubility of water in CO<sub>2</sub> is significant, but no direct consequences for pipeline transportation of CO<sub>2</sub> at concentrations of CH<sub>4</sub> below 5% and a maximum water level of 500 ppm [10].

In addition, the light hydrocarbon components have a tendency to separate from any produced water, particularly in stagnant areas, such that a thin layer of water can form under the condensate adjacent to the pipeline surface [21]. This will have consequences in terms of pipeline corrosion.

### 4.3.4 Non-condensable Gas Content Guidelines

Non-condensable gases refer to gases that typically condense at lower temperatures and/or higher pressures compared to CO<sub>2</sub>. The main non-condensable gases likely to be present in the CO<sub>2</sub> stream are nitrogen, oxygen, hydrogen and argon. Although these gases do not pose health and safety issues, their concentrations should be limited from a design and operational point of view.

Firstly, the presence of non-condensable gases result in the loss of CO<sub>2</sub> transport and storage capacity as well as the increase in pressure requirements and compression work [10]. Also, significant N<sub>2</sub> and O<sub>2</sub> components in CO<sub>2</sub> will shift the boundary of the two-phase region towards higher pressures, and will require a higher operating pressure to avoid two-phase flow [12].

Currently, a limit for non-condensable gases is set at 4 vol% [10]. Of these gases, H<sub>2</sub> requires the most additional compression work [10]. However, H<sub>2</sub> in several vol% is not expected as this will represent a clear energy loss further upstream [10]. In addition, the presence of atomic hydrogen can lead to hydrogen embrittlement of the pipeline steel or hydrogen induced cracking [14].

While the N<sub>2</sub> component may not interfere with the storage of the CO<sub>2</sub> in the geologic formation, it will still take up valuable space in the storage formation that can otherwise be used for storing the CO<sub>2</sub> and will require additional energy for injection, thereby increasing costs [3]. In this case, N<sub>2</sub> specification will involve primarily economic issues.

Based on EOR applications, O<sub>2</sub> is tolerable only in minute quantities (10 ppm), in particular where organic materials are present [1]. Even in deep saline formations organics may be present, and significant quantities of O<sub>2</sub> in the stream may result in bacterial colonies forming, thus affecting injection operations [1]. Additionally, O<sub>2</sub> may also lead to overheating at the injection point due to reaction with oil that may be present in the wells [1].



### 4.3.5 Carbon Monoxide (CO) Content Guidelines

Based on past CO<sub>2</sub> pipeline experiences, the current limit for CO is set to a level of 2000 ppm, which includes a safety factor [10]. From a design and operation point of view and within the realistic range of CO concentrations in the CCS stream from a CO<sub>2</sub> capture installation, there is no need to limit the concentration of CO to a concentration level below 2000 ppm [10].

## 4.4 Operational Impact of CO<sub>2</sub> Specification

The impact of a CO<sub>2</sub> specification (i.e. inclusion and variation of impurities) on operations has been discussed throughout this study. The presence of impurities can pose both positive and negative effects on the operation of the pipeline and storage phases of the CCS scheme. This section will further focus on specific operational issues caused by the presence of certain impurities in the CO<sub>2</sub> stream, such as pipeline capacity, corrosion risks, equipment integrity, injection issues, and hydrate formation issues.

### 4.4.1 Pipeline and Storage Capacity Issues

Pipeline capacity is a major factor for the CCS scheme, as the aim is to transport the maximum amount of CO<sub>2</sub> to the selected storage sites. Hence, fluctuations in pipeline operating conditions due to the presence of impurities will cause variations in pipeline capacity and present both control and operational difficulties.

The presence of impurities in the CO<sub>2</sub> stream shifts the boundary of the two-phase region towards higher pressures (refer to Section 4.2.2), so that higher operating pressures are required to keep CO<sub>2</sub> in the dense/supercritical phase [10]. This, in effect, increases the compression required, which depends linearly on the concentration of the gaseous impurities, with the effect of H<sub>2</sub> the greatest [10]. In order to maintain the CO<sub>2</sub> in the dense or supercritical phase throughout the entire pipeline, it is necessary to either maintain the inlet pressure to the pipeline at a high enough pressure to overcome all the losses while still above the critical pressure, increase the pipeline diameter, or install booster stations at appropriate intervals to account for the pressure losses [22]. Hence, the minimum pressure of the CO<sub>2</sub> pipeline should be set to avoid two-phase flow, which depends on the type, combination and quantity of impurities present [2].

For a given pressure drop, the presence of impurities reduces the pipeline capacity, which is more significant at larger diameters [2], [14]. Since the CO<sub>2</sub> density is sensitive to pressure and temperature changes, the pressure drop along the pipeline will reduce the CO<sub>2</sub> density and increase the velocity, which will in turn increase the pressure drop. Transport at lower densities (i.e. gas phase) is inefficient because the low density of the CO<sub>2</sub> results in greater pressure drop per unit length [5].

Temperature is another important operating variable as it markedly affects the transport properties of the CO<sub>2</sub> in terms of density, compressibility and static head losses (i.e. increasing discharge temperature lowers the static head loss). These properties and parameters change with the presence of impurities [2].



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For a given pipeline diameter, CO<sub>2</sub> binary combinations with 5% impurities other than H<sub>2</sub> and CO do not show much deviation in capacity from pure CO<sub>2</sub> [2]. For the three different capture techniques discussed in Section 3.2, oxyfuel shows the highest reduction in capacity followed by pre-combustion. The post-combustion method does not show any significant deviation [2].

Repressurisation along a pipeline is necessary to ensure CO<sub>2</sub> remains in the dense or supercritical phase [2]. The effect of impurities on the pressure and temperature profile of the CO<sub>2</sub> stream then translates into the location of repressurisation stations [2]. H<sub>2</sub> has the biggest effect on repressurisation distance, while H<sub>2</sub>S has the least effect [2]. The repressurisation distance for the oxyfuel method resulted in the shortest distance, hence the requirement for additional pumps [2].

A similar line of thought applies to storage capacity in that a decrease in density caused by impurities in the CO<sub>2</sub> stream can reduce the storage capacity at the injection sites in the range of yearly injection volumes [7]. This results in additional storage costs and/or the maximum storage capacity is reached faster than it would be by pure CO<sub>2</sub> injection [7].

#### 4.4.2 Corrosion Issues

The issue of pipeline corrosion has been reviewed in Section 4.3.1 to some detail, though corrosion can also affect other facilities in the CCS scheme, particularly the injection wells. The main factor that dictates corrosion is the presence of free water in the CO<sub>2</sub> stream, either carried over from the upstream process facilities or formulated within the pipeline due to pressure drop. The corrosion rate of carbon steel in dry supercritical CO<sub>2</sub> is low and field experience indicates very few problems with transportation of high-pressure dry CO<sub>2</sub> in carbon steel pipelines [6]. In addition, another source indicates that dry CO<sub>2</sub> does not corrode carbon steel pipelines as long as the relative humidity is less than 60% (applicable in the presence of N<sub>2</sub>, NO<sub>x</sub> and SO<sub>x</sub> contaminants) [12].

For CO<sub>2</sub>, the mass proportion of dissolved water increases with pressure and decreases with temperature [23]. In particular, there is a shift towards higher solubility of water in CO<sub>2</sub> when the pressure passes the transformation from the gas phase into the dense liquid phase [23]. Consequently, drying CO<sub>2</sub> at a higher pressure and lower temperature than the operating envelope retains a large amount of dissolved water which will drop-out as free water during operation [23]. Hence, the maximum corrosion rate is proportional to the CO<sub>2</sub> partial pressure [21].

The corrosion rate also decreases with increasing CO<sub>2</sub> pressure or decreasing temperature [24]. An increase in pH level has generally led to a reduction of the corrosion rate in CO<sub>2</sub> systems. For very high pH values a very protective carbonate film is formed on the surface that reduces the corrosion rate significantly [24]. Also, if the CO<sub>2</sub> stream contains H<sub>2</sub>S, then iron sulphide is formed as by-product from H<sub>2</sub>S corrosion, though this has a positive effect as it forms a protective thin film on the inside surface of the pipeline [10].





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Corrosion rates can be in the order of mm/year when free water is present and in the order of  $\mu\text{m}/\text{year}$  when dry  $\text{CO}_2$  is transported [10]. In addition, corrosion effects can also come from  $\text{H}_2\text{S}$ , which forms a weak acid when dissolved in water, and the combination of  $\text{CO}_2$  and  $\text{H}_2\text{S}$  is more corrosive than  $\text{H}_2\text{S}$  alone with  $\text{H}_2\text{S}$  corrosive at concentrations below 1 ppm under the right conditions [10].

It is presumed that  $\text{CO}_2$  corrosion will not take place unless there is presence of free water. Consequently, drying of  $\text{CO}_2$  to water concentrations below the dewpoint for operating conditions is thus regarded as effective corrosion prevention [23]. If free water is permitted, then it would be necessary to either increase the wall thickness of the pipeline allowing for predicted corrosion rates or utilising corrosion resistant materials where in contact with the  $\text{CO}_2$  stream. This is not considered a cost effective solution for pipeline systems of significant length.

#### 4.4.3 Equipment / Material Integrity Issues

The presence of impurities will also have a significant impact on the equipment type, operability and integrity. As has been stated previously, certain impurities necessitate higher pipeline operating pressures to avoid two-phase flow from occurring, and this has subsequent consequences on the pipeline facilities. Firstly, compression of the  $\text{CO}_2$  gas (after capture) will need to be designed to provide sufficiently high pressures prior to pipeline transport. This results in additional capital and operating (maintenance) costs for the upstream facilities. In addition, recompression stations will most likely be required along the pipeline to keep the  $\text{CO}_2$  fluid in the dense/supercritical phase.

Another important consideration is the materials used in the facilities. It is vital that all materials used be compatible with dense phase  $\text{CO}_2$  since dense phase  $\text{CO}_2$  behaves as a solvent to certain materials and diffuses into it (e.g. polymers) [14]. Some petroleum based and synthetic lubricants can harden and become ineffective in the presence of  $\text{CO}_2$  [22]. Seals and lubricants need to be also compatible and the effects of impurities accounted for considering: (1) explosive decompression of elastomers in seals and gaskets [15]; (2) low temperatures reached during depressurisation (as low as  $-79^\circ\text{C}$  from high pressures [19]); and (3) corrosion in the presence of free water [14].

#### 4.4.4 Injection Issues

Injection of the transported  $\text{CO}_2$  into the selected geological storage formations is another area of the CCS scheme that is affected by the presence of impurities. Briefly, the injectivity is dependent on the phase viscosity of the fluid, and research indicates that impurities lower the viscosity, thus improving the injectivity compared to pure  $\text{CO}_2$  [7]. However, the additional components in the  $\text{CO}_2$  stream generally reduce the density of the fluid, hence the delivery pressure (compression work) at the wellhead must be increased, which results in additional cost [7].

Some contaminants in the  $\text{CO}_2$  stream (e.g.  $\text{SO}_x$ ,  $\text{NO}_x$ ,  $\text{H}_2\text{S}$ ) are generally classified as hazardous, imposing different requirements for injection and disposal than if the stream were pure [12]. Impurities in the  $\text{CO}_2$  stream affect the compressibility of the injected  $\text{CO}_2$  (as shown in Figure 16), and hence the volume needed for storing a given amount. This reduces the capacity for storage in free phase because of the storage space taken by the impurities [12].



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The type of storage formation the CO<sub>2</sub> is injected into is also influenced by impurities, as described below in the various formation examples:

- In the case of CO<sub>2</sub> storage in deep saline formations, the presence of impurities affects the rate and amount of CO<sub>2</sub> storage through dissolution and precipitation [12].
- In the case of CO<sub>2</sub> storage in coal seams, impurities such as H<sub>2</sub>S and/or SO<sub>2</sub> will be preferentially adsorbed because they have a higher affinity to coal than CO<sub>2</sub>, thus reducing the storage capacity of CO<sub>2</sub> [12].
- In sandstone formations, inclusion of SO<sub>2</sub> can increase mineral dissolution, while H<sub>2</sub>S is not expected to affect porosity notably [7]. Therefore, neither SO<sub>2</sub> nor H<sub>2</sub>S should impact on the injectivity [7].
- In carbonate formations, inclusion of H<sub>2</sub>S can decrease the permeability due to precipitation, thereby possibly impacting the injectivity [7].

#### 4.4.5 Hydrate Formation Issues

In a similar manner to pipeline corrosion, the issue of hydrate formation has been previously discussed in Section 4.3.1. There is a risk of hydrate formation at low temperatures and high pressures, and the inclusion of impurities may cause the formation to occur at higher temperatures [7]. Also, carbon dioxide induced hydrates form up to temperatures of 10°C at current transportation pressures based on past experience with pipeline transportation of CO<sub>2</sub> [10].

The inclusion of H<sub>2</sub>S and CH<sub>4</sub> in the CO<sub>2</sub> stream can result in hydrate formation without the presence of free water [7]. Under this scenario, glycol must be injected to prevent hydrate formation in the pipeline [24].

The accumulation of hydrates can cause problems such as plugging and equipment damage. However, the maximum amount of hydrates that can be formed with dissolved water in the CCS stream will most likely be too small to cause operational problems [10].



## 4.5 Economic Considerations

One of the major hindrances to full-scale deployment of CCS is associated with the economic aspects of the scheme. The high costs associated with the capture techniques as well as the pipeline infrastructure required to transport CO<sub>2</sub> to remote areas have currently restricted the deployment of CCS.

Throughout this study, the adverse effects of impurities on the capital and operational costs associated with CCS have been presented. A summary (sourced from previous sections) of economic feasibility is presented below.

Cost estimates have been performed by different sources, which include cost of capture, compression, transport, storage and monitoring. In mostly all economic analyses carried out on CCS, the capture and compression processes dominate the cost of CCS [1]. The costs of capture from different methods often reflect the CO<sub>2</sub> concentrations in the flue gas or process stream [1]. Therefore, capture represents the largest cost associated with CCS and is a significant barrier to widespread adoption of the scheme [1].

Firstly, the widespread deployment of CO<sub>2</sub> capture will likely result in the co-capture of other chemical compounds in the process gas from industrial facilities [9]. Removing these impurities from the CO<sub>2</sub> stream to trace levels will increase costs significantly for the capture plant operators [9]. Hence, reducing the concentration of trace elements and obtaining a high purity CCS stream is often technically feasible, but purification steps most likely lead to additional costs and increased energy requirements [10].

On the other hand, if the CO<sub>2</sub> stream is not scrubbed to remove impurities, costs may increase for the downstream storage site operators in terms of injection costs, maintenance and monitoring [9]. In addition, impurities such as hydrocarbons can reduce the CO<sub>2</sub> fluid density and increase the pressure required to maintain a supercritical or dense phase, which in turn increases the energy required for additional compression work. Furthermore, recompression stations will most likely be required at more frequent intervals along the pipeline to keep the CO<sub>2</sub> fluid in the dense/supercritical phase if non-condensable gases are present in high quantities. This absolute cost increase for transport due to additional recompression stations has a more noticeable influence at longer transport distances [11].

Therefore, the economic feasibility of CCS is a crucial component to the overall successful deployment of CCS for CO<sub>2</sub> emission reduction.



## 5. HEALTH AND SAFETY IMPACT OF CO<sub>2</sub> SPECIFICATION

In any process system, the health and safety aspects of the flowing fluid must be taken into consideration in case of system leaks or due to operational or emergency venting. This is especially important for the CCS system as the CO<sub>2</sub> stream may contain toxic or harmful impurities, most notably H<sub>2</sub>S, CO, SO<sub>x</sub> and NO<sub>x</sub>, depending on the capture technique used. Pure CO<sub>2</sub> itself is non-toxic at normal atmospheric concentrations. The introduction of contaminants that might be injected with the CO<sub>2</sub>, or from the interaction of the CO<sub>2</sub> with subsurface materials in, or adjoining, an underground formation may create a risk to public safety [3].

The main safety issue for pipeline transport of large volumes of CO<sub>2</sub> is the risk of short-term, sudden leakages [10]. A property of CO<sub>2</sub> that needs to be considered when selecting a pipeline route is the fact that CO<sub>2</sub> is denser than air and can therefore accumulate to potentially dangerous concentrations in low lying areas if a pipeline rupture occurs [12]. Therefore, an appropriate risk and safety assessment should be conducted to quantify such risks from occurring. CO<sub>2</sub> is a colourless and odourless gas, and therefore, leaks or accumulations of the gas may not be readily detected. In addition, although CO<sub>2</sub> is non-explosive unlike natural gas, asphyxiation and frost burn are eminent risks associated with CO<sub>2</sub> [14]. Furthermore, exposure to concentrations of CO<sub>2</sub> higher than 10% may lead to adverse health effects, while concentrations above 25% pose a significant asphyxiation hazard [10].

Besides the safety issues of the CO<sub>2</sub> itself, other compounds such as H<sub>2</sub>S or CO provide further safety and toxicity risks [10]. There are existing and established occupational exposure limits that regulate airborne exposure to toxic compounds in working environments. One type of limit that is in common use is the Short Term Exposure Limit (STEL), which gives the maximum amount of a compound that one can be exposed to for a period of 15 minutes without adverse health effects [10]. Table 6 shows the STEL values for the likely impurities to be present in the CO<sub>2</sub> stream based on limits set by the National Occupational Health and Safety Commission (NOHSC) (from Material Safety Data Sheets – MSDS).

**Table 6 – Short Term Exposure Limits for CO<sub>2</sub> and Various Impurities**

Component	Short Term Exposure Limit	
H <sub>2</sub> S	15 ppm	0.0015 vol%
CO	200 ppm	0.02 vol%
NO <sub>2</sub>	5 ppm	0.0005 vol%
SO <sub>2</sub>	5 ppm	0.0005 vol%
CO <sub>2</sub>	30,000 ppm	3 vol%



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Exposure to CO<sub>2</sub> in case of a pipeline rupture is characterized by a short-lived, but relatively strong exposure to the leaked CO<sub>2</sub> volume [10]. Once the pipeline rupture or leak has occurred the CO<sub>2</sub> becomes diluted by air and its concentration decreases. For safe pipeline transportation it is required that once the CO<sub>2</sub> reaches its STEL value (by the dilution process), the concentration of other toxic compounds in the CO<sub>2</sub> should reach their STEL as well [10].

Facility operators must therefore be aware of the health and safety risks associated with concentrated CO<sub>2</sub>, and must be mindful of potential worker exposure to impurities in the CO<sub>2</sub> stream.



## 6. LEGISLATIONS, REGULATIONS AND GUIDELINES

Currently there are no standards to define the required quality for CO<sub>2</sub> pipelines and storage. At this present stage, there are no published regulations or standards for the quality of CO<sub>2</sub> in CCS, with most of the work performed in this area still in early stages of development. Therefore, this section will aim to outline the key bodies involved in the process of formulating a CCS guideline or standard rather than providing a CO<sub>2</sub> specification that should be used universally.

Based on past EOR experiences, there are existing legal and regulatory frameworks that address many of the issues that will need to be addressed if CCS is to be adopted [3]. Many of these CO<sub>2</sub> pipelines are based on existing hydrocarbon pipeline standards. However, there are ambiguities and gaps within these standards if applied to CO<sub>2</sub> transportation as these documents were intended for oil and gas transportation rather than CO<sub>2</sub>. For example, the Natural Gas Act in the U.S. states that a gas that is 98% pure CO<sub>2</sub> with traces of CH<sub>4</sub> in the remaining 2% is not 'natural gas' within the meaning of the Act [3].

### 6.1 Global Outlook

Many countries around the world have begun research and development in the area of CCS, with many of those countries involved establishing specialised organisations or committees to focus on the development and initiation of CCS scheme and incentives. This section will briefly outline some key organisations involved in recent CCS regulatory developments as well as existing regulations, such that these bodies/regulations may become the source of future regulations and standards used in CCS development.

- **Intergovernmental Panel on Climate Change (IPCC)** – established to provide guidelines for greenhouse gas inventories [12]. The IPCC report addressed that the process and impacts of CCS may be managed under mining, oil and gas, pollution control, waste disposal, drinking water, treatment of high-pressure gases and subsurface property rights law [25].
- **World Resources Institute** – publication of guidelines for Carbon Dioxide Capture, Transport and Storage [1].
- **International Energy Agency (IEA)** – intergovernmental organisation which acts as energy policy advisors.
- **London Protocol (1996)** – allows the geological storage of CO<sub>2</sub> under certain conditions: (1) only if injected into a sub seabed geological formation; (2) only if it consists overwhelmingly of CO<sub>2</sub>, although it may contain incidental associated substances derived from the source material and capture and sequestration processes used; and (3) only if no wastes or other matter are added for the purpose of disposal [26].



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- **European Union (EU) Directives** – publications have been produced with reference to geological storage of CO<sub>2</sub> from a Norwegian perspective [27].
- **Global Carbon Capture and Storage Institute** – established and funded by the Australian Federal Government to accelerate the worldwide development, deployment and implementation of carbon capture and storage (CCS) technologies and the sharing of information.

## 6.2 Australian Outlook

In terms of Australia's perspective on CCS regulation and legislation, there has been continual progress to allow transportation of CO<sub>2</sub> for geo-sequestration, both on a state and federal level; however there is currently a lack of existing Australian legislation that provides an adequate and discrete regime dealing with the issues of responsibility and liability for geo-sequestered gas [25].

The following progress has been made on a State Government level of authority:

- In South Australia, CO<sub>2</sub> has been defined as a regulated substance to allow it to be transported under the **Petroleum Act 2000**. However, the focus of this Act is on the *storage* of, among other regulated substances, carbon dioxide, and not on the *disposal* of carbon dioxide (as a waste product) [25]. Therefore, there are no clear provisions in relation to what happens to injected carbon dioxide on the termination of a production licence, including provisions which deal with the liability for the risks associated with the long term (indefinite) storage time proposed for geo-sequestration or on-going monitoring requirements [25].
- In Queensland, CO<sub>2</sub> transport is allowed under the **Petroleum and Gas (Production and Safety) Act 2004**. Similar to the Petroleum Act (SA), this Act expressly authorises the injection and storage of carbon dioxide in "natural underground reservoirs" but also focuses on the provisions of *storage*, rather than *disposal* [25].
- In Victoria, CO<sub>2</sub> transport is regulated by the **Victorian Pipelines Act 2005**. However, the Act does not contain detailed provisions that provide a general regime for underground gas storage or contemplate the activities associated with CCS projects [25].
- In New South Wales, pipeline transportation is regulated under the **Petroleum (Onshore) Act 1991** and **Petroleum (Offshore) Act 1982**.
- In Western Australia, the Gorgon Project CO<sub>2</sub> transport and disposal is facilitated by the **Barrow Island Act 2003**.

In addition to the features referred above, the petroleum legislation in most Australian jurisdictions contains provisions which deal to some degree with the underground storage of gas [25]. By and large, these provisions deal only with storage of naturally occurring hydrocarbons or mixtures of hydrocarbons (such as natural gas) [25]. However, Queensland and South Australia have each recently put in place provisions dealing with the underground storage of other gases, including carbon



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dioxide, as part of broader petroleum legislative reform processes [25]. Therefore, these current legislations provide a potential framework for the regulation of CCS.

The following progress has been made on current design standards:

- The current liquids pipeline code (**ASME B31.4**) is intended for carbon dioxide as well as other liquids pipelines since it considers CO<sub>2</sub> compressed above its critical pressure as a liquid.
- Currently, **AS 2885** applies to steel pipelines and associated piping and components, "that are used to transmit single-phase and multi-phase hydrocarbon fluids, such as natural and manufactured gas, liquefied petroleum gas, natural gasoline, crude oil, natural gas liquids and liquid petroleum products". Although this definition does not include CO<sub>2</sub>, a clause for inclusion under special circumstances in AS 2885.0 Section 1.2.2 Part (c) for pipelines transporting other fluids (for example non-hydrocarbon gases and slurries) has been implemented. Further research is underway to provide the basis for future amendments to fully cover CO<sub>2</sub> pipelines under AS 2885. This may take the form of an explanatory appendix.

The following progress has been made on a Federal Government level of authority:

- The **Ministerial Council on Mineral and Petroleum Resources (MCMPR)** released the Regulatory Guiding Principles ([28]) in order to achieve a nationally consistent approach to the implementation of the CCS scheme, which takes into account Ecologically Sustainable Development, the Intergovernmental Agreement on the Environment, Principles of Good Regulation and relevant Council of Australian Governments (COAG) Occupational Health and Safety Principles [25].
- **Offshore Petroleum Amendment (Greenhouse Gas Storage) Bill 2008**, which is an amendment to the Offshore Petroleum Act 2006 to include "the injection and storage of greenhouse gas substances in offshore areas" supplement to offshore petroleum activities.
- The Commonwealth Department of Environment, Water, Heritage and the Arts released a draft for the **Environmental Guidelines for Carbon Dioxide Capture and Geological Storage 2008** to build on the Regulatory Guiding Principles endorsed by MCMPR.

There are numerous existing regulations that are likely to impact on geo-sequestration projects in Australia, which arise both under domestic law (under legislation and at common law), as well as at international law, and are driven by the key risks associated with each stage of a geo-sequestration project [25]. The existing petroleum regime in Australia provides an adequate starting point for developing a legislative framework for Australian CCS projects [25].





## 7. CONCLUSION

Several variations in CO<sub>2</sub> composition due to capture technique, pipeline operating restraints and storage implications have been discussed in this study. As a result of the wide range of potential impurities possible in a CO<sub>2</sub> stream, it is not recommended to introduce legislation defining acceptable CO<sub>2</sub> composition for all possible CCS projects. Instead, it is recommended that each CCS system define their own CO<sub>2</sub> specification that carefully considers the cost and safety for the particular constraints present in the CCS system.



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