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Review

Performing Quality Assurance of Carbon Dioxide for Carbon Capture and Storage

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Abstract: Impurities in carbon dioxide can affect several aspects of the carbon capture and storage process, including storage capacity, rock erosion, accuracy of flow meters, and toxicity of potential leaks. There is an industry need for guidance on performing purity analysis before carbon dioxide is transported and stored. This paper reviews selected reports that specifically provide threshold amount fraction limits for impurities in carbon dioxide for the purpose of transport and storage, with rationales for these limits. A carbon dioxide purity specification is provided (including threshold amount fractions of impurities) on the basis of the findings, as well as recommendations on further work required to develop a suitable gas metrology infrastructure to support these measurements including primary reference materials, sampling methods, and instruments for performing purity analysis. These recommendations provide important guidance to operators and gas analysis laboratories for performing quality assurance.

Keywords: carbon capture; carbon dioxide; purity; metrology

1. Introduction

As countries around the world transform their national energy strategies to meet stringent carbon reduction targets, carbon capture and storage (CCS) is being viewed as an essential tool for reducing carbon emissions from industrial processes. Notable projects include Quest managed by Shell in Canada which managed to capture 4 million tonnes of carbon dioxide by May 2019 [1] and the Northern Lights project in Norway which aims to develop a full-scale CCS value chain in Norway by 2024 [2]. CCS could be a suitable "add-on" technology to energy processes that currently utilise hydrocarbons as the feedstock. For example, steam methane reforming which produces hydrogen from natural gas could supply the carbon dioxide byproduct to CCS to make the overall process carbon-neutral (this may a viable solution for countries with existing supplies of natural gas such as in the United Kingdom (UK)). Without CCS, such processes will not be acceptable in future.

There are specific measurement capabilities that need to be developed to support CCS. For example, flow metering is important for calculating the amount of carbon dioxide that has been sent into storage sites and this requires traceable flow metering methods and an understanding of how gas quality affects accuracy of the measurements. Setting and meeting operational conditions for CCS processes require accurate determination of physical property measurements. Leak detection or monitoring is also an important measurement to ensure carbon dioxide does not escape following storage. This paper focuses on measurement challenges for gas quality, particularly the measurement of low-level impurities in the carbon dioxide, as well as the overall composition (i.e., level of high concentration components).

Various literature is available which outlines the issues of carbon dioxide purity in CCS processes (as reviewed in Section 3). The presence of large amounts of impurities during the compression stage could lead to large inefficiencies or cause corrosion of storage/pipeline materials [3]. An additional concern is the possible leakage of hazardous impurities to the atmosphere during storage; this risk can be minimised by simply ensuring that harmful impurities are not present in the carbon dioxide before the storage step.

The relevant document that covers carbon dioxide gas quality is the International Organisation for Standardisation Technical Report ISO/TR 27921 which states that CCS operators must develop their own purity specification tailored to their process; however, there are currently no standards that provide guidance on how to perform this.

The aim of this paper is to review available literature on the required purity of carbon dioxide for the different stages of carbon capture and storage for energy processes (combustion and steam methane reforming) to develop and provide a carbon dioxide purity specification. This specification has been provided to facilitate the development of a gas metrology infrastructure to support laboratories in performing quality assurance measurements.

2. Purity across the CCS Process

2.1. Production

2.1.1. Pre-Combustion

Pre-combustion is the process where carbon dioxide is removed before the actual conversion of fuel to energy. This may involve reforming (gas) or gasifying (coal) the fuel to syngas, and utilising water gas shift to produce more hydrogen from water (which also converts carbon monoxide to carbon dioxide). The carbon dioxide can be removed leaving a hydrogen-rich fuel. In this case, the likely impurities that may be present in the carbon dioxide are nitrogen, oxygen, hydrogen, methane, carbon monoxide, and sulphur-based compounds such as hydrogen sulphide. There is not expected to be significant levels of impurities that would originate from air, such as sulphur dioxide or nitrogen oxides, as the carbon dioxide is removed before the combustion step [4]. The level of carbon dioxide in the final streams would entirely depend on the raw materials and process, but is expected to be between 5–20 $\text{cmol}\cdot\text{mol}^{-1}$ for syngas and closer to 15–50 $\text{cmol}\cdot\text{mol}^{-1}$ following water gas shift [5–7].

2.1.2. Post-Combustion

Post-combustion is the process where the fuel is directly combusted using air without an initial reforming or gasification step. The trace elements that may be present in carbon dioxide for this process are nitrogen, oxygen, water, sulphur oxides, nitrous oxides, particulates, hydrochloric acid, hydrofluoric acid, mercury, other metals, and other trace contaminants. Combustion of coal is likely to provide more sulphur oxides and nitrous oxides, but lower oxygen compared to combustion of natural gas [8].

2.1.3. Oxy-Fuel

An oxy-fuel process utilises pure oxygen instead of air to perform combustion. By removing inert nitrogen from the oxidising gas, the process can reduce fuel consumption (however, there may be additional costs from the air separation unit). The possible contaminants could be argon, oxygen, nitrogen, sulphur dioxide, sulphur trioxide, nitrogen monoxide, nitrogen dioxide, carbon monoxide, and other trace contaminants from the air [9].

2.1.4. Steam Methane Reforming

Steam methane reforming is a process similar to combustion but where methane from natural gas is reacted with water instead of air. The resulting gas then goes through a water gas shift reaction to produce a stream of hydrogen and carbon dioxide. The carbon dioxide can be separated and captured whilst the pure hydrogen can be used in chemical processes or as a clean fuel (for example for powering fuel cell hydrogen vehicles).

The expected carbon dioxide compositions from these processes (following purification) are shown in Table 1.

Table 1. Carbon dioxide compositions for typical processes (including purification step where applicable) according to the literature [10–12].

	Post-Combustion/Steam Methane Reforming ($cmol\cdot mol^{-1}$)	**Pre-Combustion ($cmol\cdot mol^{-1}$)**	**Oxy-Fuel ($cmol\cdot mol^{-1}$)**
CO_2	99.8–99.9	95–99	95–97
$N_2/O_2/Ar$	<0.1	0–1.5	1.6–4.1
CO	<0.1	0.04	<0.1
H_2S	-	0–0.6	-
SO_2	<0.1	<0.1	<0.5
NO	<0.1	-	0–0.01
H_2O	<0.1	0–1.8	-

2.2. *Capture or Separation and Transport*

The capture step refers to the stage of the process where pure carbon dioxide is extracted from the waste stream of an industrial process, whilst a separation step would remove impurities from the stream to leave pure carbon dioxide. The carbon dioxide could be present in flue gas from power plants, steam methane reforming, or chemical processes. The gas will usually go through a purification step, such as amine scrubbing, to produce a stream of pure carbon dioxide which can be liquefied before transporting for storage or utilisation [13]. According to the literature, amine scrubbing usually captures 85–90% of the carbon dioxide from flue gas [14], but it should be noted that this would entirely depend on the set-up and type of scrubbers used. The purity of the carbon dioxide following amine scrubbing can be better than 99.95% depending on the performance and lifetime of the scrubber [15]. Table 2 provides an overview of different technologies that are commonly used for the capture or separation step including typical compositions some details.

Table 2. Typical compositions following capture and separation processes [15].

	CO_2	**H_2O**	**H_2**	**CO**	**N_2**	**O_2**	**CH_4**	**Ar**
Amine scrubber (post-combustion)	94.4	5.6	0	0	0	Trace level	0	0
Amine scrubber (pre-combustion)	98.2	1.8	0	0	0	0	0	0
Water cycle	59.7	32.8	0	0.01	2.81	1	0	3.59
S-Graz cycle	61.7	30.9	0	0	2.91	0.85	0	3.69
Oxyfuel carbon capture	93.8	4.2	0	0	0.28	1.38	0	0.35
Solid oxide fuel cell and gas turbine	35.9	63.8	0	0	0.26	0	0	0
Advanced zero emission power	35.9	63.8	0	0	0.26	0	0	0
Chemical looping combustion	34.7	65.1	0	0	0.28	0	0	0
Hydrogen membrane separation reactor	62.4	35.5	0.92	0.57	0.45	0	0.12	0

Before transporting through pipelines, the carbon dioxide is usually dehydrated to ensure levels of water are below 50 µmol·mol^{-1}. According to an article by the World Resources Institute, there are three main types of pipelines that are categorised on the basis of different purity levels of carbon dioxide that can be present; the main impurities of concern are hydrogen sulphide, sulphur, methane, hydrocarbons, carbon monoxide, nitrogen, oxygen, and water [16].

As shown in Table 2, amine scrubbing appears to be one of the more suitable conventional methods for obtaining high-purity carbon dioxide from flue gas.

2.3. *Storage*

Worldwide, there are several projects that are using CCS to store carbon dioxide using different types of storage sites. There are many databases showing the CCS sites that are currently in operation including through the Scottish Carbon Capture and Storage research group (SCCS), as shown in Figure 1 [17]. This section discusses the conventional types of CCS storage sites with a focus on the possible impact of impurities in the carbon dioxide.

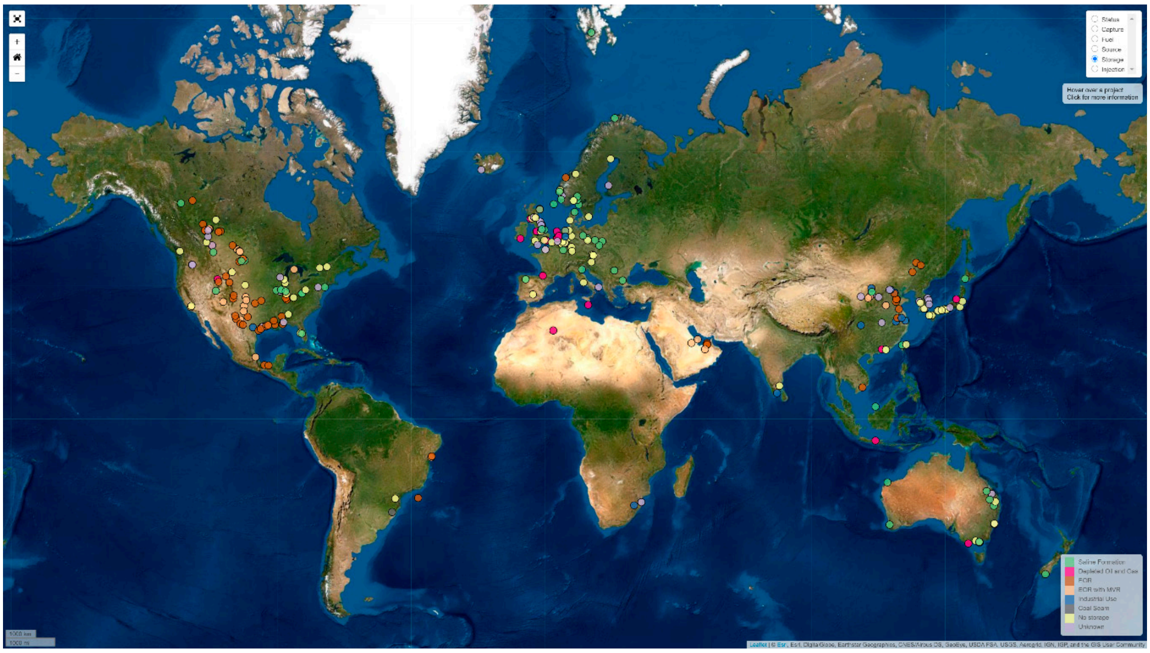

Figure 1. Location of planned or operational storage sites for carbon capture and storage (CCS) worldwide according to the Scottish Carbon Capture and Storage research group (SCCS) [17].

2.3.1. Deep Saline Aquifers

Saline aquifers are underground rocks that are water-permeable and end up saturated with brine. Storage of carbon dioxide via saline aquifers is optimised by injecting the carbon dioxide as a supercritical fluid. Once injected into the aquifers, the carbon dioxide is trapped beneath a layer of gas impermeable rock (such as caprock). The Shell Quest CCS facility in Alberta, Canada is one such process that has used this type of storage [1]. Any requirements for quality may arise from concerns around carbon dioxide leaks as some impurities present in the gas could be hazardous to humans and/or the environment. Additionally, the presence of noncondensable impurities such as nitrogen, hydrogen, and oxygen may lead to difficulties with the compression step and limit storage capacity (as these impurities may reduce overall density) [18]. Some impurities, such as water and sulphur dioxide, may react together to form sulphuric acid, which could cause mineral dissolution [18].

2.3.2. Unmineable Coal Seams

Studies have shown that porous coal is efficient at trapping carbon dioxide [19]. Therefore, coal mines that are not accessible for mining may be suitable for storing carbon dioxide. This process provides the additional benefit that the carbon dioxide can displace methane from the mine which can be extracted and utilised as a source of energy (for example, this methane could be injected into the natural gas grid following clean-up) [20]. The San Juan Basin Allison Unit Project in New Mexico is one example where unmineable coal seams were used to store carbon dioxide [21].

2.3.3. Depleted Oil and Gas Reservoirs

Enhanced oil recovery (EOR) is the process of feeding carbon dioxide into depleted oil reservoirs to extract remaining oil. This provides two benefits as the process allows carbon dioxide to be securely stored underground whilst displacing the remains of oil that otherwise would have been unobtainable. It is estimated that an additional 470 billion barrels of oil could potentially be extracted by EOR from discovered oil sites worldwide, which would lead to the sequestration of 140 billion metric tons of carbon dioxide [22]. This is already a widely used technique where carbon dioxide is readily available; however, there may be issues over the suitability of a given depleted reservoir for long-term carbon dioxide storage. One notable facility is the Century Plant in Texas which has a storage capacity of 8.4 million metric tons of carbon dioxide per annum as is being used for EOR. It is noted as one of the biggest CCS facilities worldwide currently [23].

2.4. Utilisation

There are many uses for carbon dioxide in industry that includes preparation of food and chemical processing. The European Industrial Gases Association (EIGA) have developed a purity specification for carbon dioxide (Table 3) that is widely used by the food and beverage industry, "EIGA document 70/17"; in order to meet these specifications, additional clean-up and analysis would be required following carbon dioxide capture [24]. There are several uses for carbon dioxide in chemical processing to manufacture oxygenated organics, minerals, carbon fuels, and plastics. The biggest use of carbon dioxide in industry is in the production of urea at an average of 109.5 million tonnes per years. The remaining is used for the synthesis of other important feedstock chemicals such as salicylic acid, methanol, and polycarbonates. The medical industry is the second biggest user of carbon dioxide with an average use of 400 tonnes per year, in which it is used as an insufflation gas in laparoscopic procedures (keyhole surgery). The beverage industry is also a key user of carbon dioxide, in which it is used to carbonate certain drinks like beer and cider. It is also used in its supercritical form to decaffeinate coffee.

Purity specifications and gas analysis methods for carbon dioxide utilisation are important and are already fairly established in specific industries (such as beverage); in other cases, gas quality assurance would be controlled by the individual companies receiving carbon dioxide. As this paper focuses on carbon dioxide for storage, gas quality assurance for carbon dioxide utilisation is considered outside of its scope and, as such, is not discussed further.

Table 3. Purity specifications for carbon dioxide using in beverage provided by European Industrial Gases Association (EIGA) document 70/17.

Appendix A: EIGA Limiting Characteristics For Carbon Dioxide to Be Used in Beverage for Source Specification	
Component	**Amount Fraction**
Assay	99 $\text{cmol}\cdot\text{mol}^{-1}$ min
Moisture	20 $\mu\text{mol}\cdot\text{mol}^{-1}$ max
Ammonia	2.5 $\mu\text{mol}\cdot\text{mol}^{-1}$ max
Oxygen	30 $\mu\text{mol}\cdot\text{mol}^{-1}$ max
Oxides of nitrogen (NO/NO_2)	2.5 $\mu\text{mol}\cdot\text{mol}^{-1}$ max each
Nonvolatile residues (particulates)	10 $\mu\text{mol}\cdot\text{mol}^{-1}$ max
Nonvolatile organic residues (oil and grease)	5 $\mu\text{mol}\cdot\text{mol}^{-1}$ max
Phosphine ***	0.3 $\mu\text{mol}\cdot\text{mol}^{-1}$ max
Total volatile hydrocarbons (calculated as methane)	50 $\mu\text{mol}\cdot\text{mol}^{-1}$ max of which 20 $\mu\text{mol}\cdot\text{mol}^{-1}$ max non-methane hydrocarbons
Acetaldehyde	0.2 $\mu\text{mol}\cdot\text{mol}^{-1}$ max
Aromatic hydrocarbon	0.02 $\mu\text{mol}\cdot\text{mol}^{-1}$ max
Carbon monoxide	10 $\mu\text{mol}\cdot\text{mol}^{-1}$ max
Methanol	10 $\mu\text{mol}\cdot\text{mol}^{-1}$ max
Hydrogen cyanide *	0.5 $\mu\text{mol}\cdot\text{mol}^{-1}$ max
Total sulphur (as S) **	0.1 $\mu\text{mol}\cdot\text{mol}^{-1}$ max
Taste and odour in water	No foreign taste or odour
Appearance in water	No colour or turbidity
Odour and appearance of solid CO_2 (snow)	No foreign odour or appearance

* Analysis necessary only for carbon dioxide from coal gasification sources. ** If the total sulphur content exceeds 0.1 ppm *v*/*v* as sulphur, then the species must be determined separately, and the following limits apply: carbonyl sulphide, 0.1 $\mu\text{mol}\cdot\text{mol}^{-1}$ max; hydrogen sulphide, 0.1 $\mu\text{mol}\cdot\text{mol}^{-1}$ max; sulphur dioxide, 1.0 $\mu\text{mol}\cdot\text{mol}^{-1}$ max. *** Analysis necessary only for carbon dioxide from phosphate rock sources.

3. Quality Requirements for CCS

This section reviews previous and ongoing CCS projects where the possible impurities have been identified and threshold amount fractions for compounds have been specified (Table 4). A focus of the review was to understand the amount fraction limits that have previously been used and the rationale behind these threshold limits in order to develop a draft purity specification.

Table 4. List of CCS projects providing purity specifications. USA, United States of America; UK, United Kingdom.

Author	**Description**	**Year**	**Type of Document**	**Ref.**
SNC Lavalin	This report was written by SNC for the International Energy Agency Greenhouse Gas (IEAGHG) research and development programme and is based on a study of two types of coal fired plants using conventional pulverised coal steam and an integrated gasification combined cycle plant. The report provides information on effects that some impurities may have to the process.	2004	Report	[25]

Table 4. *Cont.*

Author	Description	Year	Type of Document	Ref.
Anheden et al.	Discusses the required carbon dioxide purity specifications for a typical CCS process on the basis of transport, storage, safety, cost and environmental regulations.	2005	Paper	[26]
Metz et al.	The focus of the special report published by the Intergovernmental Panel on Climate Change is to assess current state of knowledge for important aspects of CCS which includes sources of impurities and impact on the overall process.	2005	Report	[12]
Dynamis	Written as part of the Dynamic project provides carbon dioxide purity specifications that were developed as guidance for the CCS stream of the HYPOGEN plant.	2007	Project (technical specification)	[4]
White et al.	The paper provides some guidance on possible impact of impurities in carbon dioxide for an oxyfuel process.	2007	Paper	[27]
World Resources Institute	Provides guidelines for CCS written by a group of over 80 stakeholders which includes information on effects of impurities.	2008	Report	[16]
Det Norske Veritas	Provides guidance and criteria (including recommended purity specifications) for carbon dioxide transport in steel pipelines. The guide was developed in partnership with key companies including British Petroleum, Petrobras, Shell, Statoil, Vattenfall, and Chevron.	2010	Best practice	[28]
IEAGHG	Written by the International Energy Agency, the report considers several storage scenarios including deep saline formations, depleted gas fields, and enhanced oil recovery, and provides impact assessments for impurities present in the carbon dioxide.	2011	Report	[18]
National Energy Technology Laboratory (USA)	The report provides a recommended purity specification for carbon dioxide used for general CCS processes including for transport through carbon steel pipelines, sequestration through saline aquifers, or enhanced oil recovery.	2012	Report	[29]
Wetenhall et al.	This paper studies how high-concentration inert compounds in the carbon dioxide can affect the hydraulic stage of the CCS process and overall cost.	2014	Paper	[3]
Harkin et al.	The CarbonNet Project developed a carbon dioxide purity specification to follow for its CCS hub which intended to receive carbon dioxide from various sources for storage. The specification considered pipeline, health and safety, and technical issues.	2017	Paper	[30]
The UK Health and Safety Executive	Guidance on workplace exposure limits of contaminants including flammables and toxic compounds	2018	Best practice	[31]
ISO TC 265	This technical report written within ISO TC 265 (carbon dioxide capture, transportation, and geological storage), provides guidance on the key impurities that could be present in carbon dioxide and impact to the CCS process. The report does not provide threshold amount fraction levels that could be adhered to.	2020	ISO Technical Report	[32]

3.1. Water (H_2O)

Various project reports have listed water as an impurity that must be limited; it is a common byproduct of combustion and a possible impurity in hydrogen from the steam methane-reforming process [4,16,25,26,28]. If water is present with hydrogen sulphide or sulphide dioxide, there is a risk of corrosion through the production of sulphuric acid [4,12,25]. Similarly, the reaction of water with carbon dioxide could produce carbonic acid [16]. Additionally, hydrates could form from the reaction of water with certain components which can lead to interruption to flow [26,32].

3.2. Hydrogen Sulphide (H_2S), Sulphur Oxides (SO_x), and Nitrogen Oxides (NO_x)

Hydrogen sulphide and sulphur dioxide in the presence of water can form sulphuric acid, which would be corrosive to pipelines. Similarly, nitrous oxides in the presence of water can form nitric acid [27]. Nitrogen oxide was noted to act as a catalyst for the oxidation of sulphide dioxide to sulphuric acid also leading the sulphur precipitates [18]. Hydrogen sulphide alone can cause the gas to turn sour, which would affect production equipment [25]. Additionally, if any of these gases are present in a carbon dioxide leak (from the storage site), the resulting release could be toxic [12,25]. In one report, a limit of 50 $\mu\text{mol}\cdot\text{mol}^{-1}$ for hydrogen sulphide is recommended for health and safety reasons [16]. It is also noted that hydrogen sulphide may cause severe pore blocking at geologic storage sites [18].

3.3. Carbon Monoxide (CO)

Carbon monoxide could be present in carbon dioxide at low percentage volume levels. It appears that the main concern is around toxicity if a carbon dioxide leak was to occur [29]. The CarbonNet Project [30] set a carbon monoxide range of 900–5000 $\mu\text{mol}\cdot\text{mol}^{-1}$; the lower limit and upper limit were set to allow a range of potential carbon dioxide sources to be received as part of the project.

3.4. Oxygen (O_2), Methane (CH_4), Nitrogen (N_2), Argon (Ar), and Hydrogen (H_2)

These gases are considered "light" and, if present in carbon dioxide at high levels, can increase compression power requirements and decrease carbon dioxide storage capacity by lowering the density [25,32]; therefore, a maximum level of 4–5 $\text{cmol}\cdot\text{mol}^{-1}$ has been specified in several CCS projects [4,29,30,33]. Another consideration specifically for EOR is that oxygen could lead to both combustion of hydrocarbons in the oil field [27,29] and enhanced growth of bacteria [16,29] (for both cases, a limit of 10 $\mu\text{mol}\cdot\text{mol}^{-1}$ was recommended). Oxygen was noted to have an effect on the dissolution of caprock; however, the levels required to cause this were significantly high and not likely due to its low solubility [18]. As methane and hydrogen are flammable gases, one project recommended to keep the volume of these gases low in the carbon dioxide to avoid losing useful product with high energy content [4].

The presence of high-level impurities can also affect measurements such as flow metering, density, speed of sound, viscosity, and thermal conductivity. Changes in density can reduce the amount of carbon dioxide being transported, whilst an increase in the maximum two-phase pressure could lead to increased risk of ductile fracture. This would also affect the phase behaviour of carbon dioxide [32]. As discussed later in Section 4.5, further work is required to accurately model parameters such as these to traceable gas compositions.

3.5. Ammonia (NH_3) and Amines

Ammonia and amines are potential impurities that can be present in carbon dioxide from the scrubbing stage. From the literature, the detrimental effects to the process only appear to be noted as toxicity from a carbon dioxide leak [29]; however, it is possible that these impurities could react with sulphuric acid or nitric acid to form particulates (ammonium sulphate or ammonium nitrate, respectively).

3.6. Ethane (C_2H_6) and Hydrocarbons (C_{3+})

Similarly to methane, other hydrocarbons in the carbon dioxide stream need to be kept to not only lower amount fractions to avoid explosive atmospheres, but also to reduce loss of a valuable energy product. One project noted that high levels of hydrocarbons in carbon dioxide could lead to asphyxiation, although carbon dioxide itself would also act as an asphyxiant [29].

3.7. Particulates

A purity specification set by the National Energy Technology Laboratory (NETL) in the United States of America (USA) includes particulates as one of the criteria; however, there appears to be no recommended maximum mass concentration or rationale [29]. Particulate matter could increase wear of machinery and pipelines [32], while it is also likely to induce pore blocking at the CCS site.

3.8. Other Impurities

Additional impurities that have been provided in the NETL purity specification include hydrogen cyanide, mercury, hydrochloric acid, and hydrofluoric acid as toxic components that could be hazardous in a carbon dioxide leak, as well as glycol due to its damage to seals and other equipment. The specifications also include selexol, although the effects are unknown. The authors of the report suggest further work is required to set maximum allowed levels for these impurities [29].

Table 5 provides a summary of the purity requirements identified in this section. Where different reports provide alternative maximum limits, a rationale for the selected limit is provided and the relevant references indicated. Where maximum impurity levels are selected on the basis of long-term exposure limits (for health and safety considerations), the work exposure limits provided by the UK's Health and Safety Executive (HSE) have been used to ensure they comply with UK recommended best practice [31]. The quality requirements for carbon dioxide utilisation are not included in the table as there are various uses of carbon dioxide, some of which may not adhere to national or international regulations but a company's own internal practice. Not enough information on selexol is currently known to provide maximum limits.

Table 5. Summary of purity specifications.

	Pipeline	**Storage**			**Ref.**
		Saline Reservoir Sequestration	Unmineable Coal Seams	Oil and Gas Recovery	
H_2O [a]	Use same maximum limits as storage method	300 μmol·mol^{-1}			[29]
H_2S [b]		5 μmol·mol^{-1}			[31]
CO [b]		20 μmol·mol^{-1}			[31]
O_2		4 cmol·mol^{-1}		10 μmol·mol^{-1}	[4,16,27,29]
CH_4 [c]		4 cmol·mol^{-1}		1 cmol·mol^{-1}	[4,29]
N_2 [c]		4 cmol·mol^{-1}		1 cmol·mol^{-1}	[4,29]
Ar [c]		4 cmol·mol^{-1}		1 cmol·mol^{-1}	[4,29]
H_2 [c]		4 cmol·mol^{-1}		1 cmol·mol^{-1}	[4,29]
SO_x [b]		0.5 μmol·mol^{-1}			[31]
NO_x [b]		0.5 μmol·mol^{-1}			[31]
NH_3 [b]		25 μmol·mol^{-1}			[31]

Table 5. *Cont.*

	Pipeline	Storage	Ref.
C_2H_6		1 cmol·mol^{-1}	[29]
$C_3{}^+$		1 cmol·mol^{-1}	[29]
Particulates		1 µmol·mol^{-1}	[29]
HCl [b]		1 µmol·mol^{-1}	[31]
HF [b]		1.8 µmol·mol^{-1}	[31]
HCN [b]		0.9 µmol·mol^{-1}	[31]
Hg [b]		0.02 mg·m^{-3}	[31]
Glycol		46 nmol·mol^{-1}	[29]
MEA [b]		1 µmol·mol^{-1}	[31]

[a] Water can react with sulphur-containing species to produce sulphuric acid; limiting water to less than 300 ppm will prevent damage from this product; [b] long-term exposure limits set by the Health and Safety Executive (HSE); [c] the species increase the miscibility pressure, making it more difficult to recover oil; thus, the limits for oil and gas recovery are reduced to 1 cmol·mol^{-1}.

4. Recommendations

4.1. Assessing Effects of Carbon Dioxide Quality

Further research is required to produce accurate and traceable data that can be used to assign maximum amount fraction threshold values with a sufficient degree of confidence. For example, rigorous testing of pipeline and underground storage materials is required to understand how the presence of impurities may affect, for example, corrosion. Some impurities such as nitrogen, oxygen, and argon should be limited as the presence of these components at a high level could reduce storage capacity. However, it is clear that the conditions of storage, such as temperature and pressure, also determine how much effect the presence of noncondensable gases such as nitrogen, oxygen, and hydrogen would have on storage capacity [18]. A more detailed study may be required to select an optimum condition compromising between efficiency of the compression stage and purity levels that can be achieved with conventional purification methods (ultimately looking at the economics of both). This study would require further investigation into the expected purity of carbon dioxide from amine scrubbers to understand levels of impurities on the basis of specific operation conditions. Until these studies are carried out, Table 5 probably provides the best available guidance on a suitable carbon dioxide purity specification for CCS processes.

4.2. Primary Reference Materials

When certifying the composition and purity of carbon dioxide used in the CCS process, the measurement needs to be traceable to the International System of Units (SI). This ensures that the measurements are accurate (providing confidence when transporting and storing the carbon dioxide) and internationally comparable, ensuring a common global assessment that can be easily compared to Table 5 of this report. The National Physical Laboratory (NPL) is the UK's National Metrology Institute and has the role of providing traceability for measurements of gas composition performed in UK industry. New purity requirements for CCS will require NPL to provide traceable primary reference materials containing the impurities listed in Table 5 in a carbon dioxide gas matrix. This may be challenging due to the unique properties of carbon dioxide compared to other gases frequently used as the matrix gas in primary reference materials; as shown in Figure 2, carbon dioxide liquefies at around 50 bar (at room temperature). Some laboratories would perhaps wish to use calibration standards in nitrogen (or alternative gas) matrices as opposed to carbon dioxide; however, testing would be required to ensure that changing the gas matrix would not affect accuracy of the measurement.

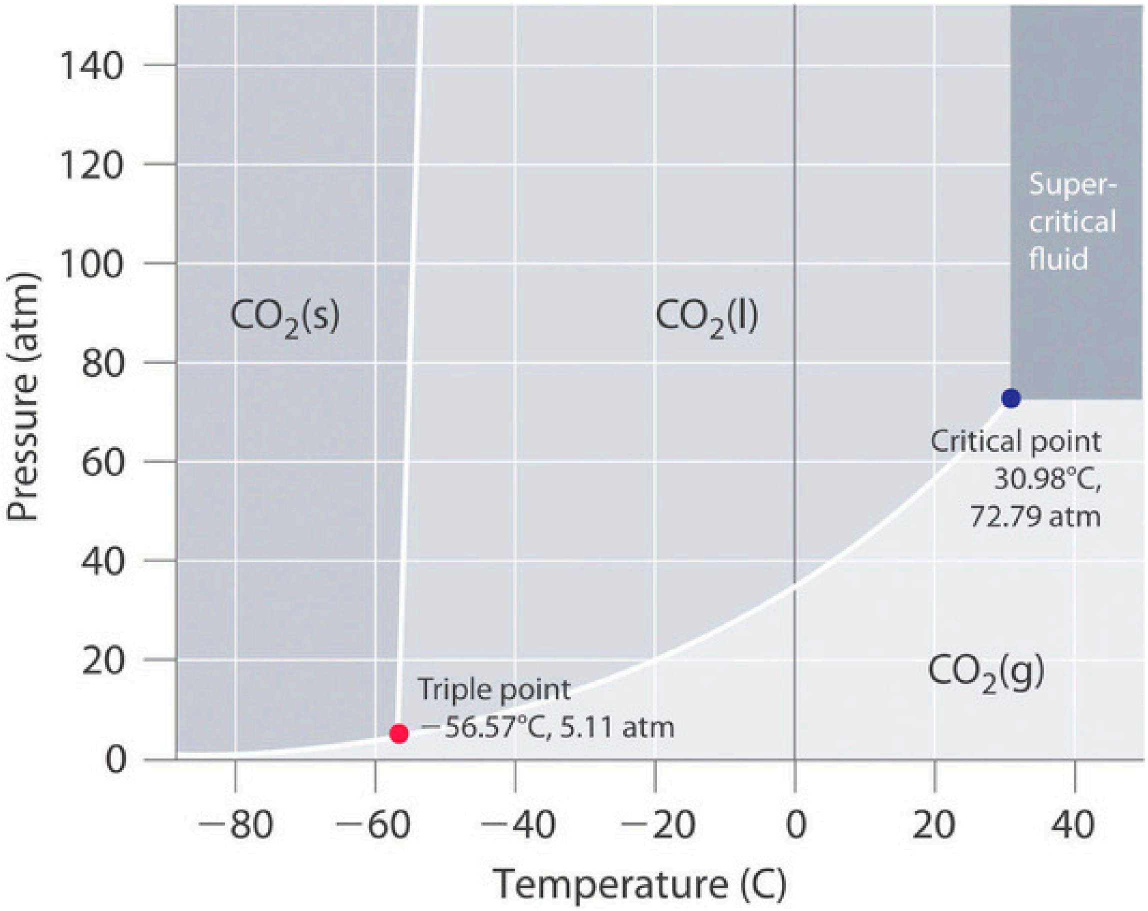

Figure 2. Carbon dioxide pressure–temperature curve.

4.3. Sampling

Carbon dioxide can be sampled as a gas or a liquid depending on conditions (such as pressure and temperature) and it can also easily change phase once it has been sampled, including becoming a supercritical fluid. One study looked into the effects that water, nitrogen, oxygen, and argon had on the thermophysical properties and phase behaviour of carbon dioxide in a CCS system. The results indicated that an impurity at a level of 10% by mole in carbon dioxide would lower the overall mixture density [34]. The potential change in phase when sampling liquid carbon dioxide from a CCS site would also raise the question of whether impurities in gas would behave the same as in liquid (i.e., if low-pressure carbon dioxide is sampled from a liquid storage site, would the impurities be present at the same level as in the original pressurised liquid?). If this did pose a problem, analytical techniques that are capable of monitoring purity whilst the carbon dioxide is in the liquid phase may need to be developed. This is a similar problem faced by liquid natural gas providers where Raman spectroscopy has been identified as a suitable technique for determining composition whilst still in the liquid phase [35]. Additionally, there is the possibility that certain impurities segregate and collect at certain locations within the storage site (such as hydrogen sulphide, which is known to absorb to surfaces); this must be studied to understand whether sampling location has an effect on composition of the carbon dioxide sample.

4.4. Gas Analysis Methods

Due to the large number of impurities that may need to be analysed, it is likely that gas analysers capable of measuring several impurities in a single method would be used (such as gas chromatography with mass spectrometer) as opposed to combining several techniques that focus on a single impurity (such as cavity ringdown spectroscopy). These new analytical methods will be important for providing initial support to UK industries that require traceable measurements to verify the purity of carbon dioxide and to validate commercially available online purity analysers. There are several methods available for performing the analysis in accordance with the purity specifications of Table 5; some options are shown in Table 6 although this should not be considered a complete list.

Table 6. Selection of analytical instruments for performing measurements of impurities in carbon dioxide for quality assurance.

Component	Upper Limit ($\mu mol\cdot mol^{-1}$)	Instrument
H_2O	300	Cavity ringdown spectroscopy (CRDS) Quartz crystal microbalance
H_2S	5	Gas chromatography with sulphur chemiluminescence
CO	20	Gas chromatography with methaniser and flame ionisation detector (GC-Meth-FID) Gas chromatography with thermal conductivity detector (GC-TCD) Nondispersive infrared (NDIR) Gas chromatography with pulsed discharge helium ionisation detector (GC-PDHID)
O_2	100	GC-PDHID
	40,000	GC-TCD
CH_4	10,000	GC-FID GC-TCD
	40,000	
N_2	10,000	GC-TCD
	40,000	
Ar	10,000	GC-TCD
	40,000	
H_2	10,000	GC-TCD
	40,000	
SO_x	0.5	Ultraviolet fluorescence spectroscopy
NO_x	0.5	Chemiluminescence analyser CRDS Cavity attenuated phase shift spectroscopy
NH_3	25	Fourier-transform infrared spectroscopy (FTIR) NDIR Selected-ion flow-tube mass spectrometry (SIFT-MS) Gas chromatography with mass spectrometry
C_2H_6	10,000	GC-Meth-FID GC-FID GC-TCD
C_3+	10,000	GC-Meth-FID GC-FID GC-TCD
Particulates	1	Filter and mass weighing
HCl	1	CRDS
HF	1.8	FTIR NDIR
HCN	0.9	Gas chromatography with flame thermionic detector SIFT-MS
Hg	0.002	Atomic absorption spectrometry
Glycol	0.046	Scanning Mobility Particle Spectrometer GC-FID
Amines	1	Gas chromatography with nitrogen chemiluminescence detector

As these methods have not been developed and tested specifically for impurity measurement in carbon dioxide, this work would need to be carried out to ensure methods are available for CCS operators to perform quality assurance measurements. There are several manufacturers who already offer gas analysers suitable for online monitoring the quality of carbon dioxide [36,37].

4.5. Impact of Gas Quality on Other Measurements

As mentioned in a paper by the National Engineering Laboratory (UK) [38], the presence of impurities will also have an adverse effect on flow metering, which is necessary for regulatory measurement under the European Union (EU) Emissions Trading System (ETS). Flow metering is required for custody transfer and fiscal purposes and for monitoring the various processes across the CCS network, including controlling the volume of carbon dioxide being injected into the geological storage formation. Flow meters are generally designed to operate in one specific phase, either gas or liquid. However, even trace levels of contaminants will invalidate the phase diagram and equations of state for pure carbon dioxide. This is important because, under the ETS, the mass of annually transferred carbon dioxide is required to be determined within a maximum uncertainty of less than ±1.5%. Without knowing the exact phase envelope and physical properties of the carbon dioxide stream, it will be extremely difficult to control the CCS processes and achieve the required measurement uncertainty. An accurate model for equations of state is also required to correctly determine other physical properties such as density, speed of sound, and carbon dioxide phase, which are required to operate the CCS process safe and efficiently [32].

5. Conclusions

CCS is a fairly new approach that is being implemented as a method for reducing carbon dioxide from energy processes, and the number of CCS operators globally is fairly low. As such, guidance and standards for carbon dioxide quality assurance are only starting to be developed; ISO/TR 27921 which provides guidance on this topic was published in 2020 and advises that each operator develops their own purity specifications on the basis of a risk assessment of their process.

In order to ensure operators can carry out gas quality assurance, they require traceable primary reference materials, suitable sampling methods, and validated purity analysis methods, which are not available. This paper provides a draft purity specification for carbon dioxide in CCS processes according to knowledge gained from previous CCS projects to support gas analysis laboratories, calibration gas producers, National Metrology Institutes, and standardisation committees to develop fit-for-purpose guidance, standards, and metrology infrastructure required for this importance measurement.

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